

WADC TECHNICAL REPORT 54-485

PART III

ASTIA DOCUMENT No. AD 110402

## **ELECTRODEPOSITION OF TITANIUM**

*WALTER E. REID, JR.*

*JEAN H. CONNOR*

*ABNER BRENNER*

*NATIONAL BUREAU OF STANDARDS*

*SEPTEMBER 1956*

**MATERIALS LABORATORY**

**CONTRACT No. AF 33(616)-53-11**

**PROJECT No. 7312**

**WRIGHT AIR DEVELOPMENT CENTER  
AIR RESEARCH AND DEVELOPMENT COMMAND  
UNITED STATES AIR FORCE  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO**

Carpenter Litho & Prtg. Co., Springfield, O.  
400 - November 1956

# Contrails

## FOREWARD

This report (NBS Report No. 4806) was prepared by the National Bureau of Standards under USAF contract No. AF(33-616)53-11. This contract was initiated under Project No. 7312, "Finishes and Materials Preservation", Task No. 73120 "Electrodeposition and Electrochemical Treatments", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with A/3C R. G. Christman acting as project engineer.

This report covers work conducted from January 1955 to March 1956.

WADC TR 54-485 Pt. III

*Contents*  
ABSTRACT

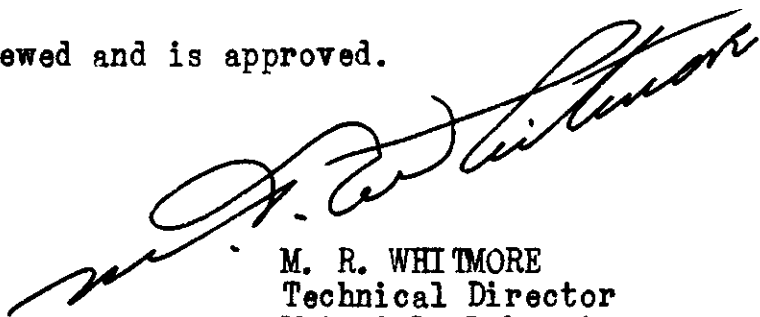
The study of titanium-aluminum alloy baths as described in previous reports [1] was extended. The possibility of using sodium or potassium borohydride instead of lithium borohydride to prepare the titanium and zirconium borohydrides was examined. Among the new compounds prepared for use in the titanium-aluminum alloy bath were chloroborohydride etherates of titanium. Some work was done on the use of organometallic aluminum compounds in a titanium alloy bath rather than the hydride aluminum bath previously used. Alloys of titanium or zirconium with magnesium were obtained from a hydride type of bath. Codeposition of some metals similar to titanium, namely hafnium and thorium, with aluminum from the borohydride bath was studied for purposes of comparison with the titanium-aluminum alloys.

A number of reactions between reactive organic compounds and titanium salts were performed in the search for a suitable titanium plating bath. This included an unsuccessful attempt to prepare ethyltitanium and a tetraphenyl borate derivative of titanium.

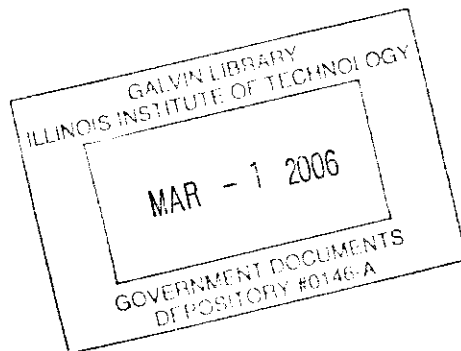
PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. WHITMORE  
Technical Director  
Materials Laboratory  
Directorate of Research



# TABLE OF CONTENTS

	Page
I. Introduction .....	1
II. Preparation of borohydrides .....	1
A. Titanium and zirconium borohydride .....	1
B. Titanium chloroborohydrides .....	2
C. Related silicon hydride compounds .....	3
III. Alloy plating solutions .....	4
A. Hafnium and thorium .....	4
B. Alloys of titanium or zirconium with magnesium and aluminum .....	4
C. Aluminum triethyl plating solutions .....	5
D. Titanium alloy baths containing titanium tetrafluoride .....	7
E. Alloys of titanium with tin .....	8
IV. Organotitanium compounds .....	8
A. Ethyltitanium .....	8
B. Phenyltitanium .....	9
C. Bis-cyclopentadienyltitanium (II) .....	10
V. Miscellaneous electrolysis experiments .....	11
A. Boron trifluoride complexes .....	11
B. Titanium tetrafluoride .....	11
C. Sodium azide .....	11
D. Sodium tetraphenyl borate .....	12
E. Triphenylmethyl sodium .....	12
VI. Bibliography .....	13

