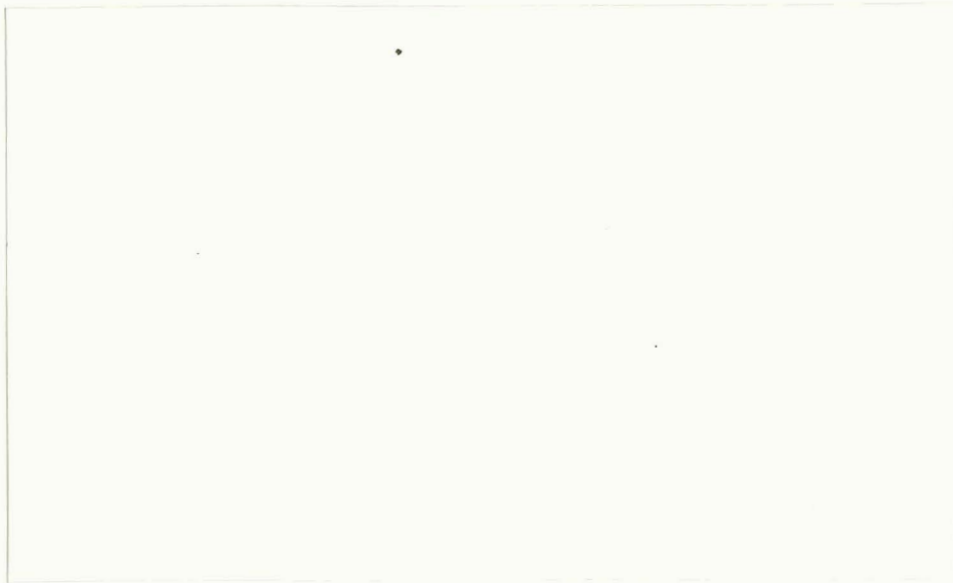


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THE DEVELOPMENT OF TECHNOLOGY
FOR THE ELECTRODEPOSITION OF
ALUMINUM ALLOYS AND BERYLLIUM

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CONTENTS

1.	INTRODUCTION	1
1.1	Abstract	1
1.2	Foreword	2
1.3	Summary	2
1.4	Discussion of Results	3
2.	TECHNICAL DISCUSSION	4
2.1	Development of Beryllium Plating Solution	4
2.1.1	Development of Be Solution Using Methyl Magnesium Bromide	4
2.1.2	Development of Be Solution Using Ethyl Magnesium Bromide	5
2.1.3	Extraction of Diethyl Beryllium by Use of Hexane	5
2.2	Electrodeposition of Beryllium	6
2.2.1	Electrodeposition Tests	6
2.2.2	Analytical Method of Beryllium Determination	9
2.2.3	Electrolysis of Diethyl Beryllium Solution	10
2.2.4	Study of Ethyl Magnesium Bromide Ratio	10
2.3	Electrodeposition of Aluminum Alloys	12
2.3.1	Plating Bath Tests	12
2.3.2	Alloying Tests	14
2.3.3	A Study of Alloying Effects of Nonaluminum Anodes	15
2.3.4	Electrolysis Test Conditions	16
2.3.5	Aluminum Plating With Various Anodes	16
2.3.6	Cell Voltage Measurements	18
2.3.7	Conductivity Measurements	19
2.3.8	Cathodic Current Efficiency	19
2.4	Long-Term Bath Stability Tests	19
2.4.1	Test Conditions	19

CONTENTS (contd)

2.4.2	Pyridine and LiAlH_4 Control	21
2.4.3	Temperature Control	21
2.5	Further Beryllium Plating Solution Studies	21
2.5.1	Beryllium Dialkyls	21
2.5.2	Ditertiary-Butylberyllium	22
2.5.3	NMR Studies of Ditertiary-Butylberyllium	23
2.5.4	Alkylberyllium Halides	24
2.5.5	Alkylberyllium Hydrides	25
3.	CONCLUSIONS	27

SECTION 1

INTRODUCTION

This final report presents the work done on the research and development of aluminum alloys and beryllium electroforming processes under contract NAS1-8953 for the period 1 March 1969 through 6 February 1970. The laboratory studies were carried out under two major tasks, namely: the electrodeposition of aluminum alloys and the electrodeposition of beryllium.

1.1 ABSTRACT

The objectives of this program were: to develop a beryllium plating solution and electrodeposit samples for further studies; to analyze methods of electrodepositing aluminum alloys; and to study long-term aluminum electrodepositing bath stability, that is, a maintainable bath.

A beryllium plating solution was attained which gave very poor electrodeposits.

Aluminum alloys were electrodeposited with very low percentages of Ti, Zn and Mn, all of which were inferior to the 100 percent Al.

Bath stability tests showed that pyridine and LiAlH_4 content must be controlled within specific limits.

1.2 FOREWORD

The work described herein was conducted by Electro-Optical Systems and performed under NASA Contract NAS1-8953 with Mr. Kenneth Lui as Project Manager.

1.3 SUMMARY

The objectives of this program were: to develop a beryllium plating solution and electrodeposit samples for further study; to analyze methods of electrodepositing aluminum alloys; and to study long-term maintainable aluminum electroplating bath stability.

A beryllium plating bath was developed which produced very poor deposits. This solution was prepared by means of hexane extraction of the diethyl beryllium from an ethereal solution. The hexane was then boiled out by means of fractional distillation. Other work on developing this plating bath was by means of nuclear magnetic resonance studies, which gave indications of reaction intermediates; more extensive work is needed to understand the problems at hand.

Aluminum alloy studies were made on anodes and different solution mixtures. The anodes studied included Al, Mg, Fe, Zn, Cu and Ni. It was found that aluminum anodes produced the best deposit structures.

Aluminum alloys electrodeposited from different solution mixtures gave very low percentages of Ti, Zn and Mn, but they did not structurally compare to the pure aluminum deposits which remained best.

Bath stability tests on the aluminum plating baths showed that the best deposits were obtained at a pyridine concentration of 0.090M. A current density of 16.15 mA/cm^2 was found to be preferable for good deposit structures. LiAlH_4 concentration should not exceed 0.5M or porous, brittle deposits are obtained. The temperature of the bath should also be controlled.

