Contrails

ELECTRODEPOSITION OF TITANIUM

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FOREWORD

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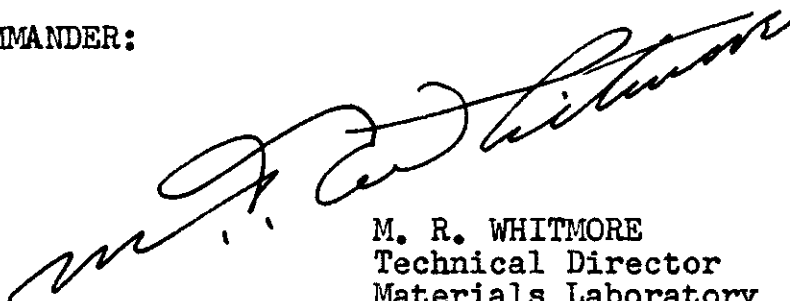
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ABSTRACT

Numerous non aqueous solutions were investigated in an attempt to electrodeposit titanium. Some work was also done with zirconium. Ether solutions containing halides, hydrides, borohydrides, and organo-metallic compounds of titanium were the most promising solutions investigated. A mixed type of bath containing both hydrides and borohydrides yielded titanium-aluminum alloys containing about six percent titanium. Similar baths containing zirconium, instead of titanium, were studied. The zirconium baths gave alloy deposits containing up to 45 percent zirconium.

New methods of preparation of titanium and zirconium borohydrides were developed.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

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

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Aqueous Media

INTRODUCTION

Of the 72 metallic elements only about 30, or less than
half, can be electrodeposited from aqueous solution. Many of
the metals which can not be deposited from aqueous solution
would have very useful applications if they could be obtained
in the form of coatings or electroformed. Among these metals
are some which are now of considerable interest, -titanium,
zirconium, molybdenum, tantalum, and tungsten. Since a major-
ity of the metals could not be deposited from aqueous solution,
electrochemists turned their attention to non-aqueous media.
These are of two types, fused salts and compounds which are
liquid at ordinary temperatures, consisting mainly of organic
compounds.

All metals can be deposited from a fused electrolyte.
However, electrodeposition from fused electrolytes has not
solved the problem of obtaining coatings of these metals
because with few exceptions the deposits are obtained in the
form of powders, crystals, sponges, or dendrites which are
of no value as coatings. Metals in this form may be of value
for electrowinning purposes. Eventually, methods for obtain-
ing smooth coatings from fused electrolytes may be developed.

Solvents which are liquid at room temperature comprise a
small number of inorganic compounds and a large number of
organic liquids. Also should be included the organic or in-
organic compounds which are solid at room temperature, but
which may be readily melted, for example, below 100°C. In
contrast to the universality with which metals have been
deposited from fused salts, few metals are depositable from
organic solvents. It is true that a number of the common
metals especially the more noble ones such as copper, silver,
or nickel can be deposited from numerous organic solvents,
but this is of no practical importance since these metals
are readily deposited from water solutions and such metals
will not be further considered here. Our interest in the
deposition of metals from organic solvents is concerned with
those metals which can not be deposited from aqueous solution.
These metals will be referred to collectively as the non-
aqueous group, and designated as NQ.

Although the literature contains a number of publications on the electrodeposition of metals from organic solvents, the studies have been rather desultory and up until recent years no satisfactory plating bath for depositing a metal as a sound coating with good mechanical properties was developed. Work reported in the literature covers a wide miscellany, ranging from the electrodeposition of the alkali metals lithium, sodium, potassium to some of the more noble metals such as copper. Of the NQ metals besides the alkali metals the literature has touched on electrodeposition of magnesium, beryllium, germanium, and aluminum, the latter probably receiving the largest amount of attention. The practical accomplishments reported in the literature are disappointing. Magnesium was deposited from Grignard reagents, but in a mossy form which probably was heavily contaminated with organic matter. The reported electrodeposition of beryllium from ammonia and other solvents has not been substantiated by us. The deposition of germanium from a glycol type bath occurs with very low cathode current efficiency. The deposition of aluminum from organo-metallic compounds of either the alkyl type or Friedel-Craft reagents did not yield good deposits. The ethyl pyridinium bromide-aluminum chloride bath of Wier and Hurley was one of the first satisfactory non-aqueous plating processes, but it is like a fused salt bath rather than the solvent type in which we are interested here. It yielded the best deposits of aluminum obtained from an organic bath up to that time. Our recent development of an organic aluminum plating bath (1) based on the utilization of hydrides encouraged further studies of baths consisting of organic solvents.

GENERAL PRINCIPLES

The failure of early workers in electrodeposition to obtain active metals like aluminum from water solutions was clearly understood. It is known that the electrodeposition of a metal usually requires a potential which is less noble than its standard electrode potential. The potentials which can be reached at the cathode in aqueous solution are limited by the discharge of hydrogen which usually occurs at a less noble potential than its true equilibrium value, in some cases amounting to a volt. This phenomenon known as overvoltage makes possible the electrodeposition of zinc from aqueous solution, since hydrogen is discharged on zinc less readily than zinc itself.

Because of the important role of hydrogen in electrolysis of water solutions in determining which metals can or can not be deposited, it was assumed that the NQ metals could be obtained by simply electrolyzing solutions of their salts dissolved in solvents which have no active hydrogen or in which the hydrogen was less easily detached. This theory is supported

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by the fact that the alkali metals are obtained by electrolysis of solutions of their salts in organic solvents.

However, the non-deposition of certain metals from aqueous media is not explained entirely by the limitation imposed by hydrogen discharge. For example, tungsten, molybdenum, tantalum, and germanium can not be deposited from aqueous solution in the pure state. Yet, their theoretical electrode potentials calculated from thermodynamic data are more noble than that of hydrogen. Therefore, these metals should be capable of being electrodeposited from aqueous solution. The fact that alloys containing 30% or more of tungsten, molybdenum, germanium and phosphorus can be obtained shows that the possibility exists of depositing these elements.

The reason that these metals do not readily deposit must be sought in a different phenomenon than electrode potentials. We believe that the basic reason for the nondeposition of these metals is the arrangement of the atoms in the ion. Even if an ion is thermodynamically capable of discharging at potentials more noble than hydrogen the structure of the ion may be such that it is incapable of complete reduction at the cathode. Partial reduction of titanium or molybdenum compounds to lower valences is observed in many solvents, but there is an oxidation state below which they cannot be taken. This would indicate that the electrode reaction for complete reduction and the reaction of the solvent with the partially reduced ion may be competitive; the reaction of the reduced ion with the solvent occurring almost completely. This vague concept is not of itself a theory, but it does serve to place the phenomenon of nondeposition in the proper category. That is, nondeposition is not a result of unfavorable electrode potentials, but rather a result of non-reactivity. The phenomenon is thus in the same category as the numerous purely chemical reactions which are thermodynamically possible, but which for some reason do not occur, for example, the combination of oxygen and nitrogen in the air to form oxides of nitrogen or with water to form nitric acid.

The latter explanation of nondeposition requires a quite different approach to the problem of deposition of the metals of the NQ group other than the alkali metals. Obviously, the use of solvents in which the hydrogen is bound more tightly, might be no more effective than water for permitting deposition of the NQ metals, if the ions do not accept electrons. Success apparently must be brought about by the discovery of new types of ions in new types of environments. Such a search is quite empirical.

The subject of non-aqueous deposition will now be considered in relation to that particular group of NQ metals in which we are mainly interested here: beryllium, aluminum, magnesium, tungsten, and molybdenum. It is possible that some of these metallic elements may be nondepositable. Others may not deposit from certain types of solvents, but for different reasons in each. For example, beryllium may not deposit from water solutions because of an unfavorable electrode potential; from another solvent because of the non-reactivity of the ions at the cathode. The work to be described in these reports indicates that the difficulty associated with the NQ metals is due to the structure of the ion rather than electrode potentials. Related to this subject and in a sense supporting these views is the work of Dr. Lyons(2), who found that deposition of metals from aqueous solutions of different complexes was determined by the electronic structure of the complex. Certain types of ions discharge readily at a cathode and others do not. It is difficult to relate the property of an ion, that makes it capable of discharging to yield a metal, with any of the properties by which complex ions are characterized, such as electrode potentials, substitution reactions, radioactive exchange, and chemical stability. On the basis of this analysis there is no simple means of bringing about the deposition of an NQ metal if its ions are non-reactive except through codeposition with another metal, for example, deposition of tungsten in presence of nickel.

A - Types of Salts and Solvents for Depositing the NQ Metals

In attempting the deposition of the NQ metals all researches have followed a similar pattern of investigation in which the available soluble salts of the desired metal were dissolved in a variety of organic solvents and the solutions electrolyzed. This sort of desultory approach has not yielded tangible success. In our work we too passed through these same initial stages, but it has gradually become clear that the solutes used in the organic solvent plating baths must be quite different from the salts used for the aqueous type of baths. Specifically, this means that an ionic salt, which yields a good aqueous plating bath, may not yield a plating bath at all when dissolved in an organic solvent, or may not even form a conducting solution. The almost exclusive study of one type of plating system - aqueous salt solutions - has resulted in the impression that certain compounds such as salts are inherently ionic and always form conducting solutions while other compounds are covalent and are inherently nonconducting. A certain amount of this lore must be unlearned. Many examples can be given of compounds that form conducting solutions in one solvent but not in another. For example, molybdenum pentachloride forms a conducting solution in water, a poorly conducting solution in ether and a nonconducting solution in toluene.

HCl forms a highly conducting solution in water but not in ether. A typical salt like silver perfluobutyrate forms a conducting solution in water but is not conducting in benzene although it is highly soluble.

Numerous observations have lead to the belief that in non-aqueous plating baths the solvent and solute must be capable of coordinating to form a complex. No pure uncoordinated organic liquid conducts electricity, and few inorganic liquids at room temperature.