## I. Introduction

The electrodeposition of titanium from organic solvents has previously been shown (1) to be most promising from baths consisting of an ether and a soluble, reactive titanium compound, such as titanium borohydride. The most promising baths contained titanium borohydride, lithium aluminum hydride, and aluminum chloride and yielded a titanium-aluminum alloy containing about 6.5% titanium. From a similar bath zirconium-aluminum alloys were obtained containing up to 45% zirconium. We have extended our study of these baths in an attempt to increase the titanium content of the alloys. In addition a number of other types of organic baths have been prepared with various titanium solutes, some of which had not previously been examined.

## II. Preparation of Borohydrides

### A. Titanium and Zirconium Borohydrides

By reacting sodium or potassium borohydride in place of lithium borohydride with titanium or zirconium halides, zirconium or titanium borohydrides were obtained directly in ether solutions. However, the yields by this method were much lower than with lithium borohydride.

#### 1. Zirconium Borohydride

Zirconium tetrachloride, potassium borohydride and ether were placed in a steel container with grinding balls. After several hours of ball-milling, the yield of zirconium borohydride in ether was about 30 to 50 percent of theoretical based on borohydride. The substitution of sodium borohydride for potassium borohydride decreased the yield to about 15 percent. The possibility of a reversible reaction was investigated and it was found that potassium chloride and zirconium borohydride did not react. Prolonged grinding and use of excess potassium borohydride did not increase the yield. Doubling the volume of ether increased the yield only slightly, as did prolonged standing at room temperature. The yield was also increased slightly by use of excess zirconium tetrachloride. The product could not be concentrated by vacuum distillation. This method of preparation was abandoned.

#### 2. Titanium Borohydride

The ball-milling of titanium tetrachloride and potassium borohydride in ether at room temperature resulted in a reaction. This was indicated by the formation of a greenish-brown solution. Hydride analysis indicated that the yield was about 30 percent. At dry ice temperature no reaction occurred. With lithium borohydride used in place of potassium borohydride the reaction proceeded almost to

completion at a slow rate and produced an ether solution, 1.24 M in titanium borohydride.

### B. Titanium Chloroborohydrides

Since titanium borohydride has been used to obtain titanium-aluminum alloy deposits, it appeared that other borohydride compounds of titanium should be tried. In order to prepare new chloroborohydride compounds, diborane was passed into ethyl ether and tetrahydrofuran solutions containing titanium esters of the type  $Ti(OR)_N Cl_{4-N}$ . The reactions are summarized below:

<u>Solvent</u>	<u>Ester Used</u>	<u>Compound isolated from solution</u>	<u>Color</u>
1. Ethyl ether	$(C_4H_9O)_2 TiCl_2$	$(C_4H_9O)TiCl_2$	Red brown solid
2. "	$(C_4H_9O)_3 TiCl$	$(C_4H_9O)_2 TiCl$	Black solid
3. Tetrahydrofuran	$(C_4H_9O)TiCl_3$	$TiCl_3 \cdot (C_4H_8O)_3$	Pale blue solid
4. "	$(C_4H_9O)_2 TiCl_2$	$TiCl_3 \cdot (C_4H_8O)_3$	Pale blue solid
5. "	$(C_4H_9O)_3 TiCl$	$Ti(BH_4)_2 Cl \cdot C_4H_8O$	Dark blue solid

In each of the above experiments the product which separated from the solution was isolated for examination. With the exception of experiment 5, an insoluble product was formed almost at once. The product from reaction 5 was quite soluble and precipitated only after concentration and cooling of the solution. Experiment 4 gave the same product as experiment 3, but the amount isolated was much less. On further standing another product separated from the solution of experiment 4 which possessed borohydride activity but it was not analyzed. It is probable that reaction 4 gives two products:  $TiCl_3 \cdot (C_4H_8O)_3$  and  $Ti(BH_4)_2 Cl \cdot C_4H_8O$ . The latter compound may be formed by a rearrangement during the reaction.

