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Electrodeposition of Metals from Fused Quaternary Ammonium Salts — Source link

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THE ELECTRODEPOSITION OF METALS IN FUSED QUATERNARY AMMONIUM SALTS

by

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Part I

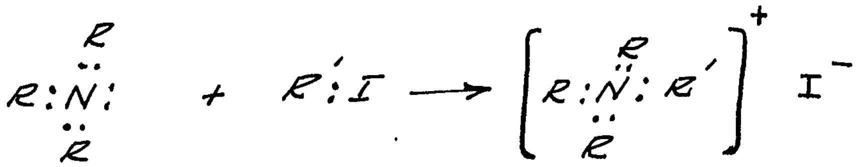
QUATERNARY AMMONIUM COMPOUNDS

I. Introduction

It has long been known (1) that tertiary amines are capable of reacting with organic halides to form a group of compounds called the quaternary ammonium salts, as illustrated in the reaction:

$$R_3N + RX \longrightarrow R_4NX$$

where R is an organic group such as alkyl and X is a halogen. The unique feature of these compounds isthat, although they are formed by the reaction between compounds having distinctly organic properties, these substances have properties analogous to those characteristic of inorganic salts. They are all crystalline solids which dissolve in water to give solutions which readily conduct an electric current. They are also highly deliquescent. The explanation of the behavior of salts of this type is seen from a consideration of their electronic structure, which may be represented as follows:



$$R:\underset{\substack{\cdot\cdot\\ R}}{\overset{\substack{R\\ \cdot\cdot}}{N}}: + R':I \longrightarrow \left[R:\underset{\substack{\cdot\cdot\\ R}}{\overset{\substack{R\\ \cdot\cdot}}{N}}:R'\right]^{+} I^{-}$$

It will be noted that although the number of electrons in the outer ring of the nitrogen atom does not change during the increase of valence from three to five, the type of valence is altered. The trivalent form is purely covalent whereas the quaternary ammonium structure contains four covalent linkages and one electrostatic valence bond. The source of the extra valence lies in the fact that the nitrogen atom can act as a "donor of electrons."

Originally, these compounds were thought to be "molecular compounds," written $(CH_3)_3\ N \cdot C_2H_5I$. The general abandonment of this view came when V. Meyer and Lecco (2) in 1876 showed that the same body was obtained from trimethylamine and ethyl iodide as from ethyldimethylamine and methyl iodide. In 1913 the distinction between the ionized valency and the non-ionized valencies was very apparent when J. Meisenheimer (3) showed that $\left[(CH_3)_3\ N \cdot OCH_3\right]OH$ and $\left[(CH_3)_3\ NOH\right]OCH_3$ were not identical compounds. However, it was the development of the electronic theory of valency by G. N. Lewis and W. Kossel and the recognition of the distinction between electrovalency and covalency that lead to a fuller understanding of the nature of the quaternary ammonium salts.

Reaction mechanisms have been proposed for the formation of these compounds, but as yet no definite conclusions have been reached, so they will not be discussed.

The nitrogen atom is not alone in showing this type of compound formation. Phosphorous, arsenic and antimony form similar compounds in which they, too, have coordination number of four, whereas oxygen, sulphur, selenium and tin have coordination number of three and that for iodine is two. The compounds formed by these elements in their highest positive valence are analogs of the ammonium series and are called onium salts.

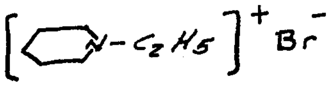
For the present study a number of quaternary ammonium salts were prepared to be used in the fused state as solvents for inorganic salts, thus giving solutions from which metals may be deposited electrolytically. The ammonium salts were principally alkyl halide derivatives of pyridine, though two derivatives of dimethyl aniline were also prepared. The preparations were accomplished by direct mixing of molar proportions of the nitrogen base and the organo-halide with stirring at room temperature or refluxing. The ease of formation varied considerably from the reactions of explosive violence to no reaction even with heating. In some cases additional tests were made for the effect of solvents on the rate of reaction.

For certain of the compounds pyrolysis experiments were performed, and these are described along with the results of the electrolysis of the pure fused salts. The electrolysis of solutions of inorganic salts in the fused ammonium salts is discussed in a later section of this paper. Pyridinium ethyl bromide has received the most attention in this study.

II. Experimental

A. Pyridinium Salts of Some Organic Bromides

1. Ethyl Pyridinium Bromide



The preparation of this material was accomplished by the mixing of equimolar proportions of pyridine (dried over solid potassium hydroxide and distilled) and ethyl bromide (dried over calcium chloride and distilled) with stirring at 25°-30°C. The mixture was protected from the atmosphere. The reaction was completed at the end of 18 to 24 hours to yield a pure white crystalline solid. This product was washed with dried benzene or toluene to remove the excess reactants, as the pyridinium salt seemed to be the least soluble in these solvents.

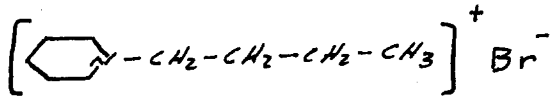
The highly deliquescent product was analyzed for bromide ion by the Volhard method with the following result:

	Calculated	Found
% Bromide ion	42.49	42.0

The material melted at 115°-116°C to give a clear, pale yellow liquid. Trowbridge and Diehl (4) had obtained a melting point of 111°-112°C on a product of almost equal purity on the basis of the bromide ion analysis. However, more recent investigators have contested the melting point data for similar compounds obtained by Trowbridge and Diehl on the basis that they, too, were low.

The use of toluene as a solvent for the reactants gave practically no increase in velocity but did yield a whiter product.

2. n-Butyl Pyridinium Bromide

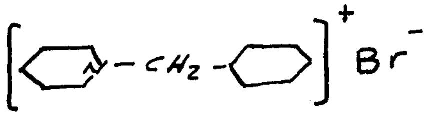


Equimolar proportions of pyridine and n-butyl bromide were gently refluxed in preparing this compound. A layer of red-brown liquid formed on the bottom of the flask after a few minutes and by the end of two hours this amounted to ninety percent of the total volume. The remaining excess milky-white layer was poured off and the reaction product cooled to give a light brown crystalline solid. A portion of this was washed with about 20 volumes of dry acetone in 4 portions to give pure white n-butyl pyridinium bromide with melting point 104º 105°C and a Br^- analysis (Volhard) as follows:

	Calculated	Found
% Bromide ion	37.0	36.5

This material was deliquescent also. No value for the melting point of this compound has been reported in the literature.

3. Benzyl Pyridinium Bromide

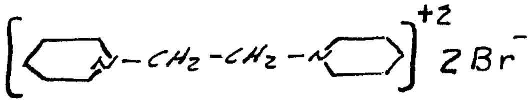


The mixing of equimolar proportions of pyridine and benzyl bromide produced a reaction of explosive violence with evolution of considerable heat. The product was a very viscous yellow mass which set to a white solid after standing a few hours. A bromide ion analysis gave:

	Calculated	Found
% Bromide ion	32.0	31.4

No sharp melting point could be observed for the benzyl pyridinium bromide. This material was very deliquescent and showed unusual supercooling. It should be pointed out that this behavior seems to be typical of the benzyl halide derivatives and that the lack of a sharp melting point may be considered a property of the compound rather than the result of impurities.

4. Ethylene Dipyridinium Dibromide



Upon mixing one mole of ethylene bromide with two moles of pyridine, a red color is produced in the solution followed by the settling out of the first crystals. Heating is required, and the end product is usually a red and pink solid. For the present research a number of preparations were made under varying conditions. The observations during the preparations and results of the analyses of the products are described in Table I. These are to be discussed under the following headings: The molar proportions of reagents, the temperature of reactions, and the method of purification of the product.

a) The Molar Proportions of Reagents.

None of the preparations was found to have a bromide

Table I. Preparation of Ethylene Pyridinium Bromide

Mol Ratio: Pyridine / Ethylene bromide	Temperature °C	Time Required	Purification	Description of product	Analysis °/o Br^-
2.00	80°	1 hour	None	Red solid, some pink	42.54
	100°	1 hour	Washed with anhyd. ether, vacuum dried	Dark pink or rose powder	42.82
	120°	5 min.	Washed with anhyd. ether, vacuum dried	Pale pink powder. M.P.= 250°-255°C (with decomp.)	41.71
			Recrystallized from EtOH, dried in Buchner funnel by suction. Spread on clay plate	Flat, light brown platelets. M.P.= 285°C (with decomp.)	43.07
			The H20 solutions from analysis before and after EtOH crystallization were evaporated to dryness	Pale, light brown platelets. M.P.= 260°±3°C	42.96
2.40	72-76°	5.5 Hrs.	Washed with anhyd. ether, vacuum dried	Dry powder, faint cream cast	36.11
0.85	85° for 5 hours, (70°/o) followed by 3 days at room temperature		Washed with anhyd. ether, vacuum dried	Dry powder, faint cream cast	34.43

Theoretical Values:

$(\text{Pyridine})_2$ Ethylene bromide = 46.20 °/o
$(\text{Pyridine})_1$ Ethylene bromide = 29.94 °/o
$(\text{Pyridine})_2$ Ethylene bromide·1 H_2O = 43.8 °/o

ion content as high as the theoretical value for ethylene dipyridinium dibromide. The highest values for the bromide ion were obtained by mixing the reagents in stoichiometrical proportions, the use of an excess of either reagent yielding a lower bromide ion content. An excess of either reagent also retarded the rate of the reaction. On the other hand, the product resulting from the mixture in which there was an excess of ethylene bromide over the stoichiometrical amount for bromoethyl pyridinium bromide contained more than the theoretical amount of bromide ion for this salt.

b) The Temperature

The effect of temperature on the speed of the reaction is well illustrated in the three cases in which stoichiometrical amounts of reagents for ethylene dipyridinium dibromide were used. At 80°C the reaction required one hour to reach completion, at 100°C considerably less than one hour was required, while at 120°C the reaction was very vigorous and was complete at the end of five minutes.

Even at room temperature the reaction of ethylene bromide with pyridine probably is faster than that of ethyl bromide, but as the solution containing ethyl bromide cannot be heated much above room temperature, the reaction rates at higher temperatures cannot be compared.

c) Method of Purification of Product

The methods employed in purifying the product of the reaction were 1) washing with ether followed by gentle heating under vacuum, and 2) recrystallization from ethyl alcohol, filtration through a Buchner funnel, followed by a quick wash with ether and drying on a clay plate.

As would be expected, the recrystallization procedure proved to be the better method. This is shown by a comparison of the analyses of the product obtained at 120°C. The ether washed product had a bromide ion content of 41.71% while the product recrystallized from alcohol contained 43.07% bromide ion. The recrystallization procedure has the disadvantage of loss of material because the solubility of ethylene dipyridinium dibromide is rather high even at 0°C

However, it should be pointed out that almost as pure a product can be obtained without any purification if stoichiometrical proportions are used and the reaction is run at a lower temperature to give a slower reaction. The product formed by reaction at 80°C contained 42.54% bromide ion without purification as compared with the value of 43.07% for the alcohol purified product previously described.

It is very important to note that ethylene dipyridinium dibromide does not form a hydrate. This is shown by the analysis and particularly by the melting point of the product resulting from the evaporation of the combined water solutions of the 43.07% and 41.71% bromide products. The analysis was 42.96% bromide ion with a melting point of 260° ± 3°C. It is very doubtful that a hydrate of this material would be stable up to such a high temperature. Any deliquescence observed with ethylene dipyridinium dibromide would probably be the result of excess pyridine remaining in the material.

B. Pyridinium Salts of Organic Chlorides.*

1. Ethyl Pyridinium Chloride

The mixing of equimolar quantities of pyridine and ethyl chloride at 25°- 30°C. produced a very slow reaction. A small amount of an oily layer appeared after several days and crystals started forming after two months. The reaction was allowed to continue for 11 months at the end of which time about 100 grams of slightly impure crystals were obtained.

A sample of this material was washed with dried toluene, the toluene decanted, then evaporated by gentle heating under vacuum. A melting point of 116°-117°C was obtained with a chloride ion (Mohr) analysis as follows:

	Calculated	Found
% Chloride ion	24.69	24.51

The preparation of this compound has not been recorded

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*- Note: The structures are similar to those of the bromides.

previously in the literature. It is deliquescent and in many ways closely resembles ethyl pyridinium bromide.