Whether or not the solution of a complex will conduct or yield a metal on discharge can not be predicted. Examples of the formation of conducting complexes which on electrolysis give metal are beryllium dimethyl in ether and sodium naphthalene in dimethoxy ethane; examples of those which do not give metal are titanium tetrachloride in acetonitrile and beryllium chloride in dimethyl aniline. Many non-aqueous solutions have good conductivity, but yield no metal on electrolysis.

A misconception that arises as a result of too much emphasis on aqueous solutions is that solvents must have a high dielectric constant in order to form conducting solutions. Water with its dielectric constant of 80 is cited as the outstanding example and contrasted with organic solvents of dielectric constants of only 5 to 10 which appear to be poorly ionizing media for salts. This misconception should be laid at rest. On the one hand we find that liquid HCN has a dielectric constant of 95 which is higher than that of water but does not appear to be as nearly as good an ionizing solvent. On the other hand ordinary diethyl ether with a dielectric constant of only 5 has proved to be our best non-aqueous solvent for plating baths. To obtain conductivity in organic solvents a different type of solute is required than for water solutions.

To summarize the ideas at this point, conductivity of, and electrodeposition from, nonaqueous media seems to depend on the specific interaction of solvent and solute to form an ionizable coordination compound rather than on physical properties such as crystal structure of the compound or the dielectric constant of the solvent. The compounds which ionize to give a conducting solution are often not isolatable, but exist only in solution. For example, the aluminum hydride plating bath is of this type. Both aluminum chloride and lithium aluminum hydride in ethyl ether are very poor conductors individually. When the two solutions are mixed, the resulting solution is a good conductor and yields a metallic deposit on electrolysis.

B - Chemical Nature of Solutes and Solvents for
    Non-Aqueous Electrodeposition

Our limited experience with the solutes and solvents required for successful electrodeposition from non-aqueous baths has pointed toward certain qualitative facts: Only certain types of metallic compounds seem to be satisfactory as solutes in non-aqueous baths. In general these must be simple compounds of low molecular weight and the radicals involved must be rather small. Actually only four classes of compounds have given any promise of success. These are metallic halides, hydrides, borohydrides, and organometallic compounds. Several features of this group will be pointed out shortly. Similarly, the group of non-aqueous solvents which can be successfully utilized as a plating bath are also very limited, the ethers being the most useful.

As pointed out above, the solvent must be capable of coordinating with the solute. This at once eliminates non-reactive liquids such as paraffin hydrocarbons and some of their halogen derivatives. A large variety of organic liquids form coordination compounds with the classes of compounds of metals mentioned above. Among these are oxygen containing compounds such as alcohols, ethers, ketones, amides, acids, etc., nitrogen containing compounds such as amines, amides, nitriles, and unsaturated hydrocarbons such as benzene and toluene. The molecules of these solvents have an active center consisting of an atom of either nitrogen, oxygen, or carbon which is not chemically saturated and is capable of coordinating with other compounds. Our experience indicates that solvents which coordinate too strongly with metal derivatives form complexes from which metals can not be electrodeposited. For example, none of the metals in which we are interested have been successfully deposited from solvents containing trivalent nitrogen. Similarly, solvents which contain the hydroxyl or carbonyl groups form too stable a complex with metallic derivatives. The ethers are the most successful solvents, because the oxygen atom apparently coordinates sufficiently, but not too strongly, with the four types of solutes mentioned above.

It will be noted that none of the four types of solutes mentioned above contain oxygen or nitrogen directly bonded to the metal. It has been our experience that metallic compounds with metal bonded to oxygen or nitrogen do not yield the metal on electrolysis of their solutions in organic solvents. Apparently, the bond between the metal and oxygen or nitrogen is too strong. For example, magnesium or aluminum perchlorate although soluble in organic solvents do not yield deposits whereas the halides may yield a deposit, although a poor one.

Consideration of the individual members of the four types of solutes above show that each class is very limited. With regard to organometallics, for example, beryllium dimethyl and diethyl in ether form conducting solutions and yield some manner of deposits, but the phenyl derivative does not. The borohydride of beryllium and aluminum in ether yields metallic looking deposits whereas borohydrides of zirconium and titanium in ether are not even conductive. Although the chloro-hydride complexes of aluminum form a good plating bath, similar hydrides of magnesium and beryllium do not. Thus, the solutes which must be used for each element seems to be rather specific and it is entirely possible that solutes and non-aqueous solvents for depositing some of these metals do not exist.

The alkali metals form conducting solutions readily when certain of their compounds such as iodides, are dissolved in organic solvents and, paradoxically, they are more readily deposited than less active metals such as titanium, tungsten, or tantalum. In particular, lithium can be deposited so readily from organic solvents that it often constitutes a nuisance when lithium complexes of metals are used for solutes.

Part II. Apparatus

The electrodeposition of metals from non-aqueous media involves the use of solutes which are very sensitive to moisture and/or to oxygen. This situation necessitates the use of special equipment for carrying out both the preparation of compounds and the electrolysis of their solutions in a moisture free and/or oxygen free atmosphere. For example, aluminum chloride very rapidly absorbs moisture from the atmosphere and may be useless for an aluminum plating bath if weighed in the open. Beryllium and aluminum borohydrides are spontaneously inflammable and the latter may explode when air is introduced into the apparatus. Beryllium dimethyl is also spontaneously inflammable and its ether solution absorbs traces of oxygen, the accumulative effect of which eventually ruins the bath. The classical way of handling these sensitive compounds is in an all glass apparatus. This necessitates using special valves, breaking internal glass seals with an iron ball and magnet, sealing off parts of the apparatus with a flame, etc.

These methods proved far too cumbersome for our purposes which had a practical objective. We had to prepare compounds in larger quantities than the gram lots which are normally handled in sealed glass apparatus and we had to be

able to run many electrolyses in solutions which were protected from the atmosphere. To do the latter it was necessary to be able to change electrodes frequently and conveniently. In order to carry on our program expeditiously we had to construct inert atmosphere chambers which at the time were not available commercially with all the features that were required. The construction of these chambers is described in a recent publication (3) and one of them is illustrated in Figure 1.

Although the inert chamber was a necessity for preparations and for handling sensitive materials, electrolysis of solutions inside the chamber proved to be rather cumbersome because of the difficulty in removing, observing, testing, cleaning, and replacing electrodes. For that reason special electrolytic cells were developed such as those shown in Figure 2. An inert atmosphere of argon was maintained or passed through the cell. When a cathode was removed for inspection, it passed upward through a long glass chimney through which a rapid stream of argon was issuing, thus preventing ingress of air. The replacement of electrodes was done similarly . These vessels operated quite satisfactorily for baths of 25-50 ml volume. For larger baths resin-reaction flasks with tubulated glass covers were used as shown in Figure 3. In those experiments in which more positive exclusion of air was required when removing or replacing electrodes, an air lock was used consisting of small rubber balloons, dime store variety, which were inflated so as to close off the chimney when the electrode was removed. This is shown diagrammatically in Figure 4. The electrodes most convenient for exploratory work were rods about 1/4 inch in diameter usually of copper or of gold. An aluminum rod anode was frequently used because it dissolved readily, and the amounts of aluminum introduced into the bath were not sufficient to affect the cathode deposits in the short time that a solution was investigated.

Part III. Preparation and Electrolysis of Titanium and
Zirconium Compounds in Non-aqueous Media

A - Literature

The lightness , corrosion resistance and strength of titanium are some of the properties which make this material very desirable for the fabrication of certain machined parts. Coatings of titanium on steel and other base metals would be of considerable value for protection against corrosion. For this reason, methods for electrodeposition of titanium have been under intensive investigation by many workers during the past few years.

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Attempts to electrodeposit titanium go back over one hundred years when Becquerel (4) claimed to have deposited a titanium-iron alloy from aqueous solution. Experiments on aqueous electrolysis have continued since that date without success. Botts (5) determined the potentials of titanium trichloride and titanous sulfate solutions; the potentials became less noble on addition of hydrofluoric acid. He found that titanium was similar to silicon in activity. Russell(6,7), investigating electrode potentials, reported that titanium amalgamated with mercury to a very slight extent. He electrolyzed an acid solution of titanium trichloride, using a water cooled rocking mercury cathode at a high current density. He claimed a deposition rate of 0.2 g of titanium per hour.

I. G. Farbenindustrie A-G (8) patented a method of plating titanium on a base metal from strongly alkaline solutions at low current density. About 20 mg of titanium were deposited in 0.1 amp-hr. Bradt (9) established optimum conditions for plating bright zirconium from solutions of zirconyl sulfate on a copper cathode. The deposits were very thin. Haissinsky (10, 11) and Emmanuel-Zavizziano (12) experimenting in a manner similar to Bradt, deposited thin, black coatings of titanium on lead, zinc, or tin cathodes from solutions of titanium sulfate and sodium sulfate. Tartaric acid solutions were also suitable. Laubengayer (13) confirmed the findings of Bradt, but Dubpernell (14) claimed results by the methods of Bradt were nugatory; Plotnikov obtained (15) only hydrogen at the cathode. Gratsianskii (16) obtained thin films of titanium on a copper cathode from sulfanilic acid solutions. A patent was issued to Dekker (17) covering the electrolysis of salts melted in their water of crystallization, titanium sulfate trihydrate being one of the salts mentioned. Fink and Jones (18) patented a bath consisting of titanium dioxide, hydrogen fluoride, hydrogen chloride and gelatin with traces of copper to depolarize the deposition of titanium. Keys and Swann (19), however, reported their inability to plate titanium from aqueous solutions.

The Virginia Institute for Scientific Research (20) investigated the feasibility of plating titanium from aqueous solutions and succeeded in electrophoretically depositing titanium from sols containing colloidal titanium but did not succeed in electrodepositing titanium from ordinary solutions of its salts. The University of Missouri School of Mines (21) was able to obtain a very thin titanium-zinc alloy deposit from aqueous solution containing peroxide and tartrate. The Bureau of Mines (22) succeeded in obtaining some alloy deposits containing titanium from anhydrous

and aqueous systems. Graham, Crowley, and Associates, Inc.,(23) were unable to obtain metallic deposits of zirconium from organic plating baths. Three general references on titanium are included in the bibliography (24, 25, 26).