The presence of the chloro radical in these esters decreases their reactivity towards diborane and they apparently yield borohydride compounds only in the presence of a strongly complexing solvent such as tetrahydrofuran as shown in the above table. It is of interest to note that the coordination number of the borohydride compound formed in tetrahydrofuran is four, but for the chloro compound it is six.

*Controls*

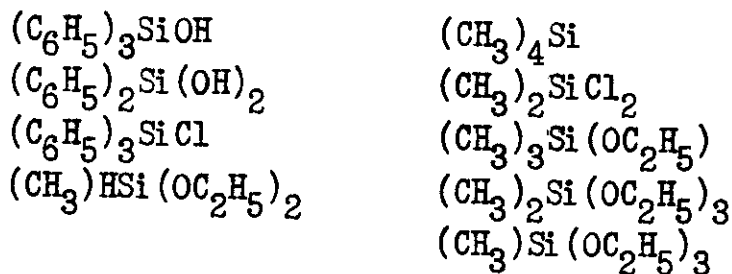
Electrolysis of the mother liquor from these reactions did not give a metallic deposit, although the solutions conducted well. Electrolysis of each of the types of compounds obtained (i.e.  $(C_4H_9O)TiCl_2$ ,  $TiCl_3 \cdot (C_4H_9O)_3$ , and  $Ti(BH_4)_2Cl \cdot C_4H_9O$ ) in aluminum-hydride plating solution gave titanium-bearing deposits, but these baths were more unstable than the titanium borohydride baths described in previous reports (1) and no improvement in the deposits was noted. For example, after the filtered solution from experiment 4 had stood for several days, some of the blue crystals which settled out were added to an aluminum-hydride plating solution. This bath gave an alloy deposit containing 7 percent of titanium, but it was poorer in appearance than the titanium alloy deposits which have been described in our earlier reports.

### C. Related Silicon Hydride Compounds

Silicon forms a series of hydrogen compounds similar to the hydrogen compounds of boron, the simplest of which is silane,  $SiH_4$ . Preliminary experiments indicated that the silicon hydride compounds may be similar to the borohydrides in reactivity. For example, methyl diethoxy silane will reduce titanium tetrachloride, presumably to the trivalent state. If silicon compounds similar to the borohydrides existed, they would be of interest as solutes in titanium plating solutions.

Attempts were made to prepare a titanium silicon hydride compound by reacting silane or methyl silane with tetraisopropyl titanate and also with titanium tetrachloride. This reaction would be analogous to the reaction of diborane ( $B_2H_6$ ) with titanium esters ( $Ti(OR)_4$ ) to form titanium borohydride. However, no reaction occurred when the silicon gases were passed through ether solutions of the titanium compounds.

A number of other silicon compounds were investigated in organic solutions containing titanium solutes. The silicon compounds investigated are listed below:



These solutes were added to ether solutions containing tetravalent or trivalent titanium halides. Titanium chlorides, bromides, and iodides were used. No titanium alloy deposits were obtained on electrolysis even when aluminum-hydride plating solution was added to the baths.

In another experiment silane reacted with pure tetrabutyl titanate to give a brown solid product containing 21.6 percent titanium (primarily in the trivalent state), apparently tributyl titanate. Lack of reactivity with water indicated that there was no hydride activity in the products. Evidently the only reaction was the reduction of the tetravalent titanium to the trivalent state. Electrolysis of the reaction products yielded no deposits of titanium.

### III. Alloy Plating Solutions

#### A. Hafnium and Thorium

To gain some insight on the possibility of increasing the titanium content of the titanium-aluminum alloys obtained from the borohydride baths, a short survey of the behavior of similar metals in the same type of solution was made. These baths were prepared in the same way as the titanium and zirconium borohydride-aluminum hydride baths described previously [1, p 24]. The maximum hafnium content of the alloy deposits obtained from such baths was about 8.5 percent. The baths containing thorium did not yield a thorium-aluminum alloy. Of the four metals investigated in the borohydride-aluminum hydride type of bath the best results were obtained with zirconium in the form of zirconium-aluminum alloys containing up to 45 percent zirconium.

