

AN EXPLORATORY INVESTIGATION OF THE POSSIBILITY FOR  
" ELECTRODEPOSITING ALUMINUM FROM MISCELLANEOUS ORGANIC SYSTEMS

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Thesis submitted to the Graduate Faculty of the  
Virginia Polytechnic Institute  
in candidacy for the degree of

MASTER OF SCIENCE

in

Chemical Engineering

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## I. INTRODUCTION

Plating of aluminum on metals which are susceptible to corrosion is a problem which is, as yet, unsolved. However, many attempts have been made to electroplate with aluminum from as early as the first of the 19th century.

Scientists from France, Germany, England, America, and other countries have made futile attempts to solve the problem of the electrodeposition of aluminum from various systems. Extensive studies have been made to determine the characteristics of prospective electrolytes with regard to their use as a source of aluminum plating.

The electrolytes investigated have included organic solutions, aqueous inorganic liquid solutions, nonaqueous inorganic liquid solutions, and molten salts baths. Most of the research has been conducted with nonaqueous inorganic liquid solutions and molten salts baths. Aluminum halides have been utilized with some success but the plate produced is susceptible to corrosion.

The purpose of this research was to make an exploratory investigation of organic solutions containing the compounds aluminum bromide, aluminum stearate, aluminum basic acetate, aluminum phenoxide and nitrophenoxide, and aluminum acetylacetonate