The foregoing literature survey shows that up to the present time no substantiated evidence has been presented for the successful electrodeposition of titanium from either aqueous or organic plating solutions. Although this metal can be deposited from high temperature fused salt baths, (27,28) the operational difficulties involved in plating from such baths make the development of a plating bath capable of operation at room temperature highly desirable.

The available evidence indicates that titanium is probably too reactive to be electrodeposited from aqueous solutions. This conclusion has focused attention on the use of organic solvents as a plating medium. Although organic plating baths have been known for many years (29), the development of the aluminum hydride plating bath by Couch and Brenner (1) has shown that it is possible to obtain good deposits consistently from an organic plating bath.

B - Solvents

In the exploratory phase of the work on electrodeposition of titanium during 1951-52, J. M. Sherfey and S. Senderoff of this laboratory dissolved the halide compounds of titanium in a number of different solvents and electrolyzed the resulting solutions. No successful deposition of the metal resulted. However, the various systems which were investigated are listed in Table I to indicate the diversity of solvents which were tried, so as to prevent duplication of similar experiments by others. The conclusions to be drawn from this preliminary work are that the titanium halides were not the proper type of compound and the titanium compound which will be successful apparently must be as specific in nature as the solvent.

Of the large number of different types of organic compounds of varied complexing ability investigated as solvents in this present study, hydrocarbons had the least complexing ability and amines the greatest. The ideal organic solvent should react with a titanium compound to form a charged complex which conducts electricity and reacts at the cathode. The hydrocarbon solvents lacked the reactivity to form charged ions, and amine complexes did not reduce at the cathode to yield metallic deposits. Of the various solvent types used, the ethers were the most suitable. They can be obtained with varying complexing ability; ordinary diethyl ether apparently being one of the weaker ones, having only moderate complexing ability. In view of this diethyl ether was the principal solvent used for further work. It has another advantage in that it is readily obtained commercially in almost pure form.

The atmospheric oxidation of ethers to peroxides and other compounds has occasionally caused difficulties. For example, the first additions of lithium aluminum hydride to 1,2 dimethoxy ethane or tetrahydrofuran reacted very vigorously. The cause of this was traced to impurities resulting from atmospheric oxidation. Acetaldehyde was identified in dimethoxy ethane. The latter is so sensitive to oxidation that even a very brief exposure to the atmosphere will result in the formation of peroxides. Ethers should be free of oxidized compounds when used as solvents for organo-metallic, hydride, or borohydride type of compounds, such as were used in this study. A necessary prerequisite of a plating bath is that a high concentration of complexed ions be maintained in solution. This has made necessary a study of the solubilities of titanium and zirconium compounds in various organic solvents. The approximate solubilities obtained at room temperature are given in Table II.

C - Electrolytic Studies

1. Titanium Borohydride Solutions

Introduction:

The borohydrides constitute a new type of electrolyte, the electrolytic properties of which have not been previously investigated. These compounds may be divided roughly into two classes; the ionic borohydrides and the covalent hydrides. The ionic borohydrides, such as sodium borohydride, are quite stable when exposed to a dry atmosphere. They are insoluble in the usual organic solvents. The covalent borohydrides, such as beryllium or aluminum, on the other hand, are unstable and are much more reactive. These borohydrides react spontaneously with the atmosphere, often with explosive violence. For this reason these compounds must be studied in an inert atmosphere. The covalent borohydrides are usually very soluble in organic solvents and this property makes them of interest as electrolytes. For example, titanium borohydride which is a covalent type, is quite soluble in diethyl ether whereas titanium trichloride is insoluble.

Titanium borohydride itself is relatively unstable at room temperature, decomposing completely within several days (30). Since the preparation of the pure compound is time consuming, titanium borohydride initially was prepared directly as etherate by the reaction of titanium halides with aluminum borohydride or lithium borohydride in ethereal solution. All experiments were performed in an inert atmosphere and no attempt was made to isolate the resulting titanium borohydride. The appearance of color in the ether solution served to indicate the formation of a titanium borohydride.

Titanium borohydride, $Ti(BH_4)_3$, is green, while titanium monochloroborohydride, $TiCl(BH_4)_2$, is blue (30). In ethyl ether solutions these compounds presumably give the same colors. This indicates that those solutions mentioned above contained titanium halo borohydrides and in some cases a mixture of the two borohydrides. This uncertainty about the borohydride compound present in the solutions being electrolyzed led us to attempt to prepare pure titanium borohydride. The method of Hoekstra and Katz which involves passing $TiCl_4$ over lithium borohydride (30) was found to be unsatisfactory when large quantities were involved so a new method was developed.

This new method involved the reaction of diborane with a titanium ester of the type $Ti(OR)_4$ in tetrahydrofuran to give titanium borohydride tetrahydrofuranate, i.e. $Ti(BH_4)_3 \cdot C_4H_8O$. The preparation of this compound is discussed in the appendix.

The results of the electrolysis experiments performed with the titanium borohydride solutions described above are included in Table III. The pure metal was not obtained. Ethereal borohydride solutions prepared from titanium halides all yielded a black, moisture sensitive deposit on electrolysis. None of the solutions conducted very well. A tetrahydrofuran solution of titanium borohydride tetrahydrofuranate did not conduct at all.

The black deposit obtained from electrolysis of the green solution of titanium tetrachloride-aluminum borohydride (Table III, No. 7) was found to contain 19% titanium which may be considered typical. It also contained aluminum and chlorine. (33% Cl, 19% Al; boron not determined). As this solution was electrolyzed the intensity of the green color diminished and a brownish-red material formed at the aluminum anode and soon discolored the solution.

Diethyl ether solutions of titanium borohydride were found to be unstable on standing for several days at room temperature as indicated by a change in color from green to brown, a decrease in the conductivity, and precipitation of a brown solid.

The addition of aluminum hydride plating bath (1) to titanium tetrachloride-aluminum borohydride solution gave a brown colored solution. (Table III, No. 9). Electrolysis of this solution gave a good metallic deposit which contained titanium, aluminum, and boron. The best alloy deposit obtained from a bath of this type contained 6.5% titanium. A deposit obtained from this same bath four days later was found to contain 1.6% titanium, 94.7% aluminum, and 2.6% boron.

An ether solution containing titanium borohydride tetrahydrofuranate and aluminum hydride plating bath was electrolyzed. The resulting alloy deposit contained 6.3% titanium. Direct addition of lithium aluminum hydride solution alone instead of the hydride aluminum bath, to titanium borohydride solution at room temperature caused decomposition as indicated by a vigorous evolution of gas and the formation of a black solid which discolored the solution. This indicates that titanium borohydride may complex with the aluminum hydride complex, present in the aluminum plating bath, but is decomposed by the more active lithium aluminum hydride itself.

2. Titanium Aluminum Hydride

In the above reaction, titanium borohydride may react with lithium aluminum hydride to form titanium aluminum hydride, $Ti(AlH_4)_4$, which apparently immediately decomposes. This seems likely because the compound has been reported in the literature (31) as being stable only at dry ice temperature or below and decomposing upon warming to room temperature. The compound is insoluble in ethyl ether at its temperature of existence. We prepared some of the compound in dimethyl ether at -80°C and electrolyzed the solution as it slowly warmed up to the boiling point of this solvent. The compound did not appear to be very soluble in this ether and the conductivity was very low. No metallic deposit was obtained.

3. Zirconium Borohydride

Zirconium borohydride is more stable than titanium borohydride and seemed to offer a better possibility of yielding a plating bath. The preparation of this compound from $KZrF_5$ and $Al(BH_4)_3$ has been described by Hoekstra and Katz (30). Initially we were interested only in preparing ether solutions of this compound in situ, which was done by adding to an ether solution the stoichiometric quantities of reactants, according to either of the following reactions:

(1) $ZrCl_4 + 2\ Al(BH_4)_3 = Zr(BH_4)_4 + 2\ AlBH_4Cl_2$

(2) $KZrF_5 + 2\ Al(BH_4)_3 = Zr(BH_4)_4 + KF + 2\ AlBH_4F_2$
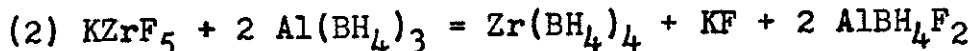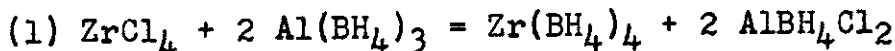
Reaction (1) has the disadvantage that both reaction products are soluble and difficult to separate.

With both reactions (1) and (2), since zirconium borohydride and aluminum borohydride are soluble, the latter contaminates the product if an excess is used. For this reason reaction (2) was carried out with a slight excess of $KZrF_5$. The potassium salt was used because a comparison of

the relative reactivities of NaZrF$_5$, KZrF$_5$5, and a product corresponding to KF·2 ZrF$_4$, showed that the potassium salt reacted more rapidly and completely.

When KZrF$_5$ was used in excess the yield was much less than expected. An examination of the reaction products showed that the reaction proceeded by a stepwise mechanism involving the intermediate formation of a compound such as Zr(BH$_4$)$_2$F$_2$, and for the reaction to go to completion an excess of aluminum borohydride must be used. Since both of the above reactions were found to be unsatisfactory for the preparation of an ether solution of zirconium borohydride, other possible methods of preparing this compound were investigated.

It was found that zirconium borohydride could be conveniently prepared by passing diborane into an ether solution of a zirconium ester of the type Zr(OR)$_4$. A product of this reaction is probably the corresponding boron ester, B(OR)$_3$ as in the similar preparation of titanium borohydride. This method is not satisfactory for the preparation of pure zirconium borohydride since the boron ester and zirconium borohydride are both present in the resulting solution.

The preparation of pure zirconium borohydride was accomplished by the dry reaction of lithium borohydride and zirconium tetrachloride at room temperature.

$$ZrCl_4 + 4 \ LiBH_4 = Zr(BH_4)_4 + 4 \ LiCl$$
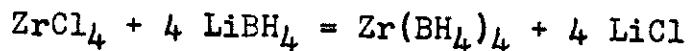
This method is convenient and rapid, and the yield is about 75% with respect to both reactants.