#### B. Alloys of Titanium or Zirconium with Magnesium and Aluminum

The possibility of obtaining titanium or zirconium alloys containing magnesium was investigated. In general, the deposits obtained were unsatisfactory, being highly stressed, and the solutions were poor conductors. Only traces of titanium were obtained in the deposits. The deposits which contained 10 percent zirconium exfoliated. The following systems were studied:

##### 1. Titanium

Titanium borohydride tetrahydrofuranate, magnesium bromide, and magnesium aluminum hydride were reacted in ethyl ether and the resulting solution electrolyzed. The conductivity of this solution was low and electrolysis of this solution gave a deposit of poor appearance.

Titanium borohydride tetrahydrofuranate and magnesium aluminum hydride reacted in ether to form a brown precipitate. The addition of aluminum chloride to this bath caused gas evolution and the



formation of a metallic deposit on the wall of the cell. Gas evolution continued during the electrolysis of this poorly conducting solution and a metallic deposit was obtained which gave a qualitative test for titanium. Only a black moisture-sensitive deposit could be obtained from the bath after gas evolution ceased.

The reaction of magnesium borohydride with titanium tetrabromide in tetrahydrofuran was vigorous and an orange colored solid settled out of solution. Electrolysis of this solution gave a magnesium deposit which did not contain titanium.

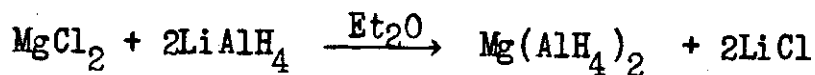
## 2. Zirconium

Magnesium aluminum hydride reacted with an ether solution of zirconium borohydride to form a white solid which did not appear to be appreciably soluble. Aluminum chloride was added and electrolysis of the solution gave a stressed metallic deposit containing 10 percent zirconium. On standing the solution separated into two layers of which the more dense layer yielded better deposits on electrolysis. Neither layer, however, yielded deposits as sound as those obtained from the freshly prepared solution.

The plating solutions described above may be summarized as follows:

<u>Solution Composition</u>	<u>Remarks</u>
1. $\text{Ti}(\text{BH}_4)_3 \cdot \text{C}_4\text{H}_8\text{O}$ ; $\text{Mg}(\text{AlH}_4)_2$ ; $\text{AlCl}_3$ ; ether	Poor deposit, low conductivity of solution
2. $\text{Ti}(\text{BH}_4)_3 \cdot \text{C}_4\text{H}_8\text{O}$ ; $\text{Mg}(\text{AlH}_4)_2$ ; $\text{AlCl}_3$ ; ether	Fair Al deposit with trace of Ti
3. $\text{TiBr}_4$ ; $\text{Mg}(\text{BH}_4)_2$ ; tetrahydrofuran	Fair Mg deposit, no Ti
4. $\text{Zr}(\text{BH}_4)_4$ ; $\text{Mg}(\text{AlH}_4)_2$ ; $\text{AlCl}_3$ ; ether	Stressed deposit, 10% Zr

The magnesium aluminum hydride used in these baths was prepared by the following reaction:

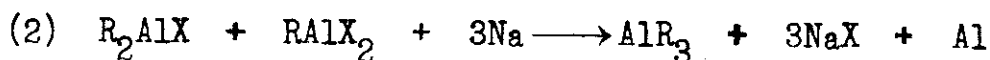


## C. Aluminum Triethyl Plating Solutions

The electrodeposition of aluminum from aluminum triethyl-sodium fluoride complex, using an aluminum anode has been claimed by Ziegler [2]. Although details of the process were not available to us at the time, attempts were made to duplicate the experiment, and to carry it further to see if titanium would codeposit with aluminum. The use

of sodium fluoride as a complexing agent is unusual. Alkali metal halides, except for the fluorides, have been used for some time to improve the conductivity of nonaqueous solutions, but little is known of their complexing ability. In order to determine if sodium fluoride complexed with other metal alkyls, this compound was reacted with beryllium alkyls which were on hand. A preliminary experiment indicated that sodium fluoride did not form a complex with beryllium alkyls.

Aluminum triethyl was prepared according to Grosse and Mavity [3]:



where RX = ethyl iodide

The aluminum alkyl, obtained on vacuum distillation, gave 97.4 percent of the theoretical quantity of gas on hydrolysis. It is a colorless, viscous liquid that is flammable in air and sensitive to minute traces of oxygen. The pure material did not conduct. The aluminum triethyl-sodium fluoride complex which was prepared by direct addition of sodium fluoride to the pure alkyl, had a fair conductivity and yielded a white deposit of aluminum on electrolysis. The complex had a lower conductivity in ether solution, but yielded a fair deposit of aluminum.