1.4 DISCUSSION OF RESULTS

By means of hexane extraction of the diethylberyllium compound from the ether solution, a plating solution was prepared which gave good molar percent beryllium yields. This shows that further efforts in this area might be fruitful. Even though the beryllium electrodeposits were poor in structure, it is possible to electroform beryllium and further work could possibly produce coherent, metallurgically sound deposits. Beryllium particles were deposited, but there was no adherence between them. If the plating solution and conditions were more closely studied, these parameters might become minor details. NMR studies on beryllium compounds gave evidence of reaction intermediates which, as of now, are not known. They also show the possibility of basic solutions different from ether which could be the key to the problem.

The aluminum alloy studies showed that alloying aluminum with various other cations is feasible, but did not show any improvements in the electrodeposited structure. It still remains that electrodeposited pure aluminum is stronger than alloyed deposits, but more work needs to be done.

Bath stability has been improved by means of controlling the pyridine concentration at 0.09M and LiAlH_4 concentrations at 0.5M along with a controlled current density at 16.15 mA/cm^2 . The temperatures of the bulk solution and cathode surface could be controlled and a correlation established so the easily controlled bath temperature can be monitored instead of the cathode surface temperature.

SECTION 2

TECHNICAL DISCUSSION

2.1 DEVELOPMENT OF BERYLLIUM PLATING SOLUTION

2.1.1 DEVELOPMENT OF Be SOLUTION USING METHYL MAGNESIUM BROMIDE

The first step of the development work was the preparation of the ethereal BeCl_2 solution. The available commercial form of BeCl_2 is granular and had to be ground, by mortar and pestle, into a fine powder. It was found that the anhydrous ether contained enough water to cause difficulties in dissolving the anhydrous BeCl_2 ; therefore, the diethyl ether was redistilled over sodium metal to ensure absolute dryness. With the combination of fine BeCl_2 and the redistilled ether, a saturated ethereal BeCl_2 solution was obtained by adding the BeCl_2 powder into the ether in 10-gram portions. Each portion was added after the previous portion had completely dissolved. It took four days to prepare one liter of the saturated solution which was analyzed to be 2.83M in BeCl_2 .

The second step of the development work was to add magnesium Grignard to the ethereal BeCl_2 solution. Two hundred-fifty mls of 3.0M ethereal methyl magnesium bromide solution was added to 137 mls of 2.83M BeCl_2 in ether, yielding an exothermic reaction.

The third step was to remove the excess ether by pulling a 5.0 mm Hg vacuum for a period of four hours. The last step was the separation of the dimethyl beryllium-ether complex from the excess Grignard by vacuum distillation at $38^\circ \text{C}/0.1 \text{ mm Hg}$.

The reduced-pressure distillation operation for the separation of dimethyl beryllium was conducted inside the glove box to avoid exposure to the atmosphere. Two hundred-fifty ml of 3.0M ethereal methyl magnesium bromide was added to 137 ml of 2.83M BeCl_2 ethereal solution. The excess ether was removed by pulling a 5.0 mm Hg vacuum for several days. The dimethyl beryllium-ether complex was separated from the reacting mixture by vacuum distillation. White crystalline powder was collected in the condenser and receiving flask. This powder was subsequently dissolved in added diethyl ether. Upon electrolysis of the solution, a thin greyish deposit was observed on the cathode. The cell voltage was 50V at a current density of 0.5 mA/cm^2 .

2.1.2 DEVELOPMENT OF Be SOLUTION USING ETHYL MAGNESIUM BROMIDE

The above development work was repeated with ethyl magnesium bromide in place of methyl magnesium bromide. Two hundred-fifty ml of 3.0M ethereal ethyl magnesium bromide was slowly added to 137 ml of 2.83M BeCl_2 ethereal solution. The excess ether was again removed by pulling and maintaining a vacuum of 5 mm Hg for a period of four days. Separating the diethyl beryllium-ether complex from the reaction products, a thick slurry, was accomplished by heating the reactor and regulating it through the use of a powerstat. A colorless liquid, which condensed at 50 to 55°C at about 3 mm Hg, was collected in the receiving flask. This was the diethyl beryllium-ether complex. It did not freeze upon cooling down to 2°C.

2.1.3 EXTRACTION OF DIETHYL BERYLLIUM BY USE OF HEXANE

By extraction of the thick slurry with a selective solvent, the diethyl beryllium was isolated from the other reaction products (MgBr_2 , MgCl_2 and BeCl_2) by filtration. The inorganic halides are insoluble in hexane, and it was appropriate both in terms of selectivity and of boiling point.

The thick slurry mixture was extracted with hexane, and a resultant mixture was filtered. The filtrate contained diethyl beryllium and ethyl magnesium bromide, both soluble in hexane. Since an excess of beryllium chloride was added, all the ethyl magnesium bromide (hopefully) reacted and none was left to go into solution when the thick slurry was extracted with hexane. The next step took advantage of the difference in boiling points between the diethyl beryllium and the hexane. The filtrate was distilled under slight vacuum. The hexane was rapidly distilled away with the residue being diethyl beryllium. The percentage of the theoretical yield was 61 percent. The percentage could have been increased by repeated extractions.

2.2 ELECTRODEPOSITION OF BERYLLIUM

2.2.1 ELECTRODEPOSITION TESTS

The diethyl beryllium ether complex was electrolyzed in small test cells with platinum electrodes, spaced at approximately 3 mm apart. Results of these tests are summarized in the following tabulation:

<u>Test No.</u>	<u>Electrolyte</u>	<u>Current Density mA/cm²</u>	<u>Cell Voltage Volts</u>	<u>Results</u>
1.	Equal volume mixture of diethyl beryllium-ether complex and anhydrous ether. Approximately 3M in Et ₂ Be	6.5	50	Black powdery deposit. Partially reactive with water.
2.	Equal volume mixture of diethyl beryllium-ether complex and 2.8M BeCl ₂ ethereal solution.	1.2	5	Black deposit. More coherent than deposit from No. 1. Partially reactive with water, containing 31% Be.
3.	Same solution used in test No. 2	2.3	7	Black deposit. Same appearance as those obtained from test No. 2. Partially reactive with water, containing 59.2% Be.