The preparation of these compounds is described in the appendix.

4. Zirconium-Aluminum Alloy Baths

Type A Bath (Zirconium borohydride and lithium aluminum hydride)

Zirconium borohydride in ether does not conduct and ether solutions of lithium aluminum hydride are only slightly conducting. When these two solutions are mixed, however, the resulting solution conducts very well. A sound metallic deposit containing about 8% zirconium was obtained from such solutions. The optimum concentrations for obtaining a metallic deposit from these ether solutions was determined by preparing baths containing different ratios of lithium aluminum hydride to zirconium borohydride. Three ratios were studied:

(a) 1.7; (b) 1.0; and (c) 0.5. Only in the case of (b) was a metallic deposit obtained on electrolysis. The other two solutions gave black moisture-sensitive deposits. Solution (a) was unstable and after standing for several hours at room temperature coated the wall of the reaction vessel with a metallic deposit. A similar decomposition occurred with solution (b) but much more slowly and to a lesser degree. Solution (c) did not decompose in this way and remained unchanged even after standing several days.

Type B Bath (Type A bath plus aluminum chloride)

The successive addition of aluminum chloride to type A baths results first in a marked increase in the amount of zirconium in the alloy deposit, and then a gradual decrease. However, even when the aluminum chloride content is relatively large, the zirconium content of the deposit is still greater than in the alloys from type A baths. From this it appears that aluminum chloride is an important component of these baths. Several baths of this type were made up with differing ratios of zirconium borohydride to aluminum chloride to determine the relation between the composition of the bath and the composition of the deposit. The results of this study are listed in Table IV. These data show that the results obtained are not consistent. The reasons for this are not yet known.

Type C Bath

In our early work with these alloy baths, aluminum borohydride and zirconium tetrachloride were used instead of pure zirconium borohydride. The deposits obtained were similar in appearance and zirconium content to the alloys from type B baths. The best deposit obtained from this type of bath contained 44.5% zirconium, 53.0% aluminum, and 2.5% boron. Due to the greater number of variables in type C baths, we did not study these baths as extensively as type B baths.

5. Characteristics and Structure of the Zirconium Plating Bath

These baths are similar to the aluminum hydride bath (1) in that they are subject to decomposition by the atmosphere. As zirconium and titanium dissolved anodically with poor current efficiency, in these solutions, aluminum anodes were used in all cases. Although this anode was soluble, some decomposition still occurred at the anodes. With zirconium and titanium anodes this decomposition was much more rapid.

The alloy baths were unstable and would give no deposit after a few weeks use. They appeared to be stabilized by aluminum chloride, which also improved the appearance of the

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deposits. Those baths containing only a small amount of aluminum chloride relative to zirconium borohydride were so unstable that metal deposition usually ceased after standing 24 hours. On prolonged electrolysis of these baths, the zirconium content of the alloys usually decreased.

At a zirconium borohydride-lithium aluminum hydride mole ratio greater than one, and also in the presence of such catalyzing materials as rubber, spontaneous decomposition of the bath occurred and a metallic mirror deposited on the inner surface of the electrolysis cell. Since this deposit is principally aluminum, it may be that the lithium aluminum hydride is catalytically decomposed by the zirconium borohydride.

If the structure of these baths was similar to that of the aluminum hydride plating bath, then lithium hydride should be equally as effective as lithium aluminum hydride, but this was not the case. Lithium hydride did not react with an ether solution of zirconium borohydride and the resulting suspension did not conduct. When this experiment was repeated with equimolar quantities of aluminum chloride, lithium hydride, and zirconium borohydride, the resulting solution gave no metallic deposit on electrolysis.

Ethyl ether plays a more important role than a mere solvent in these baths, as lithium aluminum hydride and zirconium borohydride do not react in its absence. In the presence of ether they react vigorously to form a brownish purple solution. The resulting solution conducts well and gives an alloy deposit when electrolyzed. The ether apparently serving both as a complexing and ionizing medium for the lithium aluminum hydride.

The zirconium compound responsible for the deposition of the alloys is probably a zirconium borohydride-aluminum hydride complex which is formed in solution.

This view is supported by the observation that lithium aluminum hydride conducts poorly in ethyl ether and zirconium borohydride does not conduct at all. When the two solutions were mixed a white solid was immediately formed which was found to have the empirical composition $Zr(AlH_4)_4$. In the presence of an excess of zirconium borohydride the white solid dissolved to give a solution of good conductivity. The solubility of zirconium aluminum hydride in excess of zirconium borohydride and the good conductivity of the resulting solution indicates the presence of a complex.

The preparation of the compound $Zr(AlH_4)_4$ is included in the appendix since this compound has not previously been reported in the literature.

D - Organo-metallic compounds

1. Organo-titanium Compounds

It is only within the last few years that methods have become available for the preparation of compounds containing titanium-carbon bonds (32, 33, 34). It was thought that such compounds would have greater solubility and greater stability in organic solvents than the hydride type compounds that we had previously used to prepare plating solutions. Although the preparation of such compounds is time-consuming, it was thought that their study would be of interest in view of the fact that other metals may be deposited from organo-metallic compounds (35).

Only two organo-titanium compounds were studied: bis-cyclopentadienyl titanium dibromide and phenyl titanium triisopropylate.

A quantity of bis-cyclopentadienyl titanium dibromide (32) was prepared and numerous solutions containing this compound were electrolyzed. In no case was a titanium deposit obtained. The solubility of this compound in organic solvents is very low and its solutions are weakly conducting, indicating that the compound does not form ionic complexes easily. The solubilities of this compound are listed in Table II.

Phenyl titanium triisopropylate was prepared as described by Herman and Nelson (33). The compound was not isolated but its resulting ether solution was electrolyzed. The conductivity was very small and was not improved by the addition of NaH or lithium phenyl. Electrolysis of this solution did not give a metallic deposit.

2. Organo-zirconium Compounds

Up to the present time the only organo-zirconium compound described in the literature has been the bis-cyclopentadienyl zirconium (IV) dibromide (32). In view of the lack of success with the similar titanium compound we made no attempt to synthesize this zirconium compound and turned our attention to other possible organo-zirconium compounds.

The addition of zirconium borohydride to an ether solution of lithium phenyl turned the solution black and heat was evolved. A similar reaction occurred with zirconium tetrachloride and lithium phenyl. In both cases the isolated reaction product gave a good test for carbon-metal bond. Although the exact composition of this compound was not determined, analysis indicated that it contained an appreciable amount of carbon. When the solvent was completely removed from this compound, the product was a tan powder, m.p. 175-185°C, which reacted vigorously upon exposure to the atmosphere. It was found to be soluble in phenetole,

benzene, and tetrahydrofuran, and sparingly soluble in ether and in dimethoxy ethane. The ether solutions of this compound conducted slightly but no metallic deposit was obtained on electrolysis. The compound was initially soluble in the solvents mentioned above, but upon standing for a long period of time in benzene it becomes insoluble in them. Although the compound is not very soluble in ether, it dissolves readily when lithium phenyl is added to the suspension. This may be due to the formation of a complex. The compound that had been "aged" by standing in benzene for a long period of time does not appear to dissolve in an ethereal solution of lithium phenyl.

Although the time limitation of this project did not allow a thorough study of this compound, we believe this compound is an impure zirconium phenyl derivative having the probable formula $Zr(C_6H_5)_3$. This speculation is supported by analysis and properties of the compound even though no other zirconium phenyl compound has been reported in the literature. This compound is discussed further in the appendix.

E - Perfluoroacid Salts

The presence of the fluorinated hydrocarbon chain in perfluoroacid salts enables these salts to be highly soluble in many organic solvents. For this reason the possibility of using these salts in organic plating baths was investigated.

The nickel, silver, titanium, and zirconium salts were prepared. The nickel salt was prepared as a check on the method of preparation and the silver salt was prepared as a possible intermediate in the preparation of other salts.

None of these salts yielded a conducting solution in ethyl ether or benzene. The nickel salt of perfluoroacetic acid dissolved in dimethyl formamide to give a conducting solution from which a nickel deposit was obtained. These deposits were stressed, poorly adherent, and contained organic matter. When titanium tetrachloride was added to benzene solutions of silver perfluoroacetate or silver perfluorobutyrate, a white precipitate was formed. It probably consisted of the titanium compound, which is relatively insoluble in benzene, mixed with silver chloride. A titanium derivative, containing chloride, was prepared by the direct reaction of $TiCl_4$ with trifluoroacetic acid.

Conducting solutions were obtained with titanium trifluoroacetate dissolved in 1,2 dimethoxy ethane, anisole, and dimethyl formamide. No deposit was obtained from any of these solutions on electrolysis. The preparation of these salts is described in the appendix.

F - Fused Organic Salt Systems

Several low temperature fused organic salt systems were studied during the course of this investigation.

Two quaternary ammonium tetrachlorodibromotitanates were prepared and investigated, which were the double salts of $TiCl_4$ with tetraethyl ammonium bromide and ethyl pyridinium bromide (36). These salts melt near 200°C. Melts of each of these salts at 250°C gave no deposit when electrolyzed. The addition of either of these salts to the ethyl pyridinium bromide-aluminum chloride type of aluminum plating bath (37) gave a black, tarry deposit when electrolyzed. These deposits were found to be rich in titanium.

Wier-Hurley baths (37) containing the following compounds were also electrolyzed: tetraisopropyl titanium, dicyclopentadienyl titanium dibromide, and sodium titanium chloride. In no case was a metallic deposit obtained.

When the Wier-Hurley bath was electrolyzed with a titanium anode, metallic deposits of a titanium-aluminum alloy were obtained, but with very low cathode efficiency. This bath yielded deposits containing up to 14% titanium. Alloys of higher titanium content could not be obtained; presumably due to electrolytic decomposition of the bath on prolonged electrolysis.