#### Aluminum Triethyl and Various Titanium Compounds.

Titanium tetrafluoride was found to be soluble in aluminum triethyl, but the trifluoride had very little solubility. Neither solution conducted. Addition of ether resulted in solutions which yielded good metallic deposits of aluminum containing traces of titanium. The addition of sodium fluoride greatly improved the conductivity of the baths, but did not increase the titanium content of the deposits.

The electrolysis of an ether solution of sodium titanium (III) chloride and aluminum triethyl yielded a sound titanium aluminum alloy deposit containing a small amount of titanium (determined qualitatively).

Titanium trichloride, potassium fluorotitanate, and potassium fluoro-zirconate were not satisfactory as solutes due to their low solubility and poor conductivity.

## D. Titanium Alloy Baths Containing Titanium Tetrafluoride.

### 1. Titanium-Lithium Alloys.

Alloys of titanium and lithium which were black and coherent were readily obtained from solutions of titanium tetrafluoride and either lithium borohydride or lithium halides. However, the properties of lithium make these alloys undesirable, and the solutions will be only briefly described.

Titanium tetrafluoride was fairly soluble in tetrahydrofuran. The solution was moderately conductive. Electrolysis of this solution to which lithium borohydride had been added, yielded a deposit containing titanium and lithium. The deposit could not be built up. Sodium-, potassium-, and lithium fluorides were only slightly soluble in a solution of titanium tetrafluoride in tetrahydrofuran. The lithium halides, lithium chloride and lithium iodide were quite soluble and greatly improved the conductivity. Lithium iodide yielded the best titanium-lithium alloy deposits. Such a deposit from a bath containing lithium iodide and titanium tetrafluoride in tetrahydrofuran was black and coherent. It gave a qualitative test for titanium and was comparable to the deposit from a bath containing lithium borohydride and titanium tetrafluoride in tetrahydrofuran. The same type of titanium-lithium alloy deposit was obtained from similar baths made with other solvents, namely acetonitrile, acetone, and diethylene glycol dimethyl ether.

### 2. Titanium-Aluminum Alloys.

A titanium-aluminum alloy was obtained from a bath containing titanium tetrafluoride, aluminum chloride and both ethyl ether and tetrahydrofuran. The deposits were black and metallic; the presence of titanium was indicated by qualitative tests. This work was interrupted by the closing of the project.

### 3. Codeposition of Titanium with Other Metals.

(a) Cobalt. A black deposit was obtained on electrolysis of a solution containing anhydrous cobalt chloride, and titanium tetrafluoride in tetrahydrofuran. Cobalt and titanium were identified in the deposited material. Thick deposits could not be obtained as the material exfoliated.

(b) Chromium and Nickel. Neither chromium trifluoride nor nickel acetate could be substituted for cobalt chloride in the bath described above because of their low solubility.

## E. Alloys of Titanium with Tin.

Since tin-titanium alloys were obtained in the course of preparing phenyltitanium (see below), experiments were performed to see if combinations of tin and titanium compounds would yield alloy deposits containing appreciable amounts of titanium. This work resulted in white, metallic deposits containing on an average of 2 percent of titanium.

Tin is readily deposited from organic solutions, but the deposits are generally mossy and the cathode efficiency is low. The tin compounds used were dimethyl tin dichloride and anhydrous stannous chloride. They yielded deposits from the following solvents: tetrahydrofuran, dimethyl formamide, and acetonitrile. To these solutions was added one of the following two titanium solutes: (1) tetraisopropyl titanate and (2) a titanium (III) compound formed by reduction of titanium (IV) chloride with lithium hydride, as described in Part I of this report [1, p. 54]. In general, these solutions had good conductivity and yielded thin, white, metallic deposits which dissolved very slowly in concentrated hydrochloric acid. The deposits were difficult to build up because of treeing and formation of powdery layers. Termination of the project did not allow time for studies of the effect of the concentrations of the bath constituents on the composition of the deposit, nor for an investigation of the effect of addition agents.

## IV. Organotitanium Compounds.

### A. Ethyltitanium.

The dicyclopentadienyltitanium (IV) dibromide and phenyltitanium compounds which we have described [1] did not form suitable plating baths in organic media. For this reason attempts were made to prepare an ethyltitanium derivative, which would have greater ability to form ionic complexes.