In an attempt to speed the reaction, the solvents acetone, toluene, and benzyl alcohol were used. Tests for the chloride ion after one week indicated that a large amount had been formed in benzyl alcohol whereas very little had been formed in either acetone or toluene. However, because of the high solubility of ethyl pyridinium chloride in benzyl alcohol, and the high boiling point of benzyl alcohol, no separation was accomplished.

Many tests have been made by various investigators on the rate of the addition reaction between tertiary amines and organic halides in various solvents, and, in general, the reactions are relatively slow in hydrocarbons and ethers, but in alcohols and ketones they proceed several hundred times faster.

2. Benzyl Pyridinium Chloride

The reaction between equimolar amounts of pyridine and benzyl chloride was considerably slower than that for the bromide as stirring for about 18 hours at 25°-30°C was necessary to yield almost complete reaction. The resulting white solid was deliquescent, did not give a sharp melting point and was not analyzed.

3. Tertiary Butyl Pyridinium Chloride

No reaction was observed between tertiary butyl chloride and pyridine even with refluxing.

4. Ethylene Dipyridinium Dichloride

The refluxing of the stoichiometrical proportions of two moles of pyridine and one mole of ethlyene chloride produced a cloudiness in the solution at the end of twenty minutes with a red solid beginning to be deposited after about 45 minutes. The reaction was practically complete after eight hours.

Although the product was usually used without purification, two purification methods were investigated. Washing with dry toluene gave a red and pink powder which was very deliquescent. Recrystallization from ethyl alcohol produced light brown platelets which were filtered in a Buchner funnel and washed with a little ether. The resulting product was not deliquescent and was very similar to the ethylene dipyridinium dibromide prepared in this manner. However, the method is not very useful because of the high solubility of the product in alcohol even at low temperatures. The purification was sufficient to indicate that the deliquescence of the impure product is probably caused by the excess pyridine it contains.

C. Dimethyl Anilinium Salts of Organic Bromides

Ethyl and benzyl anilinium bromides were prepared, but the general properties were so unsatisfactory that they were not considered worthy of further investigation. Both compounds dissociated on melting and excess reagents caused considerable discoloration.

D. Pyrolysis of some Pyridinium Compounds

Ethyl pyridinium bromide, n-butyl pyridinium bromide, and benzyl pyridinium bromide and chloride have been made the object of a brief study on the effect of heat on pyridinium compounds. Two types of decomposition have been observed:

1) Ethyl pyridinium bromide and n-butyl pyridinium bromide decomposed to give pyridinium hydrobromide and the unsaturated hydrocarbons ethylene and butylene, respectively while

2) benzyl pyridinium bromide and chloride dissociated into the original components, i.e., pyridine and benzyl halide. Recombination occured in this type of decomposition.

These results were obtained experimentally in the following manner for the cases of ethyl and n-butyl pyridinium bromides. A side-arm flask with receptacle was used and the salts were heated until distillation occurred (about 300°C) at atmospheric pressure. A clear liquid which set to a white solid condensed in the receptacle. In the case of ethyl pyridinium bromide, the gas formed merely was shown to be unsaturated by decolorization of a potassium permanganate solution and of bromine water. However, in the case of n-butyl pyridinium bromide, the gas formed was condensed and identified as n-butylene by the preparation of the dibromide, whose refractive index and boiling point corresponded to those of meso-2,3 dibromo butane. The solid products of the experiment were analyzed by determining the melting points and bromide ion content. Table I gives the numerical data obtained for the various materials.

It may be seen from the table that conversion to pyridinium hydrobromide and unsaturated hydrocarbon occurs in the distillation. Furthermore, the stability of ethyl pyridinium bromide is greater than that of n-butyl pyridinium bromide since the analyses of the undistilled residues indicates that almost complete conversion to the hydrobromide had taken place before distillation in the latter case whereas almost none had in the former case.

Noller and Dinsmore (5) studied the total rate of reaction between pyridine and seven alkyl bromides at 149°C using 11:1 mol ratios of alkyl bromide to pyridine. They concluded that two simultaneous, independent reactions were occurring: 1) the removal of HBr from alkyl bromides,

TABLE II. Bromide Analyses

Sample	Melting Point °C	% Bromide ion
Ethyl pyridinium bromide -- Theoretical	--	42.5
Ethyl pyridinium bromide -- Before heating	115-116	42.0
Residue after partial distillation	115 ± 5	42.6
Condensed distillate	213-215	49.1
Pyridinium hydrobromide -- Theoretical	200*	49.9
n-Butyl pyridinium bromide -- Theoretical	--	37.0
n-Butyl pyridinium bromide -- Before heating	104-105	36.5
Residue after partial distillation	210 ± 10	49.3
Condensed distillate	215-218	49.6

*- Trowbridge and Diehl (4)

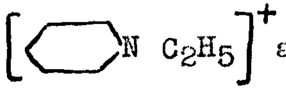
and 2) the formation of pyridinium alkyl bromides. However, the study carried out in this research was directed at the rate of removal of HBr from the fused quaternary ammonium salts from the standpoint of their usefulness as stable electrolysis mediums in the fused state.

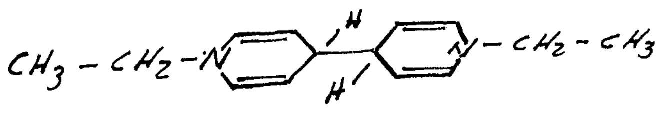
In the cases of benzyl pyridinium bromide and chloride, the same apparatus was used, with a lower temperature (about 200°C) required for distillation, but no gas was evolved.

The condensate from the distillation was a cloudy liquid which on gentle warming reacted to again produce a viscous mass. Dissociation into the original components had occurred.

E. The Electrolysis of Fused Pyridinium Salts

Several of the pyridinium salts prepared have been electrolyzed at temperatures of from 5° to 100°C above their melting points between a spiral platinum cathode and a carbon rod anode set in opposite arms of a U-tube with no diaphram. In every case a dark colored material, usually blue, was produced at the cathode with bromine being formed at the anode. Continued electrolysis produced a black, tarry mass.

In the case of ethyl pyridinium bromide, which has the ions  and Br^-, the blue material which formed was probably the same compound which Emmert (6) had obtained by the electrolysis of a water solution of ethyl pyridinium bromide and which Hofmann (7) had obtained by the action of sodium amalgam on ethyl pyridinium bromide, namely, dihydrodiethyl dipyridyl:



No attempt was made to isolate and identify this compound.

The conductivity increased with temperature nearly three-fold between 120° and 200°C. Gas was given off when the temperature reached 175°-200°C, with or without the current, as the result of the decomposition to give ethylene. Shutting off the current caused the blue color to disappear on standing several minutes, probably because of the disintegration of this compound, whereas the red bromine merely diffused through the solution, with a considerable amount settling to the bottom. Continued electrolysis produced a black tarry, water-soluble mass.

In one experiment the current was passed in the normal direction for a few minutes to produce the organic reduction product in the vicinity of the cathode and free bromine in the vicinity of the anode. The polarity and current were then reversed to give immediately a black tarry mass at both electrodes. Thus the similar mass which was previously mentioned to result from continued electrolysis is probably the result of reaction between the electrode products which have been brought together by diffusion.

The results for n-butyl pyridinium bromide were almost identical to those for ethyl pyridinium bromide, the cathode product probably being the similar compound dibutyldihydro dipyridyl.

In the case of benzyl pyridinium bromide and chloride, the dark colored cathode product, probably dibenzyldihydro dipyridyl (also obtained by Hofmann and Emmert), disintegrated to give a brown material and continued electrolysis resulted in a red-brown viscous, water-insoluble mass.

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Part II

THE ELECTROLYSIS OF INORGANIC SALTS IN FUSED PYRIDINIUM SALTS

Part II. The Electrolysis of Inorganic Salts Dissolved in Fused Pyridinium Salts

Introduction

Audrieth, Long and Edwards (1) studied qualitatively the solubility of various metals, oxides and salts in fused pyridine hydrochloride in order to show the acidic nature of the "onium" ion. They found that the metals aluminum, cadmium, calcium, magnesium, zinc, and even copper dissolved rapidly to form the corresponding chlorides and hydrogen gas; manganese, nickel, tin, lead, and iron reacted in the same manner but less rapidly; whereas arsenic, mercury, silver, and platinum were apparently unaffected. As further evidence of the acidic nature of the fused salt, the oxides of antimony, barium, bismuth, cadmium, cobalt, copper, iron, mercury, lead, magnesium, manganese, and nickel were found to dissolve readily to form the corresponding chlorides and water. Several other oxides were found to react slowly or not at all.

The acidic character of the pyridinium ion in fused pyridine hydrochloride has a theoretical foundation in the general theory of acids and bases as set forth by Bronsted (2). According to this concept, since acids are distinguished by their ability to give off hydrions and bases are characterized by their ability to take up hydrions, these substances may be schematically defined according to the equation:

$$\text{Acid} \rightleftharpoons \text{Base} + H^+$$

That is, a base is necessarily formed when a substance functions as an acid giving off hydrions. For example, consider the acetic acid-acetate ion system

$$HAc \rightleftharpoons Ac^- + H^+$$

where HAc acts as an acid and Ac^- acts as a base; or the case of

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

where NH_4^+ is the acid and NH_3 is the base.

The influence of solvent is of greatest importance, for the dissociation of an acid takes place only under the influence of the solvent. If this is included in the scheme for acetic acid given above, the result is:

$$HAc + H_2O \rightleftharpoons Ac^- + H_3O^+$$

where HAc and H_3O^+ are acting as acids and H_2O and Ac^- are acting as bases. If aniline were the solvent, the reaction would be

$$HAc + C_6H_5NH_2 \rightleftharpoons Ac^- + C_6H_5NH_3^+ .$$

With pyridine the reaction would be

$$HAc + C_5H_5N \rightleftharpoons Ac^- + C_5H_5NH^+$$

where the pyridinium ion, $C_5H_5NH^+$, would be an acid, although pyridine is a base. The experimental evidence given above confirms this statement.

In addition to the reactions mentioned above, which are characteristic of an acid solvent, the chlorides of many metals were found to be quite soluble in the fused salt. These were the chlorides of aluminum, antimony, cadmium and cobalt, copper, iron, mercury, magnesium, manganese, nickel, and zinc. The chlorides of sodium, potassium, calcium and barium were less soluble. In some cases the fusion of metallic chlorides with pyridine hydrochloride in the proper proportions led to the formation of the corresponding double chlorides. Many other salts were found to be very soluble in the fused pyridine hydrochloride, particularly the nitrates of beryllium, calcium, chromium and thorium. Some carbonates also reacted readily.

Audrieth, Long and Edwards also found that many of these melts conducted the electric current readily. However, metallic deposits were obtained only in the following instances: 1) Melts prepared by dissolving lead oxide and antimonous oxide in fused pyridine hydrochloride; 2) Melts prepared by dissolving arsenous, bismuth, mercuric, plumbous, and stannous chlorides in fused pyridine hydrochloride; and 3) From the fused double salts $AsCl_3 \cdot (C_5H_5N \cdot HCl)_3$, $BiCl_3 \cdot (C_5H_5N \cdot HCl)_2$, and $SbCl_3 \cdot (C_5H_5N \cdot HCl)_2$, and later (3) $(CoCl_2)_2 \cdot (C_5H_5N \cdot HCl)_5$. The less active metals, arsenic, bismuth, and antimony, could be readily discharged in the form of good crystalline deposits (3). Mercury collected on the cathode in the form of small globules. Cobalt gave a lustrous plate while tin deposited in the form of loose, metallic flakes. Attempts to deposit the more active metals, tungsten, molybdenum, manganese, vanadium, chromium, aluminum, iron, zinc, lead and magnesium were unsuccessful (3).