For use in fused salt electrolysis, a series of anhydrous trivalent titanium halogen derivatives of the general formula $MTiCl_4$, have been prepared. The sodium derivative is prepared by reducing $TiCl_4$, dissolved in an inert solvent, with sodium above 100°C. The green salt thus obtained reacts with many polar organic solvents, behaving much as $TiCl_3$. It dissolves in fused halide melts to form a solution from which titanium may be obtained on electrolysis. Since these compounds were described before the Electrochemical Society in April, 1953 and will be the subject of a separate publication, they will not be further discussed here.

G - Preparation of Reduced Titanium Compounds
      in Organic Solutions

The use of a trivalent titanium compound, titanium borohydride, in the titanium-aluminum alloy bath to give a titanium-containing deposit would seem to indicate that it may be possible to obtain a metallic deposit of titanium more readily from organic baths containing di- or trivalent titanium compounds.

The available lower valent titanium compounds such as the halides are not soluble in ethers. They are soluble in more polar carbonyl and hydroxyl type solvents but these solvents are too reactive for purposes of deposition.

We have prepared reduced titanium compounds in ethers by reduction of titanium tetrachloride with the following reagents: sodium naphthalene (38), diborane, lithium hydride, sodium hydride, sodium, sodium-potassium alloy, sodium dispersion, and lithium dispersion.

Sodium naphthalene in tetrahydrofuran was reacted with a tetrahydrofuran solution of $TiCl_4$. The resulting solution conducted well, but gave only a sodium deposit. A qualitative test indicated that the titanium was present in the trivalent state.

Diborane reacted with titanium tetrachloride in tetrahydrofuran to form a green colored solution of trivalent titanium chloride which did not conduct electricity. After standing for several days a blue solid crystallized out of the solution (see appendix under preparation of titanium borohydride).

In a hydrocarbon solvent such as benzene, lithium hydride and titanium tetrachloride did not react, but the addition of diethyl ether caused a reaction to occur with evolution of hydrogen and the formation of a green color which changed to reddish-brown on further reduction. The green compound could not be isolated. The hydrogen initially present in the hydride was all evolved as gas and the resulting solution gave no evidence of containing hydride when reacted with water. The reduced compound had properties similar to a lower valent titanium halide and was in no way similar to a hydride compound.

The controlling step of this reaction may be either the reaction of lithium hydride with the ether to release a hydride ion or the formation of $TiCl_4$ etherate which may be the active reagent. The reaction may be written as follows:

$$LiH + TiCl_4 \xrightarrow{\text{Et}_2\text{O}} TiCl_3 + LiCl + 1/2\ H_2$$
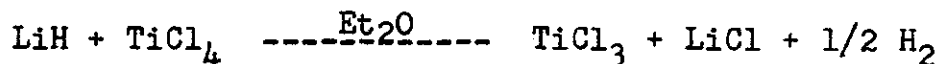
The reaction of sodium hydride with titanium tetrachloride is similar to the reaction of lithium hydride except that it is much slower. This is probably due to the lower solubility of sodium hydride in ethyl ether. The reaction of lithium, sodium, and sodium-potassium alloy with titanium tetrachloride in ether solutions appeared to produce products similar to those obtained when lithium hydride was used. Sodium and lithium were used as dispersions to obtain a more rapid and complete reaction.

Of the reducing agents listed above, only lithium hydride and sodium dispersion were used for a large number of experiments. The other reagents were examined for completeness.

The reaction of titanium tetrachloride with lithium hydride in ethyl ether resulted in the formation of two liquid layers. The more dense layer was smaller in volume and richer in titanium; on electrolysis it conducted well but gave no metallic deposit. The upper layer was low in titanium and conducted poorly.

In the more strongly complexing ethers tetrahydrofuran and tetrahydropyran, a separation of the solution into layers was not observed when titanium tetrachloride was reacted with lithium hydride, but an insoluble solid was usually formed as a product of the reaction. The composition of the solid product formed in these reactions was not determined, however it contained titanium in the reduced state. The concentration of trivalent titanium in the resulting solution was about 8 to 10 g/liter in both solvents. This is close to the content of metallic titanium (7.7 g/liter) in a saturated solution of titanium trichloride in tetrahydrofuran. These solutions yielded no metallic deposit on electrolysis although they did conduct well.

Lithium dispersion was reacted with solutions of titanium tetrachloride in ethyl ether, tetrahydrofuran, and tetrahydropyran in a 1:1 mole ratio. These solutions were not analyzed for reduced titanium, however the reactions were similar to those of sodium dispersion with titanium tetrachloride.

Table V is a summary of results obtained using various reducing agents and solvents. The mole ratio of titanium tetrachloride to reducing agent is unity in all cases.

Titanium tetrachloride in tetrahydrofuran reacted with sodium dispersion to form a blue solid. Analysis of this solid gave 12.7% titanium and 30.5% chloride, which approximates to the composition $TiCl_3 \cdot (C_4H_8O)_3$. A similar blue solid was formed when lithium hydride was reacted with titanium tetrachloride in tetrahydrofuran, but the composition of this blue solid was not determined. The reaction of diborane with titanium tetrachloride in tetrahydrofuran also formed a blue solid having the approximate composition $TiBCl_{2.6}(C_4H_8O)_{2.3}$. It is likely the same compound as above, contaminated with a boron ester formed in the reaction.

In addition to the more reactive reducing agents listed above, titanium tetrachloride solutions could be reduced by metals such as nickel, iron, copper, silver, or magnesium.

These metals are effective only when used with titanium tetrachloride in solvents such as dimethyl formamide, acetone, dimethoxy ethane, and tetrahydrofuran.

H - Preparation of $TiCl_3$

An essential part of this program is the preparation of new compounds and the simplification of present methods of preparation of compounds used in electrolysis studies. An improved method for the preparation of titanium trichloride falls under the latter category.

By reacting titanium tetrachloride with hydrogen in a bomb at 500°C and 2000 lbs/in², 12% was reduced to titanium trichloride in 30 hours. Chemical analysis of the product indicated 1.5% TiOCl and 98.5% pure $TiCl_3$. The presence of a very small amount of oxygen in the hydrogen which was not purified and the ease of formation of the compound TiOCl would explain its presence. Given enough time to go to completion this reaction may give a rather high yield of titanium trichloride. This method has certain advantages over other procedures employing hydrogen in that a lower temperature is used, so that the possibility of contamination with $TiCl_2$ is minimized, and the reaction requires no attention while in process. Presumably, the use of higher pressures, for example 1000 atmospheres, would considerably speed up the reaction.

APPENDIX

I - The Preparation of Titanium Borohydride from Titanium Tetrabutylate, $Ti(OC_4H_9)_4$ and Diborane, B_2H_6

Into a tetrahydrofuran solution containing 0.029 mole of titanium tetrabutylate (obtained from the DuPont Co.), 0.067 mole of diborane was passed. A dark blue solution was formed and beautiful blue crystals settled out of solution. The solution was filtered in the dry box and the crystals washed with petroleum ether. Yield: 5.0 grams. The filtrate was evaporated nearly to dryness and a high boiling colorless liquid remained. B. P. 225. This liquid had properties similar to those of boron esters but the amount isolated was too small to study thoroughly.

With titanium tetraisopropylate the borohydride was obtained in 90% yield. Analysis of the blue crystals gave: %C = 33.0, %H = 10.3, %B = 14.5, and % Ti = 29.1.

Theory for $Ti(BH_4)_3 \cdot C_4H_8O$: %C = 29.2, %H = 12.2, %B = 19.4, and %Ti = 28.1.

The crystalline blue solid was observed to undergo a partial decomposition at 135-140°C and upon heating to a higher temperature decomposed completely with the formation of a bright metallic mirror on the walls of the container.

It was found to be insoluble in the usual organic solvents with the exception of tetrahydrofuran but reacted readily with peroxide-containing ethers and such active solvents as water.

Titanium borohydride apparently is stabilized by coordination with tetrahydrofuran, as indicated by the fact that large crystals of the compound react rather slowly on exposure to the atmosphere (the finely divided compound occasionally ignites spontaneously) and the compound can be stored in closed containers for long periods of time without any noticeable decomposition.

II - Reaction of Diborane with Titanium and Zirconium Halide

When titanium tetrachloride or zirconium tetrachloride were reacted with diborane in tetrahydrofuran, the borohydrides were not obtained. Crystalline titanium and zirconium compounds having the approximate empirical formula $MBCl_{2.6}(C_4H_8O)_{2.3}$ were isolated from these solutions.

Analysis:

Titanium Compound: 14.5% Ti, 28.1% Cl, 4.6% B, 37.9% C, 6.4% H, by difference 10.0% O.

Zirconium Compound: 24.5% Zr, 26.1% Cl, 2.1% B, remainder organic material.

The zirconium compound was white and the titanium compound was blue.

Compounds similar to those described here were obtained by reduction of titanium tetrachloride in tetrahydrofuran as previously described. This suggests that the boron present in these compounds may be only a contaminant.

III - Preparation of Zirconium Borohydride

A. Reaction of Aluminum Borohydride with Potassium Zirconium Fluoride, $KZrF_5$

To 57.8 millimoles of $Al(BH_4)_3$ in 20 ml of ether 25.9 millimoles of $KZrF_5$ (mole ratio 2:1) was added and the flask placed in a shaking apparatus. After about 16 hours of shaking, the solution was filtered. The resulting clear solution was found to contain no fluoride. By means of hydride and zirconium analysis the yield was calculated to be 65%. When this experiment was repeated using the mole ratio of $3NaZrF_5$ to $4Al(BH_4)_3$ and 24 hours of shaking, the yield of zirconium borohydride was only 30%, thus indicating the formation of intermediate zirconium

borohydrides such as $Zr(BH_4)_2F_2$ owing to the use of insufficient aluminum borohydride.

B. Reaction of Zirconium Tetraisopropylate with Diborane

Into a tetrahydrofuran solution containing 0.02 mole of zirconium tetraisopropylate (39), 0.14 mole of diborane was passed. The resulting clear solution (34 ml) was analyzed for hydride and zirconium content. It was found to contain 0.6 millimole of zirconium and 14.7 millimoles of hydride (measured as evolved hydrogen) per milliliter. The hydride content should have been about 10 millimoles for zirconium borohydride. The analytical results indicate the solution contained zirconium borohydride and a small amount of diborane.