<u>Test No.</u>	<u>Electrolyte</u>	<u>Current Density mA/cm²</u>	<u>Cell Voltage Volts</u>	<u>Results</u>
4.	Equal volume mixture of diethyl beryllium-ether complex and tetrahydrofuran.	2.4	5.5-6	Dark deposit. Coherent, partially reactive with water containing 56.7% Be.
5.	Mixture of 1 part of diethyl beryllium-ether complex to 2 parts of tetrahydrofuran.	2.5	12-17	Dark deposit. Coherent, partially reactive with water, containing 52.2% Be.
6.	Equal volume mixture of diethyl beryllium-ether complex, 2.8M BeCl ₂ ethereal solution and tetrahydrofuran.	2.4	50	Dark deposit. Coherent, partially reactive with water.
7.	Mixture of 2 parts of diethyl beryllium-ether complex to 1 part tetrahydrofuran.	2.4	3.7-4.5	Dark deposit. Coherent, partially reactive with water, containing 61% Be.

In the first test black powdery deposits were obtained on both anode and cathode. These deposits fell from the electrode upon washing, and portions of the cathodic deposits reacted with the wash water. The unreacted portion was then dissolved in diluted HCl.

In the second test, black deposits were again obtained on both anode and cathode. The cathodic deposit was much more coherent than those from the first test. Portions of the cathodic deposit also reacted with water during washing. The unreacted portion was then dissolved in diluted HCl and was analyzed for beryllium content.

The solution from the second test was electrolyzed again with clean electrodes in order to determine if "side reactions" occurred only during initial electrolysis of the electrolyte. The same results were obtained indicating no important side reactions.

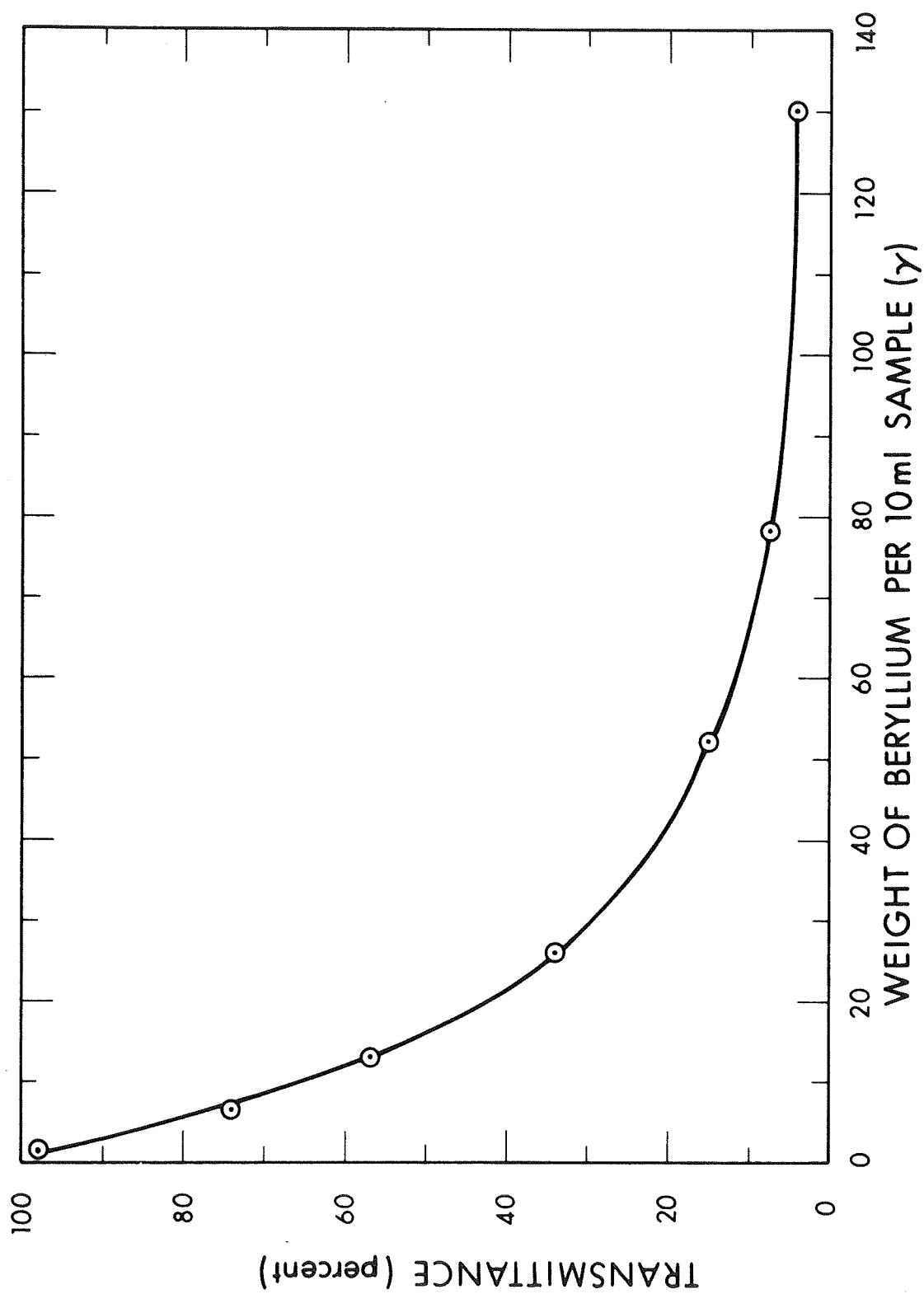


Figure 1. Standard Curve for Determination of Beryllium with p-Nitrobenzeneazo-Orcinol

In all tests, black coherent deposits were obtained upon electrolysis. These deposits were partially reactive with water during washing. Portions that did not react with water were analyzed for beryllium content. There was very little difference in appearance between the deposits. However, the beryllium content varied from 31 percent to 61 percent. They all appeared to be metallic under observation with a microscope.

2.2.2 ANALYTICAL METHOD OF BERYLLIUM DETERMINATION

The amount of beryllium in the deposits was determined through colorimetric method¹ using p-nitro-benzeneazo-orcinol as the indicator. Beryllium deposits were dissolved in a small amount of 10 percent HCl and then diluted to 500 ml in a volumetric flask. Ten ml of sample solution was transferred to a 25 ml volumetric flask, to which 2.7 mls of 2.0N sodium hydroxide and 5 mls of 0.64M boric acid and exactly 6 ml of dye solution was added. (The dye solution was prepared by stirring mechanically for several hours, 0.025g of p-nitrobenzeneazo-orcinol with 100 ml of 0.10N sodium hydroxide and then filtering.)¹ Water was added to the mark. The transmittance was determined at 525 mμ. Standards were prepared by dissolving 13.00 mg samples of beryllium metal in small amounts of 10 percent HCl and then diluting to various concentrations in volumetric flasks. A standard curve is given in Fig. 1.

From the tabulation, it can be seen that beryllium content increased (from 31 percent to 59 percent) in the deposits during successive electrolysis of the same electrolyte (test Nos. 2 and 3).

¹ Colorimetric Determination of Traces of Metals, 3rd edition p. 314, E. B. Sandell, Interscience Publishers, Inc., New York, 1965.

2.2.3 ELECTROLYSIS OF DIETHYL BERYLLIUM SOLUTION

Work was done in electrolyzing diethyl beryllium dissolved in various organic solvents. The results of these experiments are presented in Table I. Since a metal mandrel is used as the cathode for electrodepositing beryllium, the metal mandrel should be selectively dissolved. A low-melting alloy was tested as the mandrel for electrodepositing the beryllium, mainly for ease of removal. No difference in the quality of beryllium deposited on the low-melting alloy compared to other metallic mandrels, such as copper and platinum, occurred. The cohesiveness and thickness of the beryllium deposits attained did not have adequate physical properties to prevent crumbling when the low-melting alloy mandrel was melted away, so no analytical tests were performed.

2.2.4 STUDY OF ETHYL MAGNESIUM BROMIDE RATIO

Another formulation using a lower ratio of ethyl magnesium bromide to BeCl_2 was tried. Two hundred twenty-five ml of 3M ethyl magnesium bromide ethereal solution was slowly added to 150 ml of 2.7M BeCl_2 ethereal solution. The diethyl beryllium-ether complex was separated by vacuum distillation. Three parts of the diethyl beryllium-ether complex were then mixed with one part of tetrahydrofuran and electrolyzed.

The results are summarized in the following tabulation (test Nos. 8, 9, 10):

TABLE I

RESULTS OF ELECTROLYZING SEVERAL SOLUTIONS OF DIETHYL BERYLLIUM

<u>Test No.</u>	<u>Electrolyte</u>	<u>Electrodes</u>	<u>Current Density mA/cm²</u>	<u>Voltage, Volts</u>	<u>Remarks</u>
11.	2 parts of Et ₂ Be + 0 part of THF	Low m.p. alloy coated copper anode and cathode	2.5	2.5-3.2	Anode surface corroded and turned dark. A light brown cloud surrounded the anode. Black coherent deposit on anode, partially reactive with water during washing. No improvement in the quality of deposit.
12.	2 parts of Et ₂ Be + 1 part of THF	Copper cathode and Pt anode	2.4	3.2	Black coherent deposit on anode, partially reactive with water during washing. No improvement in the quality of deposit.
13.	2 parts of anisole was added to nine parts of solu- tion from No. 12	Copper cathode and Pt anode	5.0	3.7-4.0	Black coherent deposit on anode, partially reactive with water during washing. No improvement in the quality of deposit.

<u>Test No.</u>	<u>Electrolyte</u>	<u>Current Density mA/cm²</u>	<u>Cell Voltage Volts</u>	<u>Results</u>
8.	Mixture of 3 parts of diethyl beryllium-complex to 1 part of tetrahydrofuran	2.6	3.2	Dark coherent deposit, treed, partially re-active with water.
9.	Same solution as No. 8	2.6	3.2	Dark, coherent deposit, treed, partially re-active with water.
10.	Same solution as No. 9	2.3	7.3-10.5	Dark deposit. Powdery on surface. Partially reactive with water.

It is assumed that further decreasing the ratio of tetrahydrofuran to diethyl beryllium-ether complex in the electrolyte would further decrease the cell voltage, but no improvement on the quality of the deposit would be obtained. The deposits appear to be very rough and trees were observed over the entire surface. Spectrographic analysis showed that the major constituent of these deposits was beryllium.

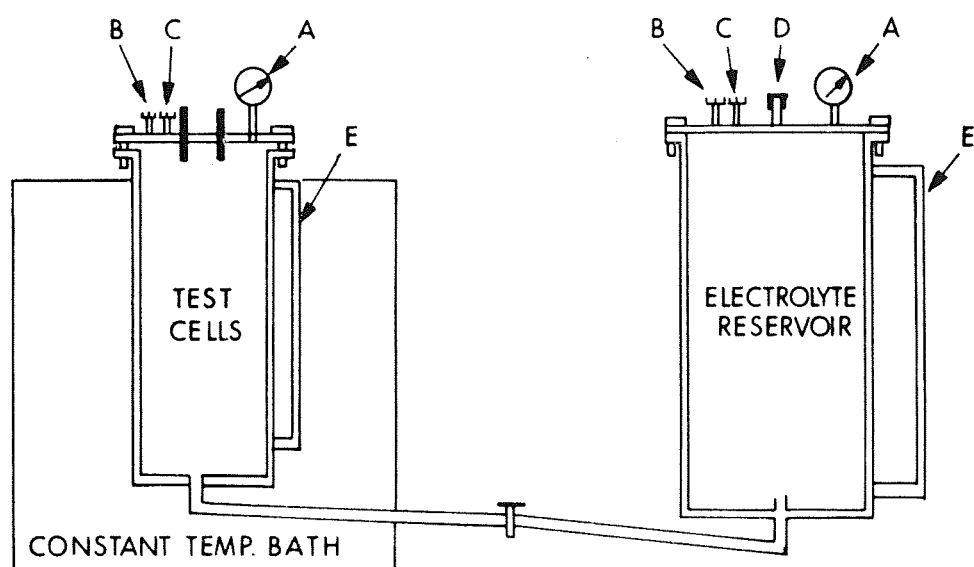
2.3 ELECTRODEPOSITION OF ALUMINUM ALLOYS

2.3.1 PLATING BATH TESTS

Modified test cells and their reservoirs, Fig. 2, as well as a constant temperature bath were assembled and tested. The following plating baths were subjected to test:

- Standard aluminum plating bath with and without LiAlH_4 .
- 0.090M pyridine in standard aluminum plating solution with and without LiAlH_4 addition.