The acidic nature of the pyridinium ion imposes a serious limitation on the activity a metal may possess if it is to be electrolytically deposited from fused salt solutions containing this ion. The purpose of this research was to employ as solvents for salts of the metals certain fused pyridinium compounds in which the hydrogen atom causing the acidity is replaced by an alkyl group, as for example, ethyl pyridinium bromide. These fused solvents would be expected to possess approximately the same properties of solubility toward the salts of the metals as pyridine hydrochloride was shown to possess. Since these alkyl pyridinium compounds would not show acidic character, the electrodeposition of the more active metals might be possible.

Experimental

The apparatus for determining the behavior of the various melted mixtures consisted simply of a round-bottom tube, 2.5 centimeters in diameter, into which were fitted a platinum cathode of one square centimeter area, and a carbon rod anode 0.4 centimeters in diameter. The volume of solution to be tested varied from five to ten cubic centimeters. The temperature was controlled by means of an oil bath and in most of the experiments was maintained at 130°-140°. Voltages ranged from six to twelve volts with currents varying between 0.01 amperes and 0.30 amperes.

In preparing the fused melts for electrolysis tests anhydrous salts were used, but only ordinary precautions were exercised to exclude moisture. The procedure was as follows: The ethyl pyridinium bromide stock was melted and 5 cc. portions poured into test tubes, which were then stoppered. The additions of the anhydrous chloride, nitrate and sulfate salts of the metals to the melted pyridinium salt were made from weighing bottles, the amount being determined by difference. Heating was usually necessary to increase the rate of solution and frequently boiling for a few minutes was required. The concentrations chosen to test were arbitrary and the maximum solubility was reached only in the cases of the chlorides of silver, manganese and beryllium and of all of the sulfates. Sodium, lithium, barium and cerium chlorides were practically insoluble. It should be pointed out that the concentrations actually used do not necessarily represent the minimums from which metal may be deposited.

A comparison of the relative solubilities of the chlorides, nitrates and sulfates of lead, nickel, cadmium and zinc showed the chlorides and nitrates to be considerably more soluble than the sulfates in every case.

It is interesting to note that a large number of the inorganic salts formed deeply colored solutions when dissolved in the fused pyridinium salts.

A. Ethyl Pyridinium Bromide

The results of the electrolysis of metallic chlorides in fused ethyl pyridinium bromide are presented in Table I, showing the relative concentrations actually used, whether a metal deposit was obtained, the relative conductivity and remarks as to whether organic reduction occurred at the cathode.

TABLE I. Results of Electrolysis of Solutions of Metallic Chlorides in Ethyl Pyridinium Bromide

Metal	Relative Concentration	Relative Conductivity	Metal Deposit	Remarks
Silver	Low	High	Yes	Organic reduction
Copper	Low	High	Yes	Organic reduction
Bismuth	High	Very high	Yes	Organic reduction
Lead	Low	Low	Yes	Organic reduction
Tin	High	High	Yes	No organic reduction
Nickel	Very low	High	Yes	Organic reduction (?)
Cobalt	Very low	Very low	No	Organic reduction
	High	Low	Yes	No organic reduction
Cadmium	High	Very high	Yes	High melting point
Iron	Very low	Low	No	Organic reduction
	High	Low	Yes	No organic reduction

(Continued)

Metal	Relative Concentration	Relative Conductivity	Metal Deposit	Remarks
Zinc	Low	Low	No	Organic reduction
	Very high	High	Yes	No organic reduction
Manganese	Low	Very low	No	Organic reduction
	High	Very low	No	No organic reduction
Aluminum	Low	Low	No	Organic reduction
	High	Very high	Yes	No organic reduction
Beryllium	Low	High	No	No organic reduction
	High	Very high	No(?)	No organic reduction

Silver, copper, bismuth, lead, tin, nickel, cobalt, cadmium, iron, zinc and aluminum were deposited from anhydrous solutions of their chlorides in fused ethyl pyridinium bromide. Mangangese was not deposited and the deposition of beryllium was doubtful.

The effect of concentration is clearly borne out by the experiments. It will be noted that in the cases of cobalt, iron, zinc and aluminum, at low concentrations of metal chloride organic reduction occurs and no metal is deposited, whereas at high concentration there is plating which is not accompanied by organic reduction. These facts indicate that there is a critical concentration, or critical molar ratio of metal chloride to ethyl pyridinium bromide, above which the metal ions react at the cathode and below which the ethyl pyridinium ions form an organic reduction product. The critical value may not be a certain singular value, but is probably a range of values in which both reactions can occur at the cathode. The use of voltages considerably in excess of the decomposition voltages of both reactions is probably the cause of this simultaneous deposition of metal and organic reduction product. However, if anodes of the metal to be plated were used, this would reduce the voltage requirement for the metal deposition and probably eliminate the disadvantage of contamination to a large extent, if not completely.

Furthermore, the order of the decomposition potentials of metals in this solvent is very probably different from that in water solutions. The case of nickel serves to demonstrate the point for, although the nickel and cobalt solutions were of exactly the same concentration and nickel is normally adjacent to cobalt in the series, nickel plated out while cobalt did not. The failure of manganese to give a plate may indicate that it has a higher potential or that the material used as manganese chloride was in reality manganese oxide.

Tables II and III give the results of the electrolyses of solutions of metal sulfates and nitrates in fused ethyl pyridinium bromide. The metals copper, lead, nickel and cadmium

TABLE II. Results of Electrolysis of Solutions of Metallic Sulfates in Ethyl Pyridinium Bromide

Metal	Relative Concentration	Relative Conductivity	Metal Deposit	Remarks
Copper	Low	High	Yes	Brown water-insoluble material also produced
Lead	Low	High	Yes	Black water-soluble, brown water-insoluble material mixed with deposit
Nickel	Very low	High	Yes	Black water-insoluble material present
Cadmium	High	Low	Yes	Brown organic matter mixed with metal
Zinc	Low	Low	No	No organic reduction

TABLE III. Results of Electrolysis of Solutions of Metallic Nitrates in Ethyl Pyridinium Bromide

Metal	Relative Concentration	Relative Conductivity	Metal Deposit	Remarks
Lead	High	High	Yes	Deposit clean although brown, water-insoluble material also produced
Nickel	High	Very high	Yes	Deposit clean but with brown matter as with lead
Cadmium	Very high	Very high	Yes	Orange solid formed at anode, but solution remained clear
Zinc	High	High	Yes	Also brown material

were deposited from solutions of their sulfates in fused ethyl pyridinium bromide and lead, nickel, cadmium and zinc were obtained from solutions of their nitrates in fused ethyl pyridinium bromide. Although tests were not made using solutions of the nitrates and sulfates of other metals, it is likely that many of the metals could be succussfully deposited electrolytically.

In Table II it is seen that nickel can be deposited from a solution of very low concentration, indicating that it probably has a relatively much lower deposition potential in this solvent. Zinc did not deposit from the solution of the sulfate because the solubility was not sufficiently high.

The sulfate and nitrate solutions produce a brown material as a by-product of the electrolysis. In the cases of lead and nickel sulfate solutions, an additional black contaminant is produced. In general, the chloride solutions are more satisfactory than the sulfate or nitrate solutions on the basis of contamination. The use of metallic sulfates has the additional disadvantage of low solubilities. However, as previously mentioned, the use of anodes of the same metal would probably reduce the difficulty of contamination.

B. Benzyl Pyridinium Bromide

The metals copper, lead and zinc were deposited electrolytically from solutions of the metallic chlorides in fused benzyl pyridinium bromide, but nickel and cadmium could not be deposited. Table IV shows the results of these electrolyses.

TABLE IV. Results of Electrolysis of Solutions of Metallic Chlorides in Benzyl Pyridinium Bromide

Metal	Relative Concentration	Relative Conductivity	Metal Deposit	Remarks
Copper	High	Very low	No	Complex formation?
	Low	High	Yes	Clean deposit
Lead	High	Low	Yes	Crystalline deposit in needles
Nickel	Low	Zero	No	
Cadmium	High	Low	No	Sharp melting point, complex formation?
	Low	High	No	Dark material produced at cathode
Zinc	High	Very low	Yes	No organic matter

The benzyl pyridinium bromide solutions showed a very different behavior from the ethyl pyridinium solutions. An examination of the data given in Table IV reveals the following information: 1) in the case of nickel, the solution did not conduct the current at all, 2) with lead and zinc, although plates were obtained, the conductivities were very low, and 3) in the cases of copper and cadmium, solutions of high concentration had a very low conductivity and produced no metal deposit. Whereas the solutions of low concentration had high conductivities and the metal was deposited from the copper solution.

This last fact suggests that the formation of a nonconducting complex is taking place and that the amount is proportional to the amount of copper or cadmium salt. The high concentrations represent practically complete formation and therefore low conductivity. In the cases of low conductivity, the current was probably carried by the pyridinium salt.

It may thus be concluded that, in general, benzyl pyridinium bromide solutions are less suitable than the ethyl pyridinium solutions of inorganic salts for the electrodeposition of metals.

Summary

Using solutions of metal chlorides in fused ethyl pyridinium bromide, the successful electrodeposition of silver, copper, bismuth, lead, tin, nickel, cobalt, cadmium, iron, zinc, and especially aluminum was accomplished in this research. Also using solutions of the sulfates of copper, lead, nickel, cadmium and zinc in fused ethyl pyridinium bromide, these metals, except zinc, were deposited electrolytically. The metals lead, nickel, cadmium and zinc also were obtained from solutions of their nitrates in melted ethyl pyridinium bromide. In addition, the electrolysis of molten solutions of the chlorides of copper, lead, nickel, cadmium and zinc in benzyl pyridinium bromide were successful in the deposition of metallic copper, lead and zinc. The chlorides of sodium, lithium, barium and cerium exhibited almost no solubility in fused ethyl pyridinium bromide and therefore could not be decomposed electrolytically.

Using solutions of metallic chlorides in fused benzyl pyridinium bromide, copper, lead and zinc were deposited electrolytically. However, nickel and cadmium could not be deposited. The formation of non-ionized complexes with the solvent seemed to be taking place in some instances.

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Part III

THE ELECTRODEPOSITION OF ALUMINUM

Part III. THE ELECTRODEPOSITION OF ALUMINUM

I. Introduction

The electrodeposition of aluminum from aqueous solutions is severely limited by the position of aluminum in the electromotive force series and by the pronounced tendency of aluminum ions to hydrolyze to form insoluble alumina. Although many earlier investigators claimed to be able to deposit aluminum electrolytically from aqueous solution, none of the processes devised was ever particularly successful and many have never been verified.

It was recognized very early that the absence of water was required for the successful deposition of aluminum from solution. The famous Hall process for the production of metallic aluminum embodies the electrolysis of a molten solution of alumina in cryolite. Many similar processes have been devised which involve solutions of an aluminum salt, usually the chloride or bromide, in various inorganic salts, such as KCl or NaCl and the like. These processes for the most part require fairly high temperatures for fusion, although not always sufficient to cause the aluminum to be molten. Since a good plating process should be capable of operation at reasonably low temperatures, say 20°C to 150°C, in recent years non-aqueous solvents, especially organic, have been investigated in the hope of obtaining these lower temperatures.

Because of the analogy of ammonia to water, Taft and Barham (1) attempted the electrodeposition of aluminum from liquid ammonia solutions of aluminum nitrate, but were not successful. Dirkse and Briscoe (2) succeeded in depositing traces of aluminum from ethanolamine solutions of aluminum salts, but were unsuccessful with acetamide, aniline, pyridine, benzoyl chloride, and glacial acetic acid solutions. Similarly, Blue and Mathers (3) found that pure aluminum could not be deposited from a solution of $AlCl_3$ in formamide, but that alloys of aluminum with iron and with zinc could be deposited, the quantity of aluminum in the alloy reaching 17%. Muller, Holzl, Knaus, Planiszig and Prett (4) also were unable to deposit the metal from a solution of $AlBr_3$ in anhydrous pyridine. However, Plotnikov and Balyasnuii (5) made a thermal analysis of the system $AlBr_3$-pyridine and found three eutectic points. Using a mixture which melted below 45°C they were able to separate aluminum. Gray, Bailey and Murray (6) electrolyzed an aluminum salt of aminobenzenesulfonic acid to obtain the metal. Attempts by Beal and Mann (7) to deposit aluminum from aluminum perchlorate solutions in the monoethyl ether of ethylene glycol were not successful. Tests by Wertyporoch and Adamus (8) and Wertyporoch and Silber (9) showed that a number of aldehydes and aromatic hydrocarbons readily dissolve $AlBr_3$ and $AlCl_3$ but that the solutions are either poor or non-conductors. Plotnikov and coworkers have made many studies of the electrochemical properties of solutions of aluminum halides in alkyl halides, aromatic hydrocarbons and their mixtures and have met with some degree of success in the deposition of aluminum. A bath containing $AlCl_3$ and toluene, xylene or acetonitrile was used by Lalbin (10) to accomplish the deposition. Plates could be made either smooth or powdery by suitable adjustment of the current density. To increase the conductivity, alkali fluorides were added to the extent of about one percent.