C. Preparation of Zirconium Borohydride from Lithium Borohydride and Zirconium Tetrachloride

Into a round bottom 500 ml flask in the dry box were placed some dry nickel balls (about 0.5 cm in diameter) for mixing the reactants. To this flask was added 15.6 g of zirconium tetrachloride and 6.0 g of lithium borohydride, both of which were finely powdered. (Mole ratio 1:4). The flask was sealed with a rubber stopper and the reaction vessel swirled by hand for about fifteen minutes at room temperature. The material in the flask became wet and heat was evolved. The flask was shaken for about five minutes more until its contents had become paste-like and the nickel balls were no longer able to produce mixing.

After cooling to room temperature the flask was placed in a vacuum system and evacuated for about thirty minutes. The zirconium borohydride was collected in a liquid nitrogen trap. The yield was 7.7 g or 77%.

If an excess of lithium borohydride is used the induction period is lessened and the yields are increased. Yields as high as 90% have been obtained by using an excess of lithium borohydride and also by breaking up the lithium chloride and evacuating again at about 50°C. The latter procedure increased the yield by 6% in one run.

Analysis of the product gave 55% zirconium, 30% boron, and 10% hydrogen. The theoretical values for zirconium borohydride are 60.6% zirconium, 28.7% boron, and 10.7% hydrogen. The melting point of the product was 28.7°C which is identical with the previously reported m.p. of zirconium borohydride (30).

For a metallic derivative, the compound shows a surprising solubility in organic solvents, including ether, petroleum ether, and benzene.

Attempts to prepare zirconium borohydride by use of sodium or potassium borohydride were unsuccessful.

IV - Preparation of Zirconium Aluminum Hydride

To a dilute ether solution of zirconium borohydride in a sintered glass filter funnel was added an ether solution of lithium aluminum hydride. The reaction was carried out in the dry box. When a sufficient amount of white solid had formed the ether solution was rapidly removed and the solid was isolated. It was found to be unstable at room temperature, decomposing within several hours to a black solid. Analysis of the white solid indicated a formula corresponding to that for zirconium aluminum hydride - $Zr(AlH_4)_4$.

Results of Analysis:

wt. sample = 41.9 mg
62 ml gas at 26°C = 2.52 millimoles H_2
13.8 mg Zr   = 0.15   "   Zr
17.6 mg Al   = 0.63   "   Al

These data would indicate an empirical formula $ZrAl_{4.2}H_{16.8}$.

V - Preparation of a Zirconium Phenyl Compound

Method A:

To an ether solution containing 0.0135 mole of lithium phenyl was added 0.0037 mole of zirconium borohydride with the formation of a black colored solution and the evolution of heat. The solution was diluted with benzene and filtered. The filtrate was then evaporated to dryness and evacuated for 1 hour at 50°C. During the drying process a small amount of biphenyl condensed on the upper wall of the container. The resulting black solid gave a positive Michler's ketone test for a carbon metal bond.

Method B:

This compound was also prepared by the reaction of lithium phenyl with a slurry of zirconium tetrachloride in ethyl ether in a manner similar to Method A above. When the solution was evaporated to a low volume and filtered, the product (a tan powder) was salted out by the addition of petroleum ether. The yield was 63% on the basis of zirconium triphenyl. This compound also gave a positive Michler's ketone test. m.p. 175-185°C.

The analysis of the compound prepared by each method gave the following results:

	Method A	Method B	Theory for $Zr(C_6H_5)_3$
% Zr	27.5	29.6	28.3
% C	49	42	67.5
% H	5.3	4.7	4.7

The compound prepared by Method A contained about 8% zirconium borohydride as impurity and the product from Method B contained about 4% lithium bromide as impurity. The reason for the low values obtained in the carbon analysis was not determined.

VI - Preparation of Titanium Trichloride

In an inert atmosphere chamber, 0.9 mole of titanium tetrachloride was placed in a one-liter capacity pressure bomb equipped with a glass liner. The bomb was then sealed and four moles of hydrogen were added. The bomb was then heated to 500°C and left at this temperature for 29 hours. The pressure was maintained at about 2000 lbs/in^2 during this time. This required that some of the gas be valved out occasionally.

At the end of the reaction the pressure was released and the bomb taken into the dry box. A yield of 16.5 g of titanium trichloride as flakey red crystals was obtained. The yield was 12% based on the amount of titanium tetrachloride initially placed in the bomb. Most of the unreacted titanium tetrachloride could have been recovered.

In the above reaction, the bomb also contained small amounts of palladium and platinum sponge in test tubes, but later observations indicated that it did not aid the reaction which occurred.

A sample of the product was dissolved in water and found to contain 1.5% insoluble matter, the soluble portion was pure titanium trichloride. The insoluble material was assumed to be titanium oxychloride, TiOCl.

This latter compound had been formed previously when the same reaction as described above had been allowed to continue for about an hour at 450°C and 1650 lbs/in^2. In this experiment a small amount of a gold colored material was formed. It was insoluble in all of the usual acids and was not affected by the atmosphere. This compound has been previously described (26, p. 322).

VII - Preparation of the Salts of Perfluoroacids

Titanium and Zirconium Salts:

The titanium and zirconium salts were prepared by the reaction of the metal tetrachlorides with trifluoroacetic acid. The preparation of the titanium salt illustrates the method used.

To 1.9 g of titanium tetrachloride was added 4.56 g of trifluoroacetic acid. The reaction mixture was heated at 65°C and evaporated to dryness. A yield of 90% or 4.5 g of white solid was obtained.

The zirconium salt was prepared in a similar manner, but in a solution of ethyl ether. Both salts contained a small amount of chlorine. Analysis of the salts for metal content gave:

Titanium 17.6%

Zirconium 25.2%

Nickel and Silver Salts:

These salts were prepared by the reaction of the metal oxides with the acids in aqueous solution and evaporation of the resulting solution to dryness. The salts were then dried at 150°C for several hours.

Nickel trifluoroacetate, silver trifluoroacetate, and silver perfluorobutyrate were prepared in this manner.

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TABLE I

Solvents in which Titanium Halides were Electrolyzed

Hydrocarbons
  Benzene
  Toluene + lithium
  Toluene + sodium

Halogenated Hydrocarbons
  Benzotrichloride
  Bis (trifluoromethyl) benzene
  Tert - butyl chloride
  Tert - butyl chloride + dry HCl
  Ethyl bromide
  Ethylidene chloride
  Ethyl pyridinium bromide +
    aluminum chloride
  Methyl chloroform
  Trichloro-fluoro-methane

Alcohols
  Butyl alcohol
  Tert-butyl alcohol
  Carbitol
  Ethanol (0°C and 25°C)
  Ethanol + boron trifluoride
  Ethanol + ethyl ether + HCl
  Ethanol + HCl
  Ethanol + HCl (aqueous)
  Ethanol + sodium
  Ethanol + tetra methyl ammonium
    hydroxide
  Ethylene glycol
  Glycerine
  Glycol
  Methanol
  Methanol + tetra ethyl lead

Ethers
  Butyl ether + aluminum chloride
  Cellosolve
  Dioxane
  1,4 dioxane + lithium
  1,4 dioxane + sodium
  Ethyl ether
  Ethyl ether + aluminum
    tribromide
  Ethyl ether + aluminum
    bromide + lithium
    aluminum hydride

Ethers Contd.
  Ethyl ether + aluminum
    trichloride
  Ethyl ether + aluminum
    chloride + lithium
    aluminum hydride
  Ethyl ether + lithium
  Ethyl ether + lithium
    borohydride
  Ethyl ether + sodium
  Ethyl ether + sodium
    borohydride
  Tetrahydrofuran

Ketones
  Acetone

Acids
  Acetic acid
  Acetic acid + acetic anhydride
  Trifluoracetic acid anhydride

Amines
  Pyridine
  Pyridine + boron trifluoride
  Amino dipropionitrile
  Ethylene diamine
   isopropyl amine

Amides
  Dimethyl acetamide
  Dimethyl cyanimide
  Dimethyl formamide
  Dimethyl formamide + lithium
  Dimethyl formamide + sodium
  N,N dimethyl trichloro acetamide

Nitriles
  Diallyl cyanamide
  Dimethyl cyanamide
  Acetonitrile
  Acrylonitrile
  Oxydipropionitrile

Table I (Contd)

Miscellaneous

Aluminum diethyl bromide + aluminum ethyl dibromide

Aluminum diethyl bromide + aluminum ethyl dibromide
+ toluene

Benzothiazole

Methyl magnesium bromide

Methyl magnesium bromide + ether

N-methyl pyridinum methyl sulfate

Methyl sulfate

Methyl trichlorosilane

3-Nitro 4-chloro benzotrifluoride

Nitro methane

Isopropyl titanate

Inorganic

Phosphorus trichloride

Sulfur chloride

Sulfuryl chloride

Thionyl chloride

Titanium tetraiodide

Water

TABLE II

Solubilities of Titanium and Zirconium Compounds in Various Organic Solvents

Solvents	Solubility (g/100 ml)
Bis-cyclopentadienyl Titanium Dibromide	
Petroleum ether	insoluble
Ethanol	very slight
Ethyl ether	0.17
Benzene	0.34
Chloroform	0.92
Phenetole	1.09
Acetone	1.15
Tetrahydrofuran	1.24
1,2-dimethoxy ethane	1.99
Dimethyl formamide	3.55
Titanium Tetrachloride	
Benzene	infinitely soluble
Acetone	very soluble
Ethanol	"
Titanium Tetrabromide	
Ethyl ether	4.4
Titanium Trifluoroacetate	
Ethyl ether	slightly soluble
Anisole	soluble
1,2-dimethoxy ethane	"
Dimethyl formamide	"
Benzene	insoluble

Table II (Contd)