We restricted our work to the reaction of ethyllithium with various titanium compounds in several solvents at different temperatures.

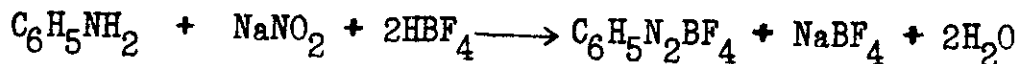
The first phase of this study involved the preparation of ethyllithium. Two methods of preparing ethyllithium were found to be satisfactory. The first involved the reaction of lithium sand with ethyl bromide in petroleum ether at reflux temperature. The second method was similar except that the reaction was carried out at room temperature in a sealed grinding mill. The yield of product by either method was about 60 percent. The second method was most rapid and convenient. In both cases the ethyllithium was extracted with hot

petroleum ether, concentrated, and dried. The solid compound was more convenient to store and handle than the solution.

The titanium compounds which were used in the attempted synthesis of a titanium alkyl derivative included:  $TiCl_4$ ,  $TiCl_3$ ,  $TiBr_3$ ,  $Ti(BH_4)_3$ , and  $Ti(OC_3H_7)_4$ . These compounds were reacted with ethyllithium in the following organic solvents: ethyl ether, xylene, benzene, petroleum ether, and tetrahydrofuran. Most of these experiments were performed at room temperature. Usually a reaction occurred immediately yielding a brown solution from which a dark solid separated. Examination of both the filtrate and residue indicated that no titanium alkyl derivatives were present. To determine if titanium alkyl derivatives were formed at a lower temperature, several experiments were performed at dry ice temperatures. However, the same results were obtained as at room temperature indicating that the reaction did not yield a product which was more stable at the low temperature. In several instances indirect evidence was obtained of the formation of an addition compound, but isolation and analysis of the solids did not reveal a compound of a definite composition. For example, under certain conditions titanium trichloride reacted with ethyllithium in xylene to form a green solid but under certain other conditions to form a black solid. When the solvent was tetrahydrofuran a powder-blue solid was isolated. All the solutions prepared were electrolyzed. In general, the conductivity was very low and in most cases they did not conduct at all. In no case was a metallic deposit obtained.

#### B. Phenyltitanium.

Phenyl derivatives of copper, mercury, arsenic, etc. have been prepared through the use of phenyl diazonium fluoborate. This compound was investigated to see if phenyltitanium could be produced similarly. Phenyl diazonium fluoborate was prepared by the method described in reference [4]:



The phenyl diazonium fluoborate was mixed with various titanium compounds in such solvents as toluene, tetrahydrofuran or butyl ether and heated to 70°C. The titanium compounds used were: titanium tetra- and trichloride, titanium dibutoxy dichloride, sodium titanium (III) chloride, and tetraisopropyl titanate. Another variant was the presence or absence of precipitated copper or stannous chloride. Reactivity was indicated by various color changes, changes in conductivity, and gas evolution.

*Conclusions*

Only with titanium tetrachloride, titanium dibutoxy dichloride and sodium titanium (III) chloride was there evidence of a reaction. Since no deposits were obtained on electrolysis of the solutions, the reaction products were not isolated. None of the reaction mixtures gave a positive Michler's ketone test for a carbon to metal bond. There was an uncertainty in some cases due to the dark colors of the product obscuring the ketone test color.

The best result was obtained with tetraisopropyl titanate. This is rather surprising because this compound has always been the least reactive of the titanium compounds under investigation. It was reacted with the diazonium compound and stannous chloride with tetrahydrofuran as solvent to yield a red solution which on electrolysis yielded a grey, metallic deposit. A spectrochemical analysis indicated that the major constituent of the deposit was tin and that it contained titanium. No deposit was obtained in the absence of stannous chloride. When the stannous chloride was added after the reaction had taken place, rather than at the beginning, the solution yielded an electrodeposit that contained much less titanium. This was roughly determined by color comparison tests.

Since these results indicated that titanium would codeposit with tin, other combinations of tin compounds and titanium compounds were tried. These are described under alloy baths.

#### C. Bis-cyclopentadienyltitanium (II).

Bis-cyclopentadienyltitanium (II) has been mentioned in the literature [5]. Birmingham, who prepared this compound, stated in an interview that this compound is appreciably more reactive than the other organo-titanium compounds which have been isolated. In view of this it was felt that this compound would be more susceptible to electrodeposition than the other cyclopentadienyltitanium compounds previously studied.