Many attempts have been made to electrolyze solutions of $AlBr_3$ in ethyl bromide alone or with other reagents, particularly benzene and related compounds. Patten (11) was able to deposit aluminum in a dull, crystalline form from a 40.95% solution of $AlBr_3$ dissolved in ethyl bromide. Katsnel'son and Aizenburg (12) reported that the electrolysis of $AlBr_3$- ethyl iodide-alkali halide mixtures gave aluminum crystals which adhered poorly. Wertyporoch and Wohl (13) and Wertyporoch (14) made many physical chemical tests on combinations of aluminum salts in various organic solvents and mixtures. They found that the conductivity of $AlBr_3$ dissolved in ethyl bromide was increased by the addition of benzene, that the conductivity increased with time, and that the reaction produced HBr. But they did not attempt to deposit metallic aluminum from any of these solutions by electrolysis. Working independently, however, Blue and Mathers (15) reported that "aluminum of high purity can be deposited easily in a bright, finely crystalline, adherent form from a solution made by dissolving metallic aluminum in ethyl bromide and benzene using $AlBr_3$ as a starter or catalyst. Toluene, xylene, b-tetrahydro-naphthalene, or kerosene may be substituted for benzene under certain conditions; and ethyl chloride, methyl chloride, and ethylene chloride for ethyl bromide. The aluminum adheres well to platinum, copper, steel and cast iron, but not to magnesium or aluminum. The bath has a current efficiency of 60% and over at both electrodes, and a throwing power of as high as 28. It does not deteriorate and can be operated indefinitely if moisture is excluded. The cell does not show a definite decomposition voltage, the potential drop varying directly and regularly with current." Later a new, cheaper and more efficient bath was reported by these workers (16). This bath contained the condensation or reaction products formed when $AlBr_3$ and $AlCl_3$ are dissolved in ethyl bromide and benzene. Also, HBr and HCl gave condensation products in benzene with $AlBr_3$ and $AlCl_3$ from which aluminum could be deposited electrolytically. The most efficient proportions were one cubic centimeter of ethyl bromide per gram of $AlBr_3$ with about two cubic centimeters of benzene. The bath had a good conductivity and gave excellent deposits at room temperature with a cathode efficiency of over 75% and an anode efficiency of 105%. A cathode current density of 0.0155 $amps/cm^2$ was employed. The aluminum anodes had an area about six times that of the cathodes, which were usually of copper, but sometimes iron. The anode loss of weight during electrolysis of this bath was greater than the cathode gain because of the reaction of ethyl bromide with the aluminum anode (which would also cut down on the cathode efficiency by attacking the deposited aluminum). However, by the addition of ethyl bromide from time to time it was possible to maintain the life of the bath for a long time. One bath of 50 cc. was operated 8-10 hours daily for a period of three months with excellent results, 3 cc. ethyl bromide being added after each 100 hours use. It was found that toluene and xylene in the plating bath had a brightening effect whereas addition of pyridine and other organic bases ruined deposits. Using this same bath but with a high aluminum concentration and a low concentration of another metal, Blue and Mathers (17) were able to deposit alloys of aluminum with copper, zinc, silver, tin, nickel, lead and mercury. A different potential series of metals was observed in this solvent which placed aluminum closer to these metals thus making the alloy deposition easier. The second metal was introduced in the bath by making it the anode for a short while.

More recently Downie (18) has described a similar process by which he deposited aluminum from a solution which consisted of $AlBr_3$, ethyl bromide, benzene and xylene, the ethyl bromide being added to prevent the solution from being affected by the atmosphere. External cooling by water and the absence of moisture were required but the metal was said to be clean, smooth and strongly adherent.

In 1940, Scheibler and Menzel (19) described a process for electrodepositing aluminum from a bath which consists of solutions of aluminum-alkyls and $AlCl_3$ in a solvent inert to the aluminum-alkyls, namely xylene. The bath liquid separates into two layers, the upper being xylene, which also acts as a protection layer, and the lower being reactants. When the bath becomes contaminated by water, it is claimed that it may be regenerated by distillation.

Keyes and Swann (20,21) and coworkers employed aluminum Grignard reagents for the electrodeposition. Smooth coats were obtained at 20°C from ether solutions of diethyl-aluminum-iodide or ethyl-aluminum-diiodide in an atmosphere of dry nitrogen although with the electrodes 1 cm. apart, 40 volts were required to produce a current density of 0.02 amps/cm^2. These investigators (20,22) have also used an electrolyte containing tetraethyl ammonium bromide and $AlBr_3$. $AlBr_3$ is added in mole to mole proportions to the tetraethyl ammonium bromide causing liquefaction to set in spontaneously at room temperature with the evolution of heat. The liquid is then heated to about 100°C and an aluminum anode and copper cathode inserted. The current density most suitably employed is 0.068 $amps/cm^2$, which required 22.6 volts. An anodic current efficiency of 100% based on the amount of aluminum dissolved is claimed although no mention is made of the cathode efficiency.

The fact that tetraethyl ammonium bromide is a quaternary ammonium salt makes this probably the closest approach to the method to be set forth in this paper, namely, the electrodeposition from solutions of aluminum chloride in fused alkyl pyridinium halides. It will be recalled from a previous section that Audrieth, Long and Edwards were not able to deposit aluminum electrolytically from a solution of $AlCl_3$ in pyridine hydrochloride because of the acidic nature of that solvent.

II. Electrolysis of Aluminum Chloride-Ethyl Pyridinium Bromide Solutions

Preliminary Experiments and Conclusions

During the first experiments on the solubility of $AlCl_3$ in ethyl pyridinium bromide and the electrolyses of the resulting solutions special precautions were taken to exclude moisture. The electrolysis cell consisted of a straight tube of 1 inch diameter with a side arm of the same size. The ethyl pyridinium bromide was placed in the bottom of the straight tube and $AlCl_3$ in the side arm, thus enabling additions of varying amounts of $AlCl_3$ by tilting without opening the cell. Dryness was insured by passing air dried over calcium chloride and phosphorous pentoxide through the apparatus continuously. Furthermore, the initial transfer of materials to the cell was performed in a dry atmosphere. However, later tests showed that such elaborate precautions with respect to moisture need not be exercised.

After the cell had been supplied with the materials, the ethyl pyridinium bromide was melted and the cell tilted so that $AlCl_3$ spilled from the side-arm in small amounts. A vigorous reaction occurred with dense white fumes given off. These were sublimed $AlCl_3$. As further additions were made the vigor of the reaction subsided and the solution took on a deep red color in the region of about 50% $AlCl_3$ by weight, while the volume of melt increased to about twice its original volume.

Using a platinum cathode of 1 cm^2 area and a 0.3 cm. carbon rod anode, several solutions prepared in the above manner were electrolyzed. The following conclusions were reached from these preliminary experiments:

1. Aluminum can be deposited electrolytically in smooth, polishable plates from solutions of $AlCl_3$ in fused ethyl pyridinium bromide. With the solutions containing high concentrations of $AlCl_3$, aluminum above was deposited below a certain voltage (about 8 volts), and above this voltage blue organic matter was deposited either alone or simultaneously with aluminum. It would appear that the Al^{+++} and (ethyl pyridinium)$^+$ ions are in competition for reduction at the cathode, and the ion in the highest relative concentration in comparison with its decomposition voltage will be the one reduced. In the case of very high concentration of the one (which necessarily implies low concentration of the other) there would probably be only one cathode product. However, there must be a range of concentrations in which the use of high voltage and current would cause a local decrease in concentration of the one and allow deposition of the other, that is, concentration polarization.

2. There is a minimum concentration of $AlCl_3$, approximately 45-50% by weight, below which the solution will not deposit aluminum electrolytically. Solutions of lower concentration form only the blue organic reduction product.

3. The solutions exhibit a decomposition voltage for

aluminum approximately between 1.5 and 2 volts between the platinum and carbon electrodes described.

4. The current is an important function of the temperature. About 90°-100°C seems to be a critical value above which the current increases very rapidly with temperature. In one experiment, at 90°C the conductivity was 1.7×10^{-3} reciprocal ohms, while at 130°C the temperature at which the best results were obtained, the conductivity was 75×10^{-3} reciprocal ohms.

It was further shown that aluminum could be deposited from $AlCl_3$-ethyl pyridinium bromide solutions using carbon rods for both electrodes and using iron and steel cathodes with carbon rod anodes. In addition, sheet aluminum anodes were used to eliminate the decomposition voltage and allow continuous electrolysis by reaction with any halide produced at the anode. Smooth, clean, adherent aluminum plates were deposited on small sheets of iron, steel and copper using aluminum anodes.

The Effect of Aluminum Chloride Concentration

A. Phase Study - Variation of melting point with composition.

Mixtures of nine different concentrations of $AlCl_3$ in fused ethyl pyridinium bromide were prepared. As previously described, these showed an initial vigor of reaction when the $AlCl_3$ was added to the melted ethyl pyridinium bromide. Table I lists these solutions, showing the weight percentage

TABLE I. Preparation of Mixtures of Aluminum Chloride In Ethyl Pyridinium Bromide

Weight % $AlCl_3$	Mol % $AlCl_3$	Melting Point (Temp. of Maximum clarity) °C	Description
20.9	27.4	61 Softened at 45	Deep orange solution at 135°
29.2	37.2	53	Deep orange-red liquid at 125°, setting to orange crystalline solid
35.1	43.6	75	Orange liquid at 125°, giving orange solid at room temperature
38.0	46.7	81	Deep orange solution at 120°
41.4	50.0	88	Deep orange solution at 140°, some solid present. Orange solid at room temperature
45.9	54.5	84	Deep red liquid at 140°
51.2	60.0	53	Brown liquid giving brown solid at room temperature
58.6	66.7	-40	Gray-brown liquid at room temperature
60.0	68.2	--	Gray-brown liquid at room temperature
70.0	76.9	127 Softened at 70	Gray-brown liquid at 140° giving gray-brown, grainy solid at room temperature

of $AlCl_3$, the mol percentage of $AlCl_3$, the temperature of maximum clarity, and a description of the solution.

It will be noted that as the concentration of $AlCl_3$ is increased, the color of the solutions changes from orange to deep red very sharply between 50.0 mol % and 54.5 mol % $AlCl_3$. The color then darkens to a gray-brown as the eutectic composition is approached. The reaction of the electrolyte when exposed to moisture gradually changes from one of watery deliquescence, similar to ethyl pyridinium bromide, to one in which a crust formation takes place because of the $AlCl_3$ present.

Figure 1 presents the melting point as a function of the concentrations of $AlCl_3$ and ethyl pyridinium bromide in mol percent. There are two eutectics and one maximum in the curve. Such a maximum indicates compound formation, and the composition at which this occurs is seen to be a 1:1 mol ratio of $AlCl_3$ to ethyl pyridinium bromide. It is also interesting to note that the two eutectics appear at almost exactly 1:2 and 2:1 mol ratios. The eutectic temperature at the 1:2 mol ratio of $AlCl_3$ to ethyl pyridinium bromide was taken to be 45°C because the 27.4 mol % and 37.2 mol % solutions both softened sharply at this temperature. This is indicated on the curve by the dotted line connecting the squares. The remarkably low melting point of the eutectic at the 2:1 mol ratio should be noted especially.

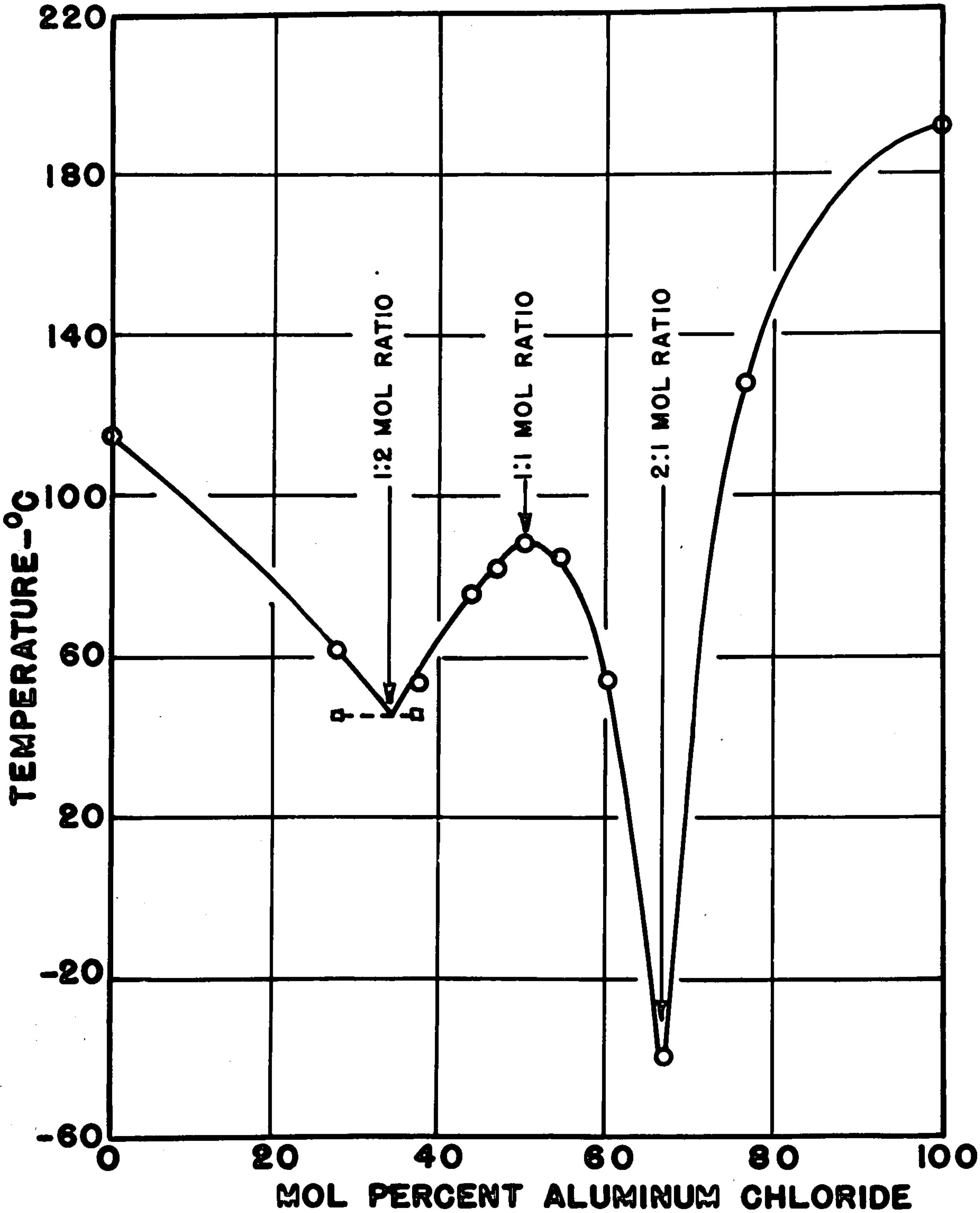


FIGURE I. MELTING POINT CURVE FOR ALUMINUM CHLORIDE—ETHYL PYRIDINIUM BROMIDE MIXTURES

B. Minimum Aluminum Chloride Concentration for Plating

In performing the electrolyses to find the minimum concentration of $AlCl_3$ that can be used to electrodeposit aluminum, the cell used consisted of a simple glass tube of about one inch diameter and 10 cc. volume with a circular aluminum anode surrounding a 1 cm.^{2} flat iron cathode. The temperature was 120°-130°C for all of these electrolyses.

Table II gives the results of these electrolyses. The lower limit of aluminum plating concentrations is between 50.0 and 54.5 mol % $AlCl_3$, although a very poor deposit was obtained from the 54.5 mol % solution. There must be an upper concentration limit also for pure $AlCl_3$ does not give an Al deposit. However, this upper limit is not easily established because at 125°-130°the solubility limit of $AlCl_3$ is reached at 77 mol % as can be seen from the phase diagram. This is further borne out by the fact that aluminum was obtained in a uniform adherent deposit from the 76.9 mol % $AlCl_3$ solution at a temperature of 150°C although at 130°C $AlCl_3$ was occluded in the deposit. Temperatures above about 150°C cause slow sublimation of the $AlCl_3$.

Table II. Electrolysis Results at 120°-130°C

Mol % $AlCl_3$	Description of deposit
43.6	Blue organic reduction product
50.0	No aluminum, no blue material
54.5	Very poor, dark gray, non-adherent aluminum deposit
60.0	Clean, adherent aluminum plate
66.7	Very shiny, adherent aluminum plate
68.2	White, adherent aluminum plate
76.9	Crystalline, non-adherent aluminum deposit with occluded $AlCl_3$

It will be noted that at a 1:1 mol ratio of $AlCl_3$ to ethyl pyridinium bromide neither metallic aluminum nor organic reduction product was formed. This is the concentration for which compound formation was indicated by the composition-temperature phase diagram.

C. Direct Current Conductivities at Various Temperatures

The direct current conductivities of three solutions were measured at various temperatures and the results plotted in graphical form. These were freshly prepared solutions of 54.5, 58.6, and 66.7 mol percent $AlCl_3$ in ethyl pyridinium bromide. It should be realized that these conductivities can be interpreted only in a practical sense as any theoretical interpretation would necessarily involve a knowledge of such quantities as the kinds of ions carrying the current, the viscosity at the various temperatures, and so forth. Furthermore, the conductivities are merely expressed in reciprocal ohms and therefore are comparable only among themselves. Nevertheless, they show the desired relationship. For this purpose it was necessary to standardize the cell and electrode dimensions, the volume of electrolyte and the current density. The conditions used were chosen largely because of their convenience.

Cell: Glass tube, 2.5 cm. in diameter
Volume of electrolyte: 10 cc.
Anode: Aluminum sheet, 0.025 cm. thick, 1.6 cm wide, in circular form against the wall of the cell. Total area of exposed side was 12.0 cm^2.
Cathode: Thin square iron sheet, total area 2 cm^2.
Current density: 0.5 $amps/dm^2$.

Table III contains the values obtained for the conductivity at various temperatures of the 66.7, 58.6, and 54.5 mol percent $AlCl_3$ solutions. These data are plotted in graphical form in Figure 2. At all temperatures, the conductivity of the 66.7 mol percent solution is greater than that of the 58.6 mol percent solution, which, in turn, is greater than the conductivity of the 54.5 mol percent solution.

TABLE III. Conductivity of Aluminum Chloride-Ethyl Pyridinium Bromide Solutions at Various Temperatures

Composition Mol % $AlCl_3$	Temperature ^oC	Conductivity Reciprocal ohms
66.7	125	7.7×10^{-2}
	102	5.6×10^{-2}
	82	$3.7_5 \times 10^{-2}$
	65	$2.6_9 \times 10^{-2}$
	58	$1.3_2 \times 10^{-2}$
58.6	130	6.3×10^{-2}
	111	3.0×10^{-2}
	101	$2.1_8 \times 10^{-2}$
	91	$0.9_7 \times 10^{-2}$
54.5	142	1.89×10^{-2}
	127	1.62×10^{-2}
	112	1.17×10^{-2}
	(100)	(0.5×10^{-2})

(current density = 0.5 amps/dm^2.)

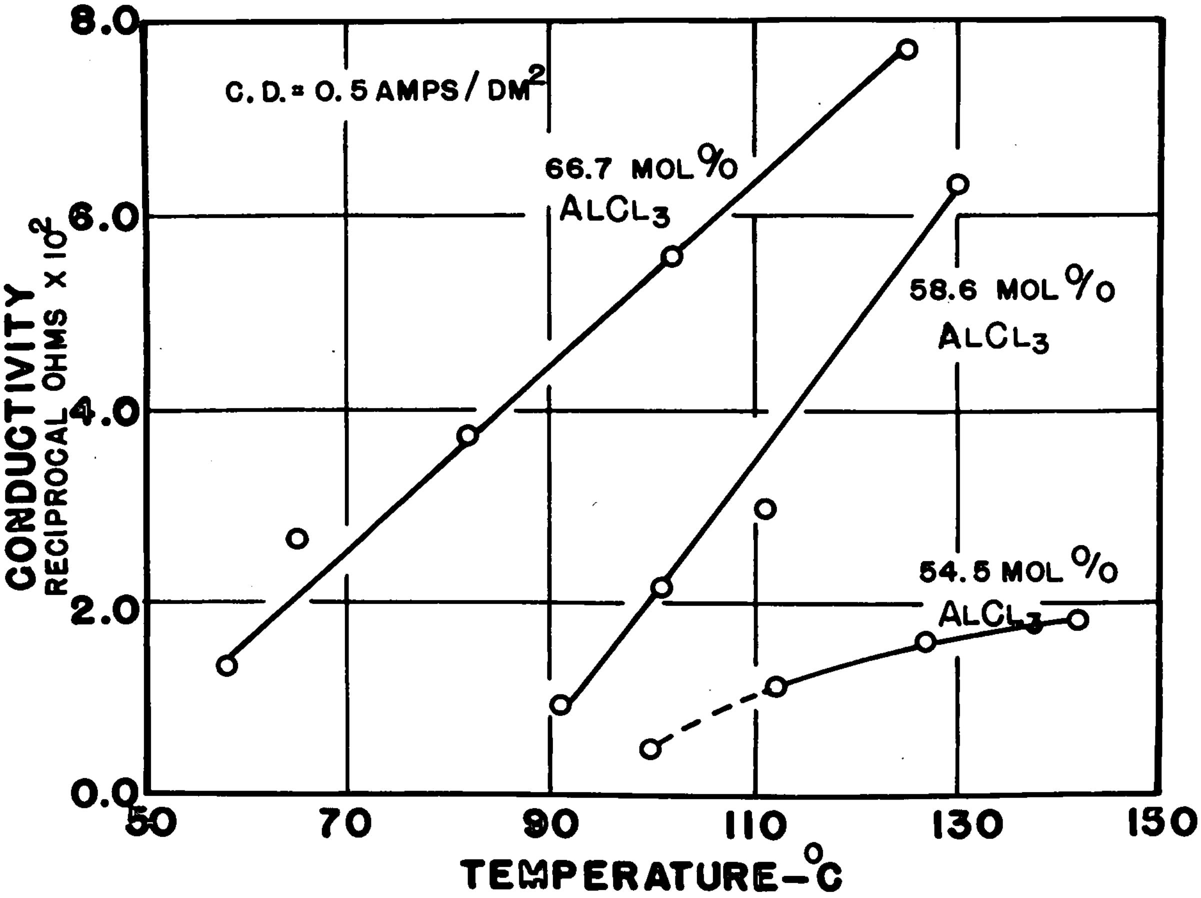


FIGURE 2. CONDUCTIVITY OF ALUMINUM CHLORIDE-ETHYL PYRIDINIUM BROMIDE SOLUTIONS

This increase of conductivity with increase in $AlCl_3$ concentration is seen by comparing the conductivities of the three solutions at a temperature of 120°. The increase is about three-fold between 54.5 mol percent and 58.6 mol percent, and the value for the 66.7 mol percent solution is about five times that of the 54.5 mol percent solution. It will be noted that the temperature range is shorter for the 58.6 mol percent solution than for the 66.7 mol percent solution, and it is shifted slightly in the direction of higher temperatures. This is because of the higher melting point of this solution. For the 54.5 mol percent $AlCl_3$ solution, the conductivity decreases markedly with temperature in the neighborhood of 110° because the plating temperature is very close to the melting point of the solution.

In general, the conductivity of fused salts or their mixtures increases very rapidly just above the melting point. At temperatures somewhat higher the conductivity usually assumes a straightline relationship with the temperature. This behavior was observed with the fused mixtures of $AlCl_3$ in ethyl pyridinium bromide and is shown in the accompanying table and graph.

D. The Effect of Temperature on Plating Properties

In addition to the change of conductivity of the various solutions with temperature, there is a change in the type of deposit obtained. In order to determine the minimum temperature at which smooth, clean, adherent plates could be obtained from the solutions of 54.5, 60.0, 66.7, 68.2, and 76.9 mol percent $AlCl_3$, electrolyses were conducted at intervals of fifteen to twenty degrees from 125°C down. It was necessary to use lower current densities as the temperature was decreased. At the temperature at which a poor deposit resulted, several current densities were usually tested. The results are described below.

a) 54.5 mol percent $AlCl_3$: The plates obtained at 125° and 140° were only partly adherent because too high a current density was used. However, 125° probably represents the minimum plating temperature even with lower current densities because of the high melting point of the solution.

b) 60.0 mol percent $AlCl_3$: Good plates were obtained at temperatures as low as 80°. At 65° a spongy gray deposit of aluminum was obtained which was only slowly soluble in concentrated hydrochloric acid. It was easily dispersed in water to a high degree to give a gray, silky appearance. This is probably due to the presence of numerous small platelets of aluminum along with some aluminum particles of almost colloidal dimensions.

c) 66.7 mol percent $AlCl_3$: With this solution it was possible to obtain smooth, white plates at temperatures as low as 40°, although the conductivities were very low.

At 30° a spongy deposit was obtained similar to that resulting from the electrolysis of the 60.0 mol percent $AlCl_3$ solution at 65°.

d) <u>68.2 mol percent $AlCl_3$</u>: Plates were obtained as low as 80° although at this temperature they were granular and only partly adherent.

e) <u>76.9 mol percent $AlCl_3$</u>: As previously mentioned, a temperature of 150° was necessary to produce a smooth plate as the deposit at 135° contained occluded electrolyte.

It has now been shown that solutions in the neighborhood of 66.7 mol percent are optimum from the standpoints both of conductivity and of minimum plating temperature.

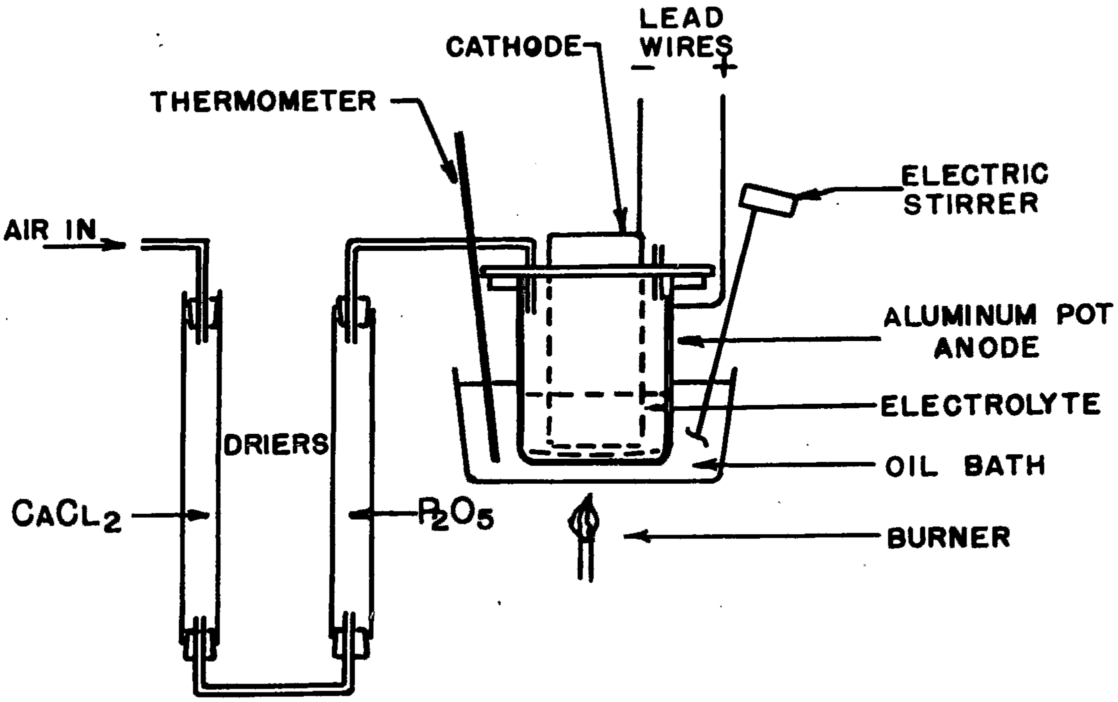
The Effect of Current Density

In order to determine the optimum current density at which plating operations should be conducted, a number of experiments were made on a scale sufficiently large to show that the process can be carried out practically and at the same time make it possible to obtain a better measure of the current density and the type of deposit.

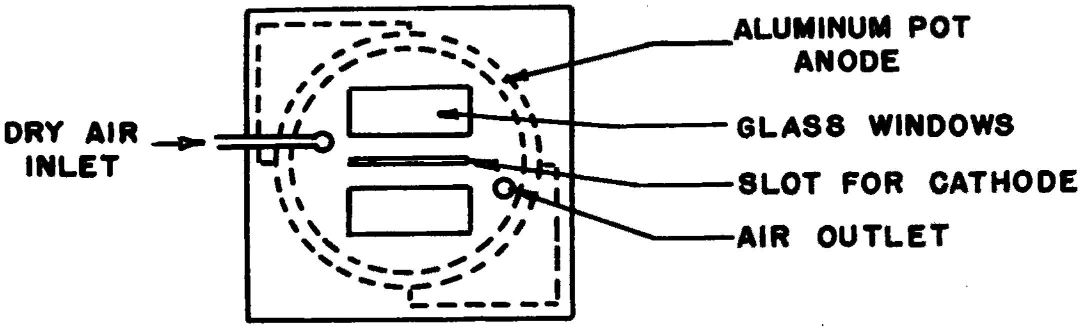
A. Apparatus

The apparatus used is illustrated by figure 3. The cell consisted of an aluminum pot which also served as anode. This was fitted with a wooden top slotted to allow

FIGURE 3. ELECTROLYSIS APPARATUS



DETAIL OF WOODEN TOP



passage of the flat cathode and supplied with two glass windows to allow observation of the electrolyte on either side of the electrode. The cathodes were sheets of steel, brass, and bronze, 5 cm. wide and 14 cm. long with the depth of immersion of the cathodes in the electrolyte being 3.5 cm. A watch glass was placed on the bottom of the aluminum cell to prevent contact of the cathode with the bottom, which would result in a short-circuiting of the cell. The temperature was maintained at 125° by the use of a large oil bath. In order to prevent the diffusion of moisture into the cell, a slow continuous stream of air dried over calcium chloride and phosphorous pentoxide was gently blown in.

The electrolyte was an anhydrous 63.0 mol percent solution of $AlCl_3$ in ethyl pyridinium bromide.

B. Procedure

1. Preliminary treatment of the cathode:

Three general procedures were used to prepare the surface of the cathode for plating. These were a) sanding with emery paper, b) etching in 6N hydrochloric acid or a combination of sanding and acid etching, or c) making the iron surface passive in concentrated nitric acid. After each treatment the surface was dried with clean cloth before inserting in the electrolyte.

2. Electrolysis:

The factors varied in the electrolyses were the current density and the time of electrolysis. This resulted in the deposition of various amounts of aluminum, and from the data it was possible to determine the amount of aluminum which can be plated most satisfactorily as well as the optimum current density.

3. Subsequent Treatment of Plates:

An important feature of the process involved the immediate removal of the adhering film of electrolyte by washing in benzene. The benzene dissolves this film and thus prevents attack of the plate by hydrochloric acid produced by the reaction of the electrolyte with moisture of the air.

The corrosion resistance of the plates could be improved by the subsequent controlled oxidation of the surface using concentrated nitric acid or anodic oxidation in a chromic acid bath. However, this was not generally done.

C. Results and Discussion

1. Aluminum Plating on Steel:

The results are divided into two sections, namely, the effect of current density and the effect of the amount of aluminum deposited.

Observations on the effect of current density in a number of tests with steel cathodes on which approximately the same amount of aluminum was deposited (equivalent to 0.43 -0.51 ampere-hours/square decimeter) showed that:

a) at a current density of 1.00 amps/dm^2, the plates are uniform but gray and the crystal size is fairly large;

b) at 0.90 amps/dm^2, the crystalline character is still slightly granular in some places;

c) at 0.63 amps/dm^2, the plates are uniform, but not shiny;

d) at 0.46 amps/dm^2, the plates are at an optimum, being uniform, very finely crystalline, and shiny; and

e) at 0.30 amps/dm^2, the plate is not uniform, being partly shiny and partly dull.

On considering the cases in which various amounts of aluminum were deposited under conditions of optimum current density, the following observations were made:

a) at the end of 0.23 ampere-hour/square decimeter (amp~~ere~~-hours/dm^2) the plate was white, but dull, and shiny only at the edges;

b) at the end of 0.43-0.49 amp-hours/dm^2 shiny, adherent, uniform plates were obtained; and

c) at the end of 0.69 amp-hours/dm^2 the plate was still shiny but the edges had become crystalline.

The optimum length of electrolysis is seen to be equivalent to about 0.5 amp-hours/dm^2. In electroplating aluminum on steel a current density of 0.5 amps/dm^2 for one hour should be used. Assuming a cathode efficiency of 100% and the density of the electrodeposited aluminum to be 2.7, the same as cast aluminum, this amount of current will deposit a layer of aluminum 0.006 mm thick. The cathode efficiency has been assumed to be 100 percent for calculating the plate thickness. This should be true as long as moisture is excluded and no colored organic reduction product is formed since the electrolyte does not react with aluminum when dry.

It must be realized that these optimum values apply only for this concentration of $AlCl_3$, but it is expected that the values for other neighboring concentrations would be of the same order of magnitude.

2. Aluminum Plating on Brass and Bronze

In a number of tests aluminum was plated on brass and bronze sheets. Inspection of the plates and electrolysis data showed that the values of the optimum current density and amount of aluminum which may be deposited are lower for plates on brass and bronze than the values for aluminum plates on steel. Furthermore, the deposit is much less uniform and adherent.

Adherence and Corrosion Resistance of Aluminum Plates

The adherence of the aluminum to the steel, brass, or bronze is an important function of the preliminary treatment of the cathode. This variable has not been completely studied as only three processes were used. Passivity of the cathode seems to have no effect.

Corrosion resistance of aluminum surfaces is very dependent on the treatment the plated surface receives after it is formed. This variable has not been studied in this paper, but the corrosion resistance is definitely improved by the controlled formation of an oxide coating, whether it is done by concentrated nitric acid, anodic oxidation in a cromic acid bath, or otherwise.

Contamination and Deterioration of the Electrolyte

It is possible that a freshly prepared sample of the electrolyte might contain water, excess ethyl bromide or excess pyridine if it has not been prepared carefully. The water and the ethyl bromide would lower the cathode efficiency by reaction with the aluminum deposited and increase the anode efficiency by increasing the rate of solution there. These impurities may be rendered ineffective by allowing them to react with the aluminum anode for a while before placing the cathode in the electrolyte. The presence of free pyridine would possibly result in the formation of a gum or resin on electrolysis. However, the amounts of these impurities should be small in a properly prepared bath.

In addition to the contamination of the electrolyte by excess reagents or water, there can be contamination by the introduction of foreign metal ions. The source of these may be the iron or other metal cathode, metal containing vessels, or impurities in the $AlCl_3$. In order to determine the extent to which this might be expected to occur, solubility tests of the metals were made. These tests showed that even a sample of electrolyte which has been exposed to the atmosphere through use will attack only slightly the metals iron, copper, brass, lead and tin. The slight etching that was observed was attributed to the presence of moisture in the electrolyte. No effect was observed on steel, bronze, or aluminum.

The effects of small amounts of copper and iron on the character of the deposit were studied in more detail and it was found that relatively low concentrations ruined the deposits. Immediately after obtaining very good plates with a sample of the $AlCl_3$-ethyl pyridinium bromide electrolyte, 0.1% cuprous ion (as Cu_2Cl_2) was added. This caused the subsequent deposits to be black, grainy and non-adherent. Both continued electrolysis and galvanic reaction with an aluminum strip failed to restore the original plating properties of the bath. With a second sample of the electrolyte, ferrous ions to a concentration of 0.1% were introduced by reversing the electrode polarity for the calculated length of time. Immediately thereafter black, non-adherent deposits were obtained. In one case, continued electrolysis succeeded in again producing shiny plates, while in another case at a slightly higher concentration, continued electrolysis had no beneficial effect.

It has been found that the properties of the bath change over a period of time with continued electrolysis at the required temperature. There is a change in the character of the electrolyte and of the plates, and a lowering of the usable current density. The change in character of the electrolyte results in a slight drop in the viscosity and the melting point. However, the deposits become more crystalline and finally become contaminated with organic matter.

In order to determine whether this change is caused by the electrolysis or by the prolonged heating, the following test was made. A sample of freshly prepared electrolyte was heated continuously for nearly 150 hours. The sample was electrolyzed only long enough to make one or two plates at the end of every 24 hours. Good adherent aluminum plates were obtained at the start of the test. Plates at the end of 24, 48, and 72 hours showed an increasing amount of crystalline character and were becoming less adherent. At the end of 96 hours deposits of mixed aluminum and organic reduction product were obtained and at the end of 144 hours only purple organic matter was deposited on the cathode.

It was thus established that prolonged heating is sufficient to cause deterioration of the bath. It was also found that the deterioration is not caused by a change in concentration of $AlCl_3$ or ethyl pyridinium bromide for the addition of these substances did not improve the deposits after deterioration had occurred.

III. Electrolysis of Aluminum Chloride-Ethylene Dipyridinium Dibromide Solutions

Aluminum may also be deposited electrolytically from solutions of $AlCl_3$ in ethylene dipyridinium dibromide. A study has been conducted to determine the operating conditions for electroplating aluminum from these solutions.

A. Phase Study

Mixtures of six different concentrations of $AlCl_3$ in ethylene dipyridinium dibromide were prepared. These are listed in Table IV, showing the weight percentage of $AlCl_3$, the mol percentage of $AlCl_3$, the temperature of maximum clarity, and a description of the product. The compositions shown vary from a 1:1 mol ratio to a 5:1 mol ratio of $AlCl_3$ to ethylene dipyridinium dibromide. The color of the solutions varied only slightly during this very large variation in the mol ratio of the components. There is a slight darkening of the brown color with increase in $AlCl_3$ concentration.

In view of the fact that it was impossible to obtain a sample of ethylene dipyridinium dibromide which contained as much as the theoretical bromide ion content, it was necessary to calculate an "apparent molecular weight" from analytical data in order to provide a basis for comparison. The sample used in the experiments described here were found to contain 41.71% bromide ion. As a result the data cannot be considered as accurate as those for $AlCl_3$ in solutions of ethyl pyridinium bromide.

Figure 4 shows the melting point as a function of the concentration of $AlCl_3$ and ethylene dipyridinium dibromide in mol percentages. There seems to be only one eutectic and no compound formation. Melting points of mixtures of very low $AlCl_3$ concentration could not be obtained because of the ready decomposition of these mixtures. For this reason, the possibility of the formation of a compound with a 1:1 or lower mol ratio of $AlCl_3$ to pyridinium salt cannot be completely excluded, although the general behavior makes the existence of such a compound seem unlikely. The eutectic occurs at almost exactly a 4:1 mol ratio of $AlCl_3$ to ethylene dipyridinium dibromide. The mol ratio of $AlCl_3$ to pyridinium groups or bromide ions is 2:1 at this point. This is the same ratio previously observed at one of the eutectics of $AlCl_3$ in ethyl pyridinium bromide. Also, as will be shown

TABLE IV. Preparation of Mixtures of Aluminum Chloride In Ethylene Dipyridinium Dibromide

Weight % $AlCl_3$	Mol % $AlCl_3$	Melting Point (Temp. of Maximum clarity) °C	Description
17.7	38		Decomposed on heating
25.9	50.0	200 ± 5	Red-brown solution, decomposed on heating to give black material
34.2	60.0	190-195	Red-brown liquid, setting to brown solid
41.1	66.8	140±2	Brown liquid setting to brown solid
51.3	75.4	112±3 softened below 70	Dark brown liquid giving dark brown solid
58.4	80.0	70 ± 5	<u>Dark</u> brown liquid of low viscosity, which supercooled. Dark brown solid.
62.3	82.6	95 softened at 65 - 70	Dark brown liquid giving dark brown solid.

later, the ratio of $AlCl_3$ to pyridinium groups seems to be 2:1 at the eutectic of $AlCl_3$ and ethylene dipyridinium dichloride. Taking all of these values into account it would appear that there is some special significance attached to these eutectics.

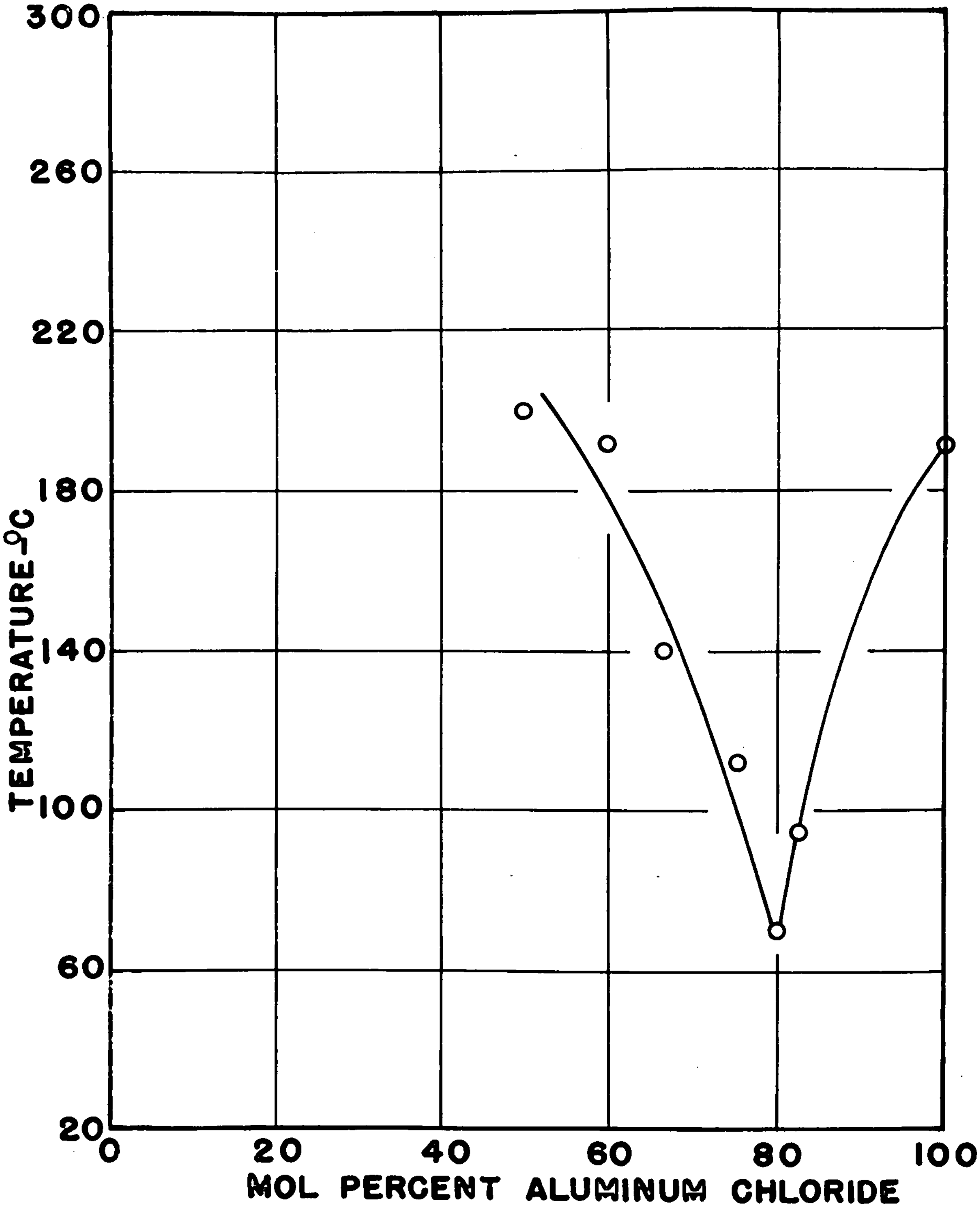


FIGURE 4. MELTING POINT CURVE FOR ALUMINUM CHLORIDE ETHYLENE DIPYRIDINIUM DIBROMIDE MIXTURES

B. Minimum Aluminum Chloride Concentration for Plating

Using a small cell similar to that used for conductivity tests, the 82.0, 80.0, and 75.4 mol percent $AlCl_3$ solutions were electrolyzed at several temperatures from 100° to 145°. The following observations were made:

a) 82.6 mol percent $AlCl_3$, only thin plates were obtained with appreciable sublimation of $AlCl_3$ at all temperatures above 100°.

b) 80.0 mol percent $AlCl_3$, excellent shiny or white adherent plates obtained at temperatures between 115° and 145°.

c) 75.4 mol percent $AlCl_3$, unsatisfactory dark gray, non-adherent deposits were obtained.

The minimum concentration of $AlCl_3$ is thus found to be between 75.4 mol percent, which corresponds to a 3:1 mol ratio of $AlCl_3$ to ethylene dipyridinium dibromide, and 80.0 mol percent $AlCl_3$, which corresponds to a 4:1 mol ratio. On the other hand, the plates at 82.6 mol percent $AlCl_3$ (5:1 mol ratio) were poor, and sublimation of $AlCl_3$ was appreciable. So it is readily seen that the range of concentration which can be used in practice is rather narrow.

C. Direct Current Conductivities at Various Temperatures

The direct current conductivity of three solutions were measured at various temperatures and the results plotted in graphical form. These were freshly prepared solutions of

75.4, 80.0, and 82.6 mol percent $AlCl_3$ in ethylene dipyridinium dibromide. The cell and electrode dimensions, volume of electrolyte, and current density have been standardized. The same experimental conditions were used for these solutions as for solutions of $AlCl_3$ in ethyl pyridinium bromide except that the cathode area was 1.8 cm^2 instead of 2.0 cm^2.

Table V presents the values obtained for the conductivity of various temperatures of the 75.4, 80.0 and 82.6 mol percent $AlCl_3$ solutions. These data are plotted in graphical form in Figure 5. From the curves there is seen to be a straight-line relationship between the conductivity and temperature for each of the solutions. At temperatures below about 115°, the eutectic mixture (80.0 mol percent $AlCl_3$ solution) exhibits the highest conductivity of any of the solutions. But at a temperature of about 115°, the curves for the eutectic and for the 82.6 mol percent solution cross and above this temperature the 82.6 mol percent solution has the highest conductivity. The conductivity of the 75.4 mol percent $AlCl_3$ solution at this temperature, obtained by extrapolation of the curve, is approximately zero. However, the slope of this line is so great that when a temperature of 150° is reached, the conductivity of the 75.4 mol percent $AlCl_3$ solution exceeds that of the 80.0 mol percent solution. Above a temperature of about 155° the 75.4 mol percent solution would possess the highest conductivity of the three solutions tested.

TABLE V. Conductivity of Aluminum Chloride-Ethylene Dipyridinium Dibromide Solutions at Various Temperatures

(Current density = 0.5 amps/dm^2)

Mol % $AlCl_3$	Temperature C°	Conductivity - Reciprocal ohms
75.4	130	2.3×10^{-2}
	145	5.0×10^{-2}
	160	7.5×10^{-2}
80.0	90	2.2×10^{-2}
	100	2.7×10^{-2}
	115	4.1×10^{-2}
	130	4.5×10^{-2}
	145	5.0×10^{-2}
82.6	100	2.5×10^{-2}
	115	3.9×10^{-2}
	130	4.1×10^{-2}
	145	6.0×10^{-2}

This behavior of solutions containing less $AlCl_3$ than the eutectic composition is very different from the behavior of solutions of $AlCl_3$ in ethyl pyridinium bromide of corresponding composition. The values of the conductivity of the solutions of $AlCl_3$ in ethylene dipyridinium dibromide are

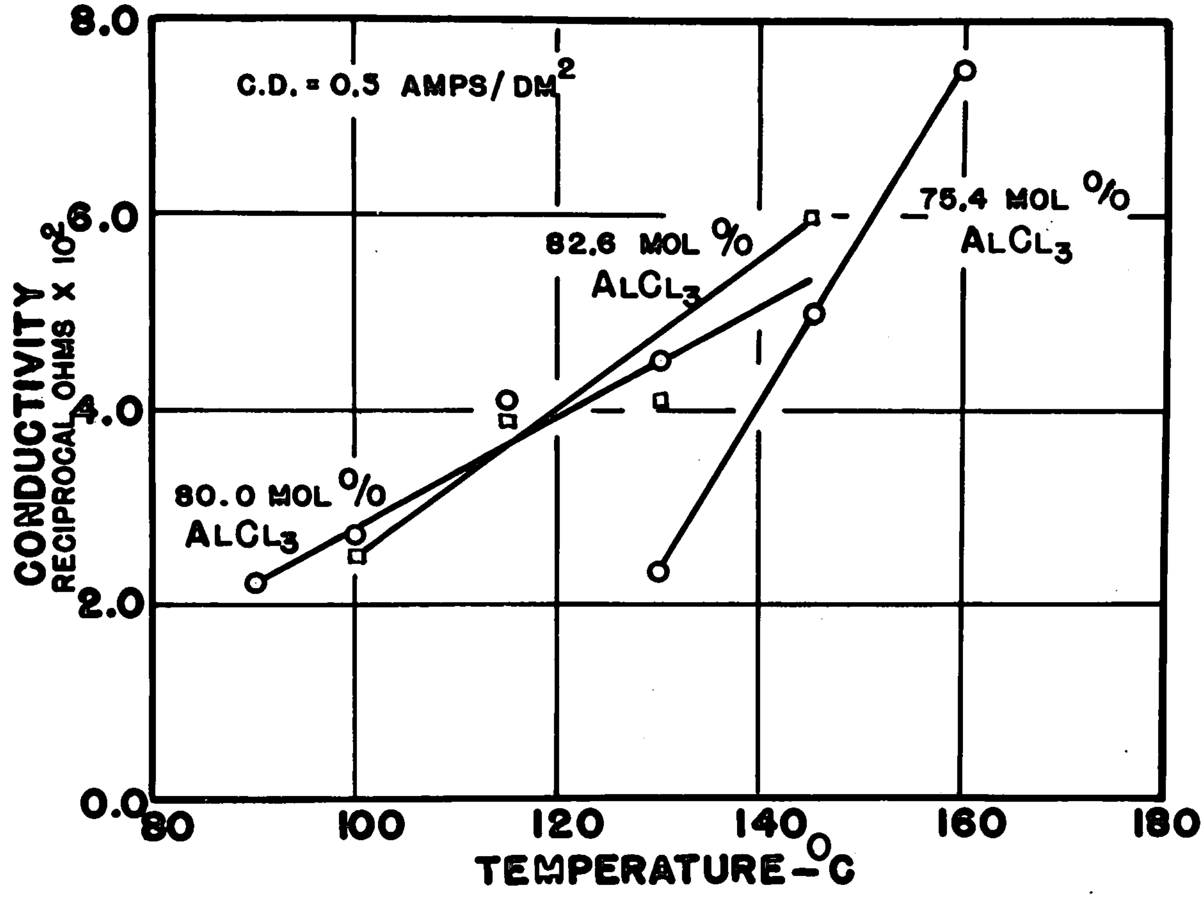


FIGURE 5. CONDUCTIVITY OF ALUMINUM CHLORIDE ETHYLENE DIPYRIDINIUM DIBROMIDE SOLUTIONS

of the same order of magnitude as the solutions of $AlCl_3$ in ethyl pyridinium bromide but the temperature range is shifted slightly in the direction of higher temperatures.

D. Optimum Operating Conditions

Solutions whose composition is in the immediate neighborhood of the eutectic at 80.0 mol percent $AlCl_3$ have been shown to be the only ones from which good plates could be obtained. The optimum conditions for operating a bath of this composition have been determined by performing tests at several current densities at a number of temperatures between 90° and 145°. It was found that the best plates were obtained at a temperature of 145° using a current density of 0.5 amps/dm^2 for 30 minutes. Temperatures above this were not used because of the sublimation of $AlCl_3$. The maximum current density at any temperature at which an adherent plate could be obtained was 1.5 amps/dm^2 at 145°, but these were not as finely crystalline as the plates made at 0.5 amps/dm^2.

IV. Electrolysis of Aluminum Chloride-Ethylene Dipyridinium Dichloride Solutions

The system of $AlCl_3$ and ethylene dipyridinium dichloride has not received extensive study yet because of the difficulty of preparing reasonably pure ethylene dipyridinium dichloride, which was mentioned in Part I. This difficulty led to the use of a direct method of preparation of the electrolyte using pyridine, ethylene chloride and $AlCl_3$. The method has been found to be reasonably satisfactory but is more susceptible to an excess of reagents. The procedure for preparing the electrolyte is to mix the stoichiometrical amounts of pyridine and ethylene chloride and allow them to react at room temperature until a yellow color appears, which is accompanied by a slight increase in the viscosity. This may require 24 hours. Weighed amounts of $AlCl_3$ are then added slowly with vigorous stirring. Considerable heat is evolved. The solution changes in color to a red-brown and as more $AlCl_3$ is added becomes very dark brown, or black. A rough indication of the phase diagram may be obtained by taking the melting point of the mixtures at various stages in the addition of $AlCl_3$. It was found that there is definitely a eutectic in the neighborhood of a 4:1 mol ratio of $AlCl_3$ to ethylene dipyridinium dichloride. Observations on two preparations showed that this eutectic melts fairly sharply at 27°. The presence of excess reagents at the beginning of the addition of $AlCl_3$ makes melting point data for low percentages of $AlCl_3$ of no value.

The conductivity of the 80 mol percent $AlCl_3$ solution has been measured at several temperatures using the same current density and conductivity apparatus as that described for the ethylene dipyridinium dibromide. Table VI presents the data obtained. These data have been plotted in graphical form in Figure 6. A straightline relationship between conductivity and temperature is found to hold for this solution above a temperature of about 90°, but below this temperature the conductivity falls off more rapidly with further decrease in temperature. For the purpose of reference, the line obtained for ethylene dipyridinium dibromide at 80.0 mol percent $AlCl_3$ has been drawn on the same graph. The two lines are found to be practically coincident.

TABLE VI. CONDUCTIVITY OF ALUMINUM CHLORIDE-ETHYLENE DIPYRIDINIUM DICHLORIDE

80 mol percent $AlCl_3$
Current density = 0.5 amps/dm^2

Temperature C°	Conductivity Reciprocal Ohms
70	0.5×10^{-2}
90	2.4×10^{-2}
115	3.6×10^{-2}
129	4.6×10^{-2}

VI. Electrolysis of Aluminum Chloride-Ethyl Pyridinium Chloride Solutions

The study of the system of $AlCl_3$ and ethyl pyridinium chloride has been directed only toward the establishment of the feasibility of depositing aluminum from such solutions.

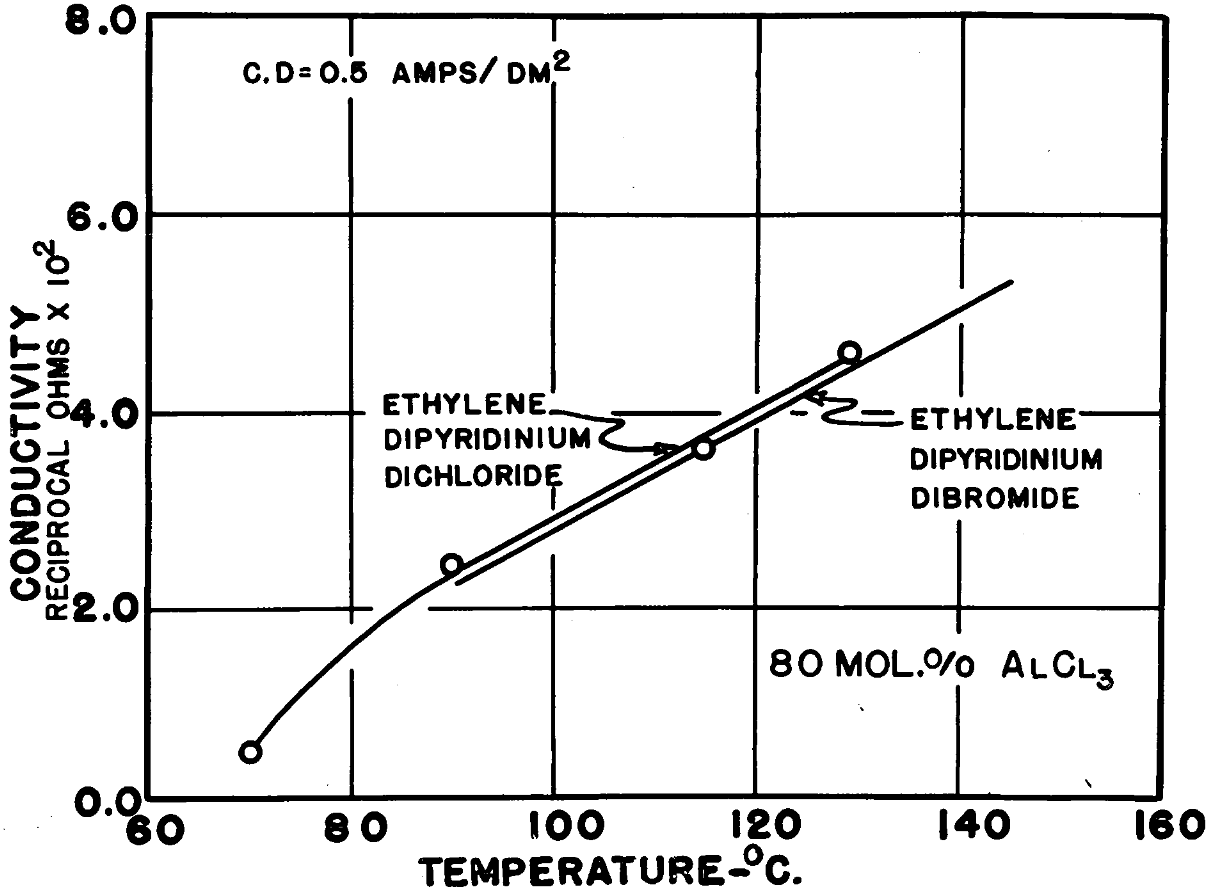


FIGURE 6. CONDUCTIVITY OF ALUMINUM CHLORIDE-ETHYLENE DIPYRIDINIUM DICHLORIDE MIXTURE

The addition of $AlCl_3$ to fused ethyl pyridinium chloride produced a red-brown solution which was a liquid of low viscosity at room temperature. The electrolysis of this solution at a temperature of 110° using a current density of 0.5 $amps/dm^2$ produced a bright deposit of metallic aluminum in large crystals.

VI. Summary:

The results of the present research show that aluminum can be deposited electrolytically on other metals from solutions of anhydrous $AlCl_3$ in any one of several fused pyridinium compounds, namely, ethyl pyridinium bromide or chloride and ethylene dipyridinium dibromide or dichloride. Furthermore, the plates are smooth, and very finely crystalline, and may be produced on iron, steel, copper, bronze, brass, platinum, lead and tin using aluminum anodes. Other metals were not tested. The case of $AlCl_3$ in fused ethyl pyridinium bromide has been studied in considerable detail with respect to the effects of $AlCl_3$ concentration, current density, temperature, current efficiency, and the ease of contamination of the plating solution.

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