Solvent	Solubility (g/100 ml)
Zirconium Tetrachloride	
Ethanol	soluble
Ethyl ether	1.1
Methyl ether	5.4 at 23.6°C
Benzene	very low (less than ether)
Anisole	2.7
Dimethoxy ethane	6.8
Phenetole	7.1
Tetrahydrofuran	14.1
Zirconium Tetrabromide	
P-xylene	0.2
Ethyl ether	1.2
Dimethoxy ethane	50.3
Tetrahydrofuran	53.0
Titanium Trichloride	
Tetrahydrofuran	2.5
Silver Trifluoroacetate	
Benzene	17.8
Ether	47.1

TABLE III

Electrolysis of Ethereal Solutions of Titanium and Zirconium Borohydride

	Preparation of Electrolyte			
	Ti or Zr Salt Present	Reagent Added	Color of Solution	Nature of Deposit	% Ti or Zr in Deposit
1.	K_2TiF_6	$Al(BH_4)_3$	Colorless	None	-
2.	$TiCl_3$	$LiBH_4$	Blue	Black, moisture sensitive	-
3.	$NaTiCl_4$	$LiBH_4$	Colorless	None	-
4.	TiF_3	$LiBH_4$	-	Li deposit	-
5.	TiF_4	$LiBH_4$	Blue	Black, moisture sensitive	-
6.	$TiCl_3$	$Al(BH_4)_3$	Blue	Black, moisture sensitive	22.4
7.	$TiCl_4$	$Al(BH_4)_3$	Green	Black, moisture sensitive	19.1
8.	$TiBr_3$	$LiBH_4$	Blue	Black, moisture sensitive	-
9.	$TiCl_4$	$Al(BH_4)_3$ + Al hydride bath	Brown	Metallic	6.5
10.	$ZrCl_4$	$Al(BH_4)_3$ + Al hydride bath	Brown	Metallic	22.9
11.	$ZrCl_4$	$Al(BH_4)_3$	Colorless*	Black, moisture sensitive	34.2

*Zirconium borohydride solutions are colorless.

TABLE IV

Electrodeposited Zirconium - Aluminum Alloys from Plating Baths Containing Hydrides, Borohydrides and Chloride

	Bath Composition (mole/liter)						Composition of Deposit		
	$Zr(BH_4)_4$	$AlCl_3$	$LiAlH_4$	$ZrCl_4$	$Al(BH_4)_3$	$Zr/AlCl_3$	% Zr	% Al	% B
1.	0.335	-	0.335	-	-	-	8.1	85.2	1.9
2.	0.223	0.057	0.153	-	-	4:1	11.8	90.8	2.5
3.	0.335	0.150	0.235	-	-	2:1	42.1	48.6	-
4.	0.804	0.784	0.616	-	-	1:1	9.5	-	-
5.	0.335	0.450	0.305	0.112	-	1:1	26.3	74.5	3.4
6.	0.168	0.168	0.108	-	-	1:1	14.0	82.6	2.5
7.	0.335	0.670	0.305	-	-	1:2	19.2	70.0	4.5
8.	0.335	2.01	0.305	-	-	1:6	15.1	-	-
9.	-	0.653	0.720	0.287	0.440	1:2	8.9	71.5	-
10.	0.335	0.650	0.525	0.335	-	1:2	9.3	89.0	6.4

After bath No. 9 (above) had been prepared a metallic deposit formed on the wall of the electrolysis cell. On analysis, this deposit was found to contain 12.4% Zr, 78.8% Al, and 9.2% B.

TABLE V

Reduction of Titanium Tetrachloride in Solution

Reducing Agent	Solvent	Conc. of Ti in Reacted Soln. in g/l	
		Total	Reduced (as Titanous Ti)
1. Sodium dispersion	Tetrahydrofuran	14.3	9.6
2. Sodium dispersion	Ether	1.8	2.2
3. Sodium dispersion	(50% tetrahydrofuran) (50% benzene)	15.0	5.8
4. Sodium[a]	Tetrahydrofuran	15.4	24.1
5. Sodium-potassium[b] alloy	Anisole	5.0	0.0
6. Lithium hydride	Tetrahydrofuran	11.2	8.3

[a] In experiment 4, metallic sodium was added to a tetrahydrofuran solution of titanium tetrachloride in a steel bomb and the resulting solution was ball milled at 100°C.

[b] Reduction occurred in experiment 5, but reduced titanium was found only in a black solid formed as a product of the reaction.

In two cases the reduced titanium content calculated as titanous ion was greater than the total titanium concentration. From this it would appear that a mixture of di and trivalent titanium is formed in these reduced solutions.
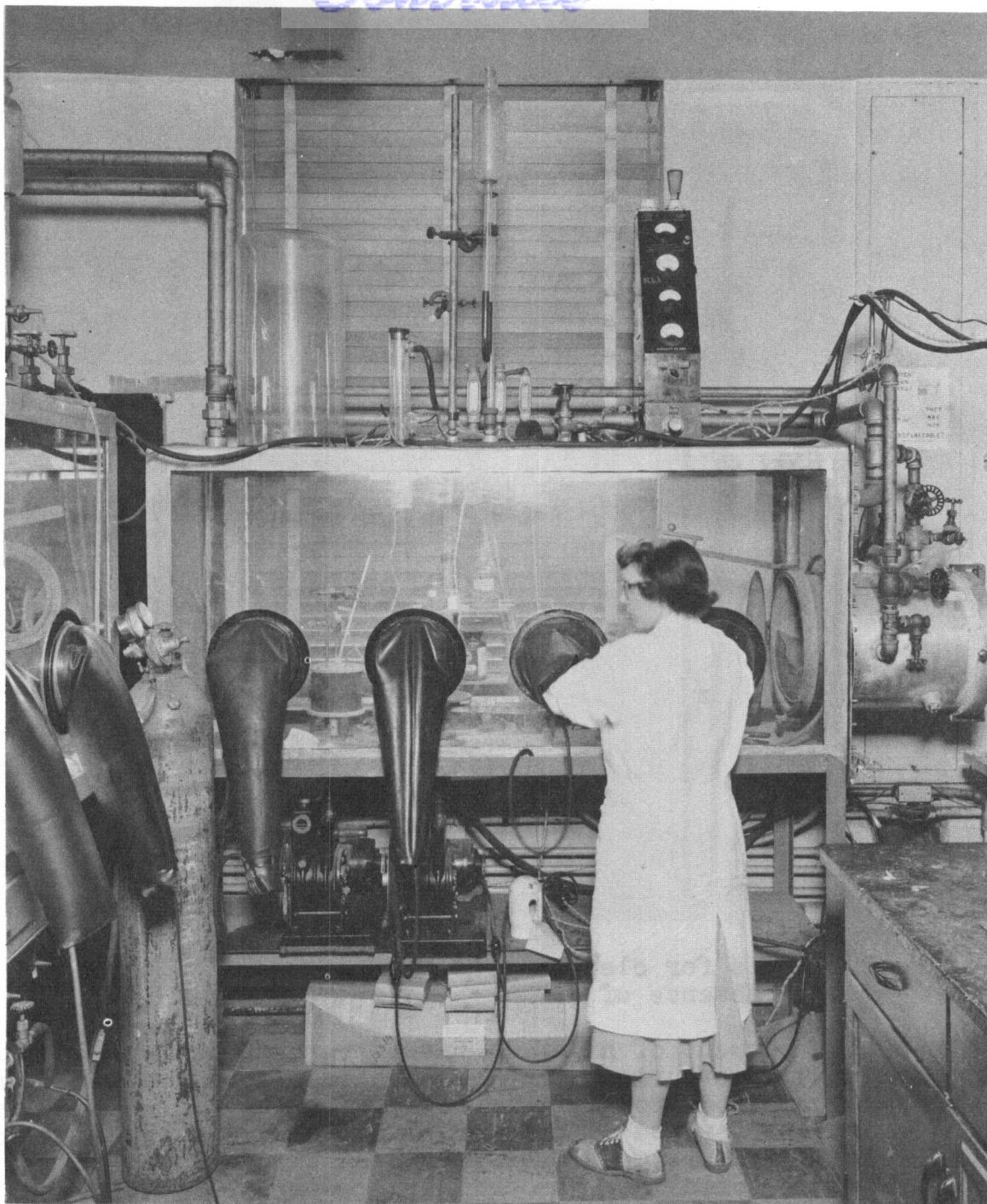
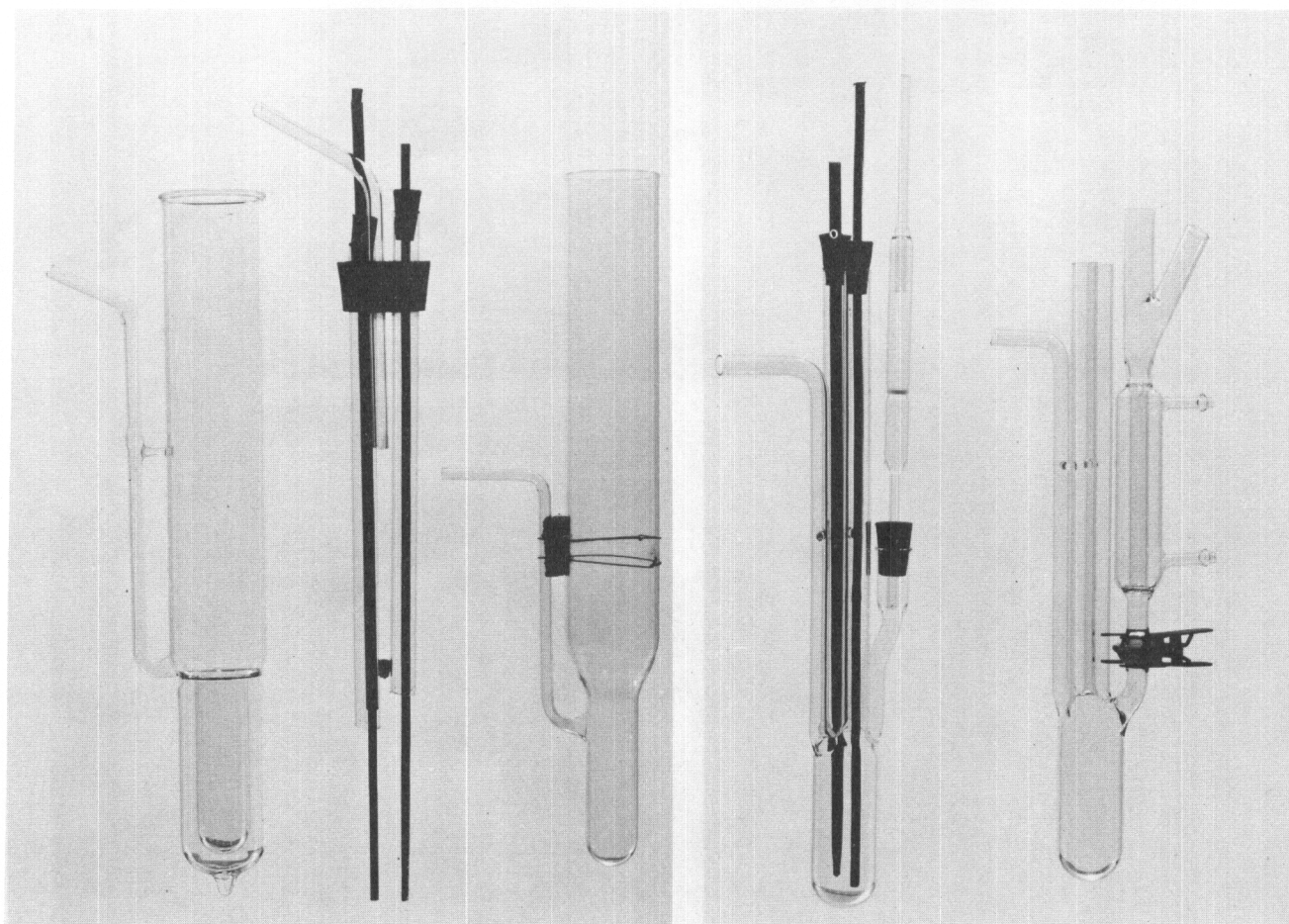Figure 1. Inert atmosphere chamber (3) or "Dry Box"

Figure 2. Cells for electrolysis of nonaqueous solutions
in absence of air

A slow current of argon is passed through each cell during
operation; a fast current when electrodes are removed or introduced.
Cells are numbered from left to right 1 through 4. Cell 1 is of
the Dewar type for use with low boiling liquids such as ammonia.
Cell 2 is a simpler type. Between these two cells are shown the
electrodes enclosed in glass chimneys. Cells 3 and 4 are of all
glass construction. Cell 3 has a mercury seal valve for escape
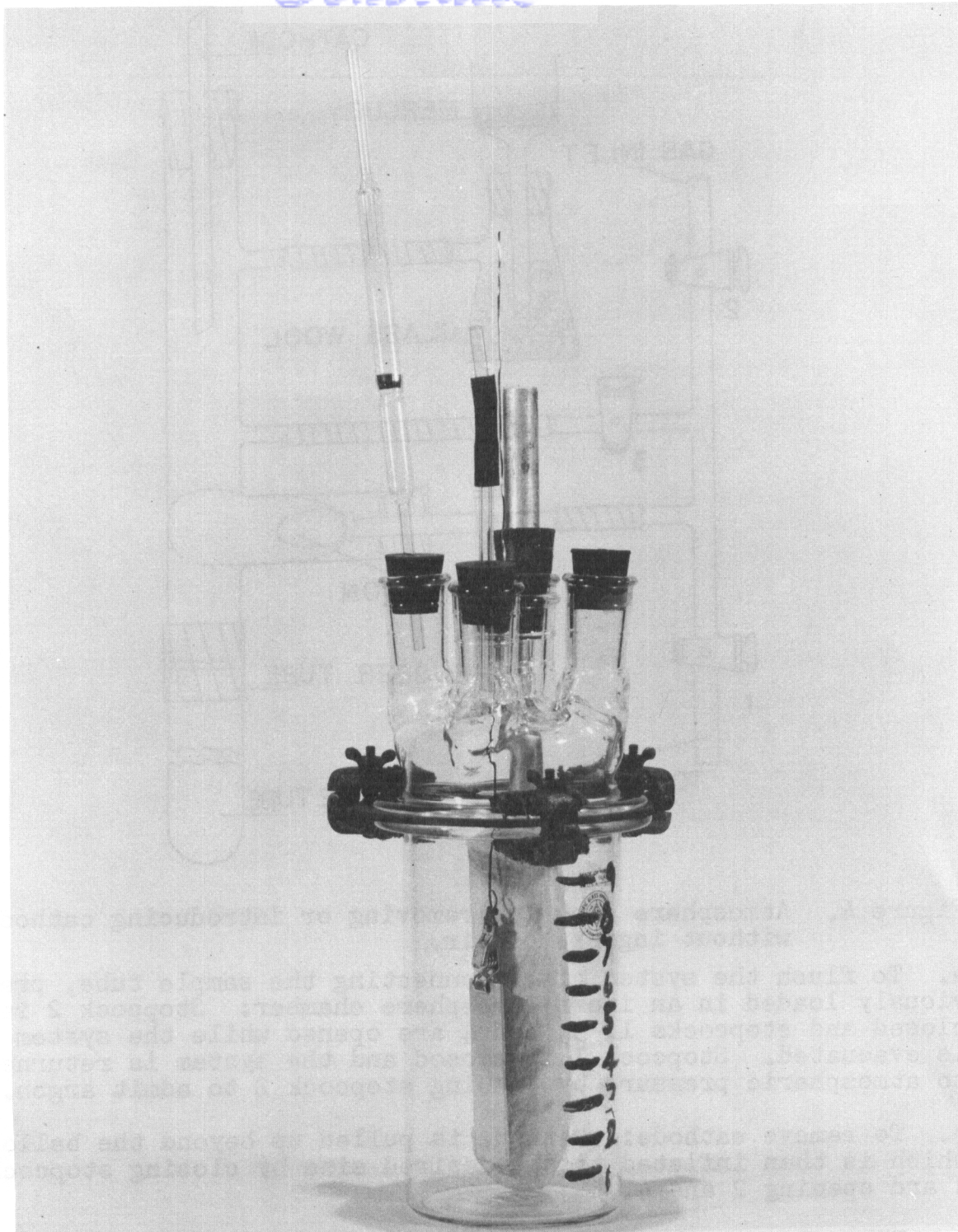of excess pressure. Cell 4 has a condenser for volatile liquids.

Figure 3. Resin reaction vessel used as electrolytic cell for larger volumes of solution than can be handled by cells in figure 2.
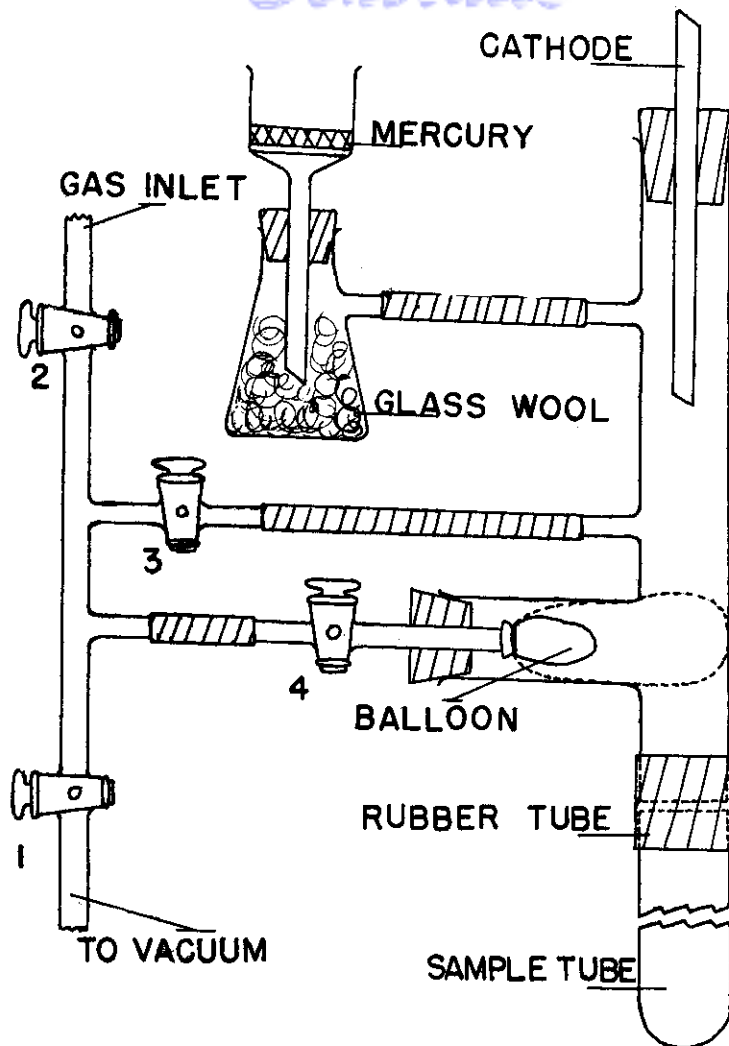
Figure 4. Atmosphere lock for removing or introducing cathodes
without ingress of air.

a. To flush the system after connecting the sample tube, pre-
viously loaded in an inert atmosphere chamber: Stopcock 2 is
closed and stopcocks 1, 3, and 4 are opened while the system
is evacuated. Stopcock 1 is closed and the system is returned
to atmospheric pressure by opening stopcock 2 to admit argon.

b. To remove cathode: Cathode is pulled up beyond the balloon
which is then inflated to the desired size by closing stopcock
3 and opening 2 and 4.

c. To replace cathode: Stopcocks 2 and 3 are opened and the
chimney flushed while the balloon is inflated. Stopcock 2
is then closed and 4 is opened so that the balloon reduces to
original size. Cathode can then be lowered into sample bath.

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