Each plating bath was electrolyzed for approximately 20 ampere hours and all deposits appeared to be normal with electrolyte temperatures kept at $18 \pm 2^\circ\text{C}$.



A. PRESSURE GAGES
 B. N₂ LINES
 C. VACUUM LINES

D. Li Al H₄ ADDITION PORT
 E. SIDE GLASSES

Figure 2. Schematic of Test Cell and Reservoir

Aluminum plating baths with Mg, Mn, Ti and Zr salt additives were prepared and tested in the modified test cells. The results are discussed below.

2.3.2 ALLOYING TESTS

2.3.2.1 MgBr₂

Anhydrous MgBr₂ is readily soluble in standard aluminum plating solution (APS). A solution containing 0.6M of MgBr₂ in standard APS was prepared and electrolyzed. No apparent variation on the deposit was observed. Spectrographic analysis gave no positive identification of magnesium in the deposit.

2.3.2.2 MnI₂

Anhydrous MnI₂ is only slightly soluble in standard APS. A saturated MnI₂ solution (0.16M) in APS was prepared. Upon electrolysis, a very brittle metallic deposit of fine grain was obtained. It is suspected that the salt concentration was too high. Dilution with standard APS to the ratios of 2:1, 5:1, 10:1, 20:1, 30:1 and 60:1 was made. None of these solutions yielded good aluminum deposits. The best deposits were obtained with the last dilution ratio given; spectrographic analysis showed the deposit contained 0.028 percent of Mn.

2.3.2.3 TiCl₃

Anhydrous TiCl₃ is only slightly soluble in standard APS, yielding a dark-colored solution. A saturated solution was prepared. Upon electrolysis, a very soft, granular metallic deposit was obtained. Spectrographic analysis showed that the deposit contained 0.015 percent of Ti.

2.3.2.4 ZrCl₄

Anhydrous ZrCl₄ dissolved in standard APS yielded a dark colored solution. A 0.27M solution was prepared. Upon electrolysis, a greyish brittle metallic deposit with fine grain was obtained. It was suspected that the salt concentration was too high. Dilution with standard APS to the ratios of 2:1, and 5:1 was made. These solutions, upon electrolysis, yielded a slightly harder deposit. Spectrographic analysis of the deposit obtained from the last solutions contained 0.02 percent of Zr.

2.3.3 A STUDY OF ALLOYING EFFECTS OF NONALUMINUM ANODES

The use of metals other than aluminum was evaluated as anodes to ascertain if any alloying effect could be found in the aluminum deposits. The use of insoluble or only partially soluble anodes, in place of aluminum anodes, was observed to have a visibly deleterious effect upon the aluminum plating solution and the aluminum electrodeposits. The order of decreasing anodic solubility was found to be as follows: Al > Mg (est) > Fe > Zn > Cu > Ni. The anode with the lowest current efficiency was nickel (0.48 percent), while iron had the highest (36.1 percent) not considering Al and Mg. The anodic current efficiency of magnesium was not determined but it is estimated to be higher than that for iron. A reduction of cathodic current efficiency was observed to accompany reduced anode current efficiency: Al > Mg (est) > Fe > Cu > Zn > Ni. Acceptable aluminum electrodeposits were obtained only when using anodes of aluminum, magnesium and zinc. The use of zinc anodes caused the aluminum electrodeposit to be considerably rougher than usual. Since none of the anodes yielded an electrodeposit comparable to that obtained from aluminum anodes, no qualitative tests were made to determine any alloying contents of the electrodeposits or of the solutions to determine Fe, Zn, Cu, or Ni ion contents. The details of this study are discussed in the following sections.

2.3.4 ELECTROLYSIS TEST CONDITIONS

The anodes studied included nickel, iron, copper, magnesium, and electrodeposited zinc. A test cell with a 6061 aluminum anode was used as a control. Electrolysis was carried out in small glass test cells under the following conditions:

Temperature	Ambient (23-25°C)
Current Density	20 mA/cm ²
Electrode Spacing	6.5 mm
Solution Volume	60 cm ³
Electrolysis Time	15 hr at 150 mA (2.25 A-hr)
Cathode	(3.8 cm x 1.9 cm in area)
Electrolyte	APS

2.3.5 ALUMINUM PLATING WITH VARIOUS ANODES

The test results using various anodes are presented in Table II.

The most soluble anode material (other than aluminum) was iron (35 percent based on two electron transfers) which, as an element, resembles aluminum quite closely in its chemical properties. It was noted that a considerable amount of white precipitate was formed at the iron anode during the course of the test.

The anodic current efficiency of zinc was only about one-third that of iron.

The anodic current efficiency of copper was observed to be 2.94 percent. The copper anode was covered with a black, brittle crust during electrolysis. The crust was found to be water soluble, and in physical appearance resembled copper oxide, but CuO is not water soluble.

TABLE II

ANODE TEST DATA (2.25 A-HR TEST)

<u>Anode</u>	<u>V_{cell} At 1.12A-Hr (Volts)</u>	<u>Conductivity After 2.25 A-hr -3 -1 -1 (X10 Ω cm)</u>	<u>Anode Weight Loss (g)</u>	<u>Anode Current Efficiency</u>	<u>Cathode Current Efficiency (%)</u>	<u>Remarks</u>
Ni	6.85	6.54	0.00538	0.484 (2e ⁻)	41.3	Black, powdery, poor deposit. Anode covered with brown, rubbery film.
Fe	5.95	6.96	0.369	36.1 (2e ⁻)	71.0	Black, "burned", powdery de- posit. Considerable anode corrosion with much white ppt. at anode.
Mg	2.10	-	-	-	-	Good Al deposit; good back- side coverage (ribbon). Thin anode severely corroded caus- ing loss of contact during electrolysis.
Cu	2.01	6.72	0.0697	2.94 (1e ⁻) 5.90 (2e ⁻)	52.4	Stressed, dark-gray deposit. Reduced backside coverage. Anode covered black crust.
Zn	1.39	6.50	0.133	10.9 (2e ⁻)	49.0	Good Al deposit; good back- side coverage. Considerable anode corrosion.
Al (6061)	1.28	6.40	0.313	89-90 (3e ⁻)	99.8	Typical soft Al deposit.

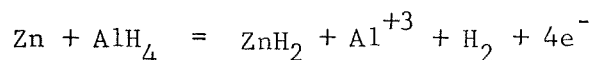
Nickel had the lowest anodic current efficiency of the metals evaluated in APS, (0.48 percent for two electron transfers) and is very nearly an "inert" anode. Apparently, organic oxidation reactions predominate at the nickel anode, as it was covered with a brown rubber-like film which was insoluble in water.

2.3.6 CELL VOLTAGE MEASUREMENTS

Measurement of cell voltages during electrolysis gave a measure of the anode polarization characteristics and APS condition as well. There was no direct correlation between cell voltage and anodic current efficiency, although the highest cell voltage was observed for the case of the nickel, the most inert anode material of the study. For example, the highly soluble iron anode also had a high cell voltage. However, the best aluminum electrodeposits were obtained for the cases of the cells with the lower voltages (i.e., Mg, Zn, Cu, and of course, Al anodes).

Although initially some of the cells (e.g., Ni and Cu) exhibited similar cell voltages, relative to the control, these values increased toward the end of the run due to deterioration of the APS, changes in the anode surface, and nonconducting films which covered the anode surfaces.

The iron anode exhibited high initial and terminal cell voltages, indicative of extensive, continuous anodic polarization. The anode of electrodeposited zinc also exhibited a high initial cell voltage which sharply decreased after less than an hour of electrolysis. This is attributed to initial formation of an insoluble ZnH_2 film on the anode, possibly by the following reaction:



2.3.7 CONDUCTIVITY MEASUREMENTS

Conductivity measurements gave no indication of solution deterioration, as there were substantial differences in the nature of the aluminum electrodeposits from solutions of similar conductivity (see Table II, nickel and zinc, for example).

2.3.8 CATHODIC CURRENT EFFICIENCY

Reduction of anodic current efficiency during electrolysis of the standard APS through the use of inert or partially insoluble anodes was also reflected in the cathodic current efficiency. As the anode became more inert, the cathodic current efficiency generally decreased. On the other hand, the quantities of nonaluminum ions or particles would appear to have no suppressing effect on cathodic efficiency. The predominant effect was that the inert anodes had high polarization (note the higher cell voltage for Ni as compared to Al). At higher voltages, the decomposition of the solvents and/or organic species occurred at both electrodes in conjunction with the corrosion of the anode and the deposition of the aluminum at the cathode. The proportions of the plating cell current that went into decomposition of organic species and solvent molecules appeared to be directly related to anodic and cathodic polarizations, but this is not conclusive.

2.4 LONG-TERM BATH STABILITY TESTS

2.4.1 TEST CONDITIONS

Long-term bath stability was evaluated by subjecting a fixed volume (1000 ml) of plating solutions to the following test conditions.

- a. Plating 10-mil specimens consecutively until no coherent aluminum can be electrodeposited.

- b. Plating 10-mil specimens consecutively, but adding a fixed quantity of LiAlH_4 after each plating, until no coherent aluminum can be electrodeposited. A continuous addition process is possible when the amount of LiAlH_4 is optimized through intermittent addition.

An electroformed 5 x 15-cm flat aluminum specimen was obtained from each plating.

Long-term bath stability tests on the following six plating baths were run:

- 1 and 2. Standard aluminum plating baths (APS), i.e., 3.4M aluminum chloride and 0.35M LiAlH_4 in diethyl ether solution, with and without LiAlH_4 addition.
- 3 and 4. 0.125M pyridine in APS with and without LiAlH_4 addition.
- 5 and 6. 0.0625M pyridine in APS, with and without LiAlH_4 addition.

Each bath was subjected to approximately 60 ampere-hours of electrolysis. Addition of LiAlH_4 was made at 20 ampere-hours, at a rate of 0.0012M or 0.045 gm ampere-hours of electrolysis. No apparent sign of deterioration was observed in these baths, with the exception of the APS with 0.125M pyridine. A brittle deposit was obtained from this bath at the very beginning. It is evident that the pyridine content of the bath has a very narrow and critical range. In order to obtain good aluminum deposits, the concentration of pyridine must be controlled very close to 0.10M. Gassing from the anode had been observed in all six test cells.

No attempt was made to control bath temperatures, and the steady state temperature was observed to be about 36°C. Frequent addition of anhydrous diethyl ether was necessary to replenish the loss of the solvent due to evaporation. It is known that variation in temperature can change the mechanical properties of electrodeposits; also, the necessary

frequent addition of diethyl ether can bring in a significant amount of moisture (0.1 percent in "anhydrous" ether) which reacts with the LiAlH_4 . Therefore error was introduced into the LiAlH_4 additions for rejuvenation.

2.4.2 PYRIDINE AND LiAlH_4 CONTROL

A study was made to optimize the operating parameters of the pyridine bath. Solutions with pyridine concentration of 0.125, 0.115, 0.105, 0.095, 0.090, 0.085 and 0.075 molar were prepared and electrolyzed at 21.5, 16.15 and 10.75 mA/cm^2 , respectively. It was found that the best deposit, on a plate structure basis, was obtained at a concentration of 0.090M and a current density of 16.15 mA/cm^2 . Additions of LiAlH_4 to the above solution did not improve the quality of the deposit. Porous brittle deposits were observed when LiAlH_4 concentration exceeds 0.5M.

2.4.3 TEMPERATURE CONTROL

During the three electrolysis runs (Nos. 11, 12 and 13), it was observed that the temperature in the bulk of the solution and the temperature on the cathode surface were different during electrolysis. The magnitude of such difference is dependent upon the configuration of the electrode assembly, the geometry of the test cell, and the circulation and/or agitation of electrolyte.

2.5 FURTHER BERYLLIUM PLATING SOLUTION STUDIES

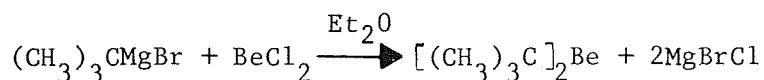
2.5.1 BERYLLIUM DIALKYLs

The experimental effort was concentrated on the beryllium dialkyls because they are very soluble and stable in ethers, their preparative and characterization techniques are fairly well known, and they are precursors to the other classes of organo beryllium compounds.

Three batches of diethyl beryllium were prepared from the reaction:
 $2\text{C}_2\text{H}_5\text{MgBr} + \text{BeCl}_2 \xrightarrow{\text{Et}_2\text{O}} (\text{C}_2\text{H}_5)_2\text{Be} + 2\text{MgBrCl}$. Yields of diethylberyllium were generally about 60 mole percent based upon BeCl_2 used. To obtain yields this high the reaction sludge had to be extracted with a hydrocarbon solvent such as hexane at the stage just prior to ether removal by distillation. The extraction removed the diethylberyllium from the sludge before it solidified into an intractable mass.

2.5.2 DITERTIARY-BUTYLBERYLLIUM

Three batches of ditertiary-butylberyllium were prepared from the reaction:



Yields from this reaction were about 30 mole percent, based on BeCl_2 used. The ether was removed under vacuum at room temperature rather than by distillation and the reaction mixture was extracted with hexane before the ether was completely removed. The vacuum distillation of the hexane extract at 75 to 85°C (0.001 mm Hg) was complicated by the deposition of large quantities of salt (possibly MgBrCl) as the last traces of ether were removed. A considerable amount of $[(\text{CH}_3)_3\text{C}]_2\text{Be}$ was pyrolyzed to either BeH_2 or $(\text{CH}_3)_3\text{CBeH}$, both of which are non-volatile. A crystalline sublimate was observed in the side arm of the distillation apparatus, but attempts to recover it proved fruitless, as the material decomposed vigorously when exposed to the dry-box atmosphere. This sublimate may have been tertiary-butylberyllium chloride.

Ditertiary-butylberyllium distills as an etherate of nonstoichiometric composition. To determine the ratio of beryllium alkyl to diethylether, NMR spectra of the neat distillates were taken. By integration of the areas of the methyl resonances of diethylether and the methyl resonances

of ditertiary-butylberyllium the $\text{Et}_2\text{O}/\text{t-Bu}_2\text{Be}$ ratio was determined to an accuracy of ± 2 percent. The results of these measurements and the chemical shifts of the tertiary-butyl protons are shown in Table III.

TABLE III
RATIO OF DIETHYLEETHER ASSOCIATED WITH
DITERTIARY-BUTYLBERYLLIUM

<u>Batch</u>	<u>$\text{CH}_3\text{Et}_2\text{O}$ Area</u>	<u>CH_3+Bu Area</u>	<u>$\text{CH}_3\text{Et}_2\text{O}/\text{CH}_3+\text{Bu}$</u>	<u>Formula</u>	<u>T (ppm)</u>
1	20	92	$20/92 = 0.22$	$\text{fBu}_2\text{Be} \cdot 0.7\text{Et}_2\text{O}$	--
2	43	118	$43/118 = 0.36$	$\text{fBu}_2\text{Be} \cdot 1.0\text{Et}_2\text{O}$	9.10*
3	54	116	$54/116 = 0.46$	$\text{fBu}_2\text{Be} \cdot 1.5\text{Et}_2\text{O}$	8.83 ⁺

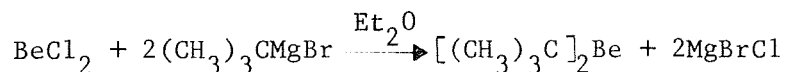
* Internal Me_4Si reference

+ External Me_4Si reference

In all three batches the tertiary-butyl proton resonance was a sharp singlet, indicating the distilled products contained only ditertiary-butylberyllium etherate.

2.5.3 NMR STUDIES OF DITERTIARY-BUTYLBERYLLIUM

Some preliminary NMR studies were made on the reaction:



to see whether kinetic studies could be made. A solution of $\text{BeCl}_2\text{Et}_2\text{O}$ was introduced into a capillary which was placed in an NMR tube containing an ether solution of $(\text{CH}_3)_3\text{CMgBr}$. The contents were frozen in liquid nitrogen and the tube was evacuated and sealed off. When the contents thawed, they were mixed vigorously and NMR measurements started. The first scan taken immediately after mixing showed only the protons

of $(\text{CH}_3)_3\text{CMgBr}$. After five minutes the resonance for $[(\text{CH}_3)_3\text{C}]_2\text{Be}$ appeared 5 cps upfield from $(\text{CH}_3)_3\text{CMgBr}$.

The two peaks were of approximately equal area. After 30 minutes, the $(\text{CH}_3)_3\text{CMgBr}$ resonance had disappeared and only the $[(\text{CH}_3)_3\text{C}]_2\text{Be}$ resonance remained. These results indicate that, with solutions of known concentration, quantitative kinetic measurements can be made and the nature of reaction intermediates may be determined.

An attempt was made to prepare either free ditertiary-butylberyllium by a procedure described by Head, Holley and Rabideau (J.A.C.S. 79, 3687 (1957)).

A sample of ditertiary-butylberyllium etherate was mixed with sufficient BeCl_2 to remove one mole of ether from one mole of ditertiary-butylberyllium. The mixture was stirred with warming at about 40°C overnight. As soon as the reagents were mixed an immediate reaction occurred with the precipitation of a grey sludge (probably beryllium metal). The subsequent vacuum distillation at $75^\circ - 85^\circ\text{C}$ yielded a crystalline sublimate, nonvolatile residue, and a small amount of distillate. An NMR spectrum of the distillate showed that ether was present and at least three tertiary-butyl resonances were detected. Apparently this reaction is more complicated than is indicated in the literature. Further study might lead to the preparation of ether-free $[(\text{CH}_3)_3\text{C}]_2\text{Be}$.

2.5.4 ALKYLBERYLLIUM HALIDES

No preparations of compounds with the formula RBeX , where $\text{R} = \text{Alkyl}$, and $\text{X} = \text{Cl or Br}$, were made, but the reaction $[(\text{CH}_3)_3\text{C}]_2\text{Be} + \text{BeCl}_2 \xrightarrow{\text{Et}_2\text{O}} 2(\text{CH}_3)_3\text{CBeCl}$ was carried out in an NMR tube in the same manner as described above for the preparation of ditertiary-butylberyllium. A scan taken at the time of mixing and another scan ten minutes later

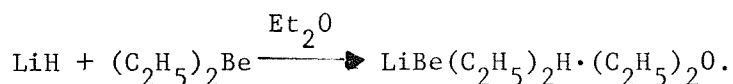
showed no change in position or number of tertiary-butyl resonances. After standing four days at 25°C the mixture was scanned again and a single tertiary-butyl resonance was observed 4 cps downfield from the $[(\text{CH}_3)_3\text{C}]_2\text{Be}$ resonance. The tertiary-butyl resonance did not split when the mixture was cooled to the freezing point of ether (-116°C).

If inductive effects influence the chemical shift of the tertiary-butyl protons (see Kover and Morgan, J.A.C.S. 91, 7269 (1969)) then $(\text{CH}_3)_3\text{C BeCl}$ may have been formed.

2.5.5 ALKYLBERYLLIUM HYDRIDES

Two batches, totalling approximately 3 grams of $\text{NaBe}(\text{C}_2\text{H}_5)_2\text{H}$ were prepared by the reaction $\text{NaH} + (\text{C}_2\text{H}_5)_2\text{Be} \xrightarrow{\text{Et}_2\text{O}} \text{NaBe}(\text{C}_2\text{H}_5)_2\text{H} \cdot \text{X}(\text{C}_2\text{H}_5)_2\text{O}$. A mixture of approximately 0.25 mole of Et_2Be and 2.0 moles of NaH was stirred in diethylether (100 ml) at reflux for 24 hours. The mixture was filtered to remove unreacted NaH and the product was recovered by removing the ether, under vacuum. The product was a sticky white solid, indicating some unreacted diethylberyllium was present. The product was extracted with hexane and filtered; a dry white solid was obtained. The product did not melt (lit.m.p. 257°C) but at about 275°C turned brown and diethylberyllium collected on the cool portion of the melting point tube. No further characterization was made.

One batch of $\text{LiBe}(\text{C}_2\text{H}_5)_2\text{H}$ was made by the reaction:



The reaction conditions and workup were the same as for the sodium salt, but the final product was a clear liquid. Even after additional heating at 50°C for two days under vacuum, the product remained a clear viscous liquid.

An NMR spectrum of this liquid showed the presence of diethyl ether (CH_3 centered at $T = 8.4$ ppm) and another broad methyl resonance centered at $T = 8.1$ ppm. The methylene resonance is a complex multiplet suggesting two overlapping quartets. If the broad methyl triplet can be assigned to ethylberyllium, and the methylene region consists of CH_2 resonances of both diethylether and diethylberyllium, then the conclusion may be made that the liquid product is not diethylberyllium etherate. The NMR spectrum of diethylberyllium shows the methylene protons upfield from the methyl protons. Until further characterization can be made the product is presumed to be $\text{LiBe}(\text{C}_2\text{H}_5)_2^{\text{H}} \cdot (\text{C}_2\text{H}_5)_2\text{O}$.

SECTION 3

CONCLUSIONS

With the hexane extraction technique, large volumes of beryllium plating solutions with high concentrations of diethyl beryllium were prepared. The results on electrolyzing the larger bath of high concentrations yielded only very disappointing thick black powdery deposits.

The beryllium content of plated samples increased from 31 percent to 59 percent (test Nos. 2 and 3) in the deposit upon successive electrolysis of the same solution. Decreasing tetrahydrofuran to diethyl ether ratio from 2 to 0.5 increased the beryllium content from 52.2 percent to 61 percent in the deposit. The deposit with the highest beryllium content (61 percent) was obtained from a bath containing two parts of diethyl beryllium-ether complex, 2.8M BeCl_2 ethereal solution to one part of tetrahydrofuran (test No. 7). On the work done on electrolyzing beryllium chloride dissolved in various organic solvents, no improvement upon the quality of the deposits was noted.

In order to obtain good aluminum deposits, the pyridine concentration had to be maintained at 0.090M and at a current density of 16.15 mA/cm^2 . LiAlH_4 concentration could not exceed 0.5M. It is also apparent that the bath temperature should be controlled, but no work was done in this area. In order to obtain a correlation between the cathode surface temperature and bulk solution temperature, experimental runs must be performed using a thermometer to detect the bulk solution temperature and thermocouples to detect the cathode surface temperature. Once a correlation has been established, the more readily obtainable bulk temperature can be monitored instead of the cathode surface temperature, and can be applied to different configurations of electrode assembly, geometry of test cells, and the circulation and/or agitation of electrolyte, depending upon the magnitude of such differences.

In the study of alloying effects using nonaluminum anodes on the electrodeposition of aluminum, none of the results favorably compared to those obtained from aluminum anodes. In alloying Mg, attempts could be made to introduce MgBr_2 at different stages of electrolyte preparations, such as before the addition of LiAlH_4 to the aluminum chloride ethereal solution. This was not done on this contract.

The nuclear magnetic resonance (NMR) studies of di-tertiary-butylberyllium indicate that, with solutions of known concentration, quantitative kinetic measurements can be made and the nature of reaction intermediates may be determined. It also seems possible that an ether-free $[(\text{CH}_3)_3\text{C}]_2\text{Be}$ can be prepared by mixing di-tertiary-butylberyllium with BeCl_2 . These NMR studies show that many possibilities are yet to be uncovered.