The compound was prepared in this laboratory by reacting sodium cyclopentadiene with a titanous salt ( $\text{NaTiCl}_4$ ) in tetrahydrofuran. An excess of sodium was required. The product was isolated by evaporation of the tetrahydrofuran and extraction of the residue with ether.

The compound was only slightly soluble in organic solvents, ranging from about 0.1 g/100 ml in petroleum ether to about 7 g/100 ml in tetrahydrofuran. The solvents investigated were: petroleum

ether, ethyl ether, propylene glycol, benzene, dimethylformamide, anisole, tetrahydrofuran. No conducting solutions were obtained. The addition of various complexing solutes such as hydrides and borohydrides to these solutions did not yield titanium or titanium alloy plating solutions.

## V. Miscellaneous Electrolysis Experiments

In the following experiments, which were essentially of an exploratory nature, no titanium electrodeposits were obtained. They are included to show the variety of systems investigated.

### A. Boron Trifluoride Complexes

A number of boron trifluoride complexes were electrolyzed using sodium titanium (III) chloride and also titanium tetrachloride as the solute. The boron trifluoride complexes investigated included those of ammonia, urea, trimethyl amine, piperidine, ethyl amine, hexamethylenetetramine, para-cresol, acetic acid, ethyl cellosolve, and triethanolamine. Those complexes which are solids at room temperature melted between 200° and 300°C to give fluid baths. No satisfactory deposits were obtained from any of the baths nor from baths which were diluted with ether.

### B. Titanium Tetrafluoride.

The electrolysis of titanium tetrafluoride in the following solvents could not be investigated either because of insolubility or formation of an insoluble reaction product.

ether	bromobenzene
tetraethylene glycol dimethyl ether	toluene
triethylene glycol dimethyl ether	diethylamine
ethylene glycol dibenzyl ether	pyridine
phenetole	ethylene diamine
dioxane	dimethylaniline
butyl alcohol	tripropylamine
methyl butynol	dimethylformamide
p-xylene	dimethylcyanamide
benzene	chlorothiophene

The reaction of titanium tetrafluoride in tetrahydrofuran is described under alloy baths, above.

### C. Sodium Azide

Sodium azide ( $\text{NaN}_3$ ) was added to titanium tetrachloride in ether and the resulting solution on electrolysis yielded at the cathode

a black nonmetallic material containing titanium and chloride. This material was not obtained from the electrolysis of titanium tetrachloride in ether alone. When titanium tetrafluoride was used in place of titanium tetrachloride a solution of trivalent titanium formed; there was no similar reaction with tetraisopropyl titanate. Because of the inability to obtain a thick deposit and the low conductivity of these solutions, they were not investigated further.

#### D. Sodium Tetraphenyl Borate

No metallic deposits were obtained from solutions of titanium tetrachloride, containing sodium tetraphenyl borate, in ether.

#### E. Triphenylmethyl sodium. (Na C (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>).

The preparation of this compound [6] was modified by using a steel container and shaking the reactants for 3 to 4 hours. A 50 percent yield was obtained.

The solution of triphenylmethyl sodium in ether was moderately conductive. The ether solution was reacted with the following compounds:

titanium tetrafluoride	titanium trifluoride
titanium tetrachloride	triisopropyl titanate
sodium titanium chloride	tributyl titanate
titanium trichloride	lithium titanium bromide
cyclopentadienyl titanium dibromide	titanium hydride
	zirconium tetrabromide
	molybdenum trichloride

The resulting solutions had very low conductivity, usually around 2 ma/110 v. However, with titanium tetrachloride, the resulting black solution had much better conductivity, and with an excess of the tetrachloride a black oil was formed. No metallic deposits were obtained.



VI. Bibliography

- [1] WADC-TR-54-485, Parts I (September, 1954) and II (February, 1955).
- [2] Chem. and Eng. News 33, 3486 (1955).
- [3] A. V. Grosse and J. M. Mavity, J. Org. Chem. 5, 106-21 (1940).
- [4] Org. Syntheses Coll. Vol. II, Wiley and Sons, P. 225 (1943).
- [5] G. Wilkinson and J. M. Birmingham, J. Am. Chem. Soc. 76, 4281 (1954).
- [6] Org. Syntheses Coll. Vol. II, Wiley and Sons, P. 607 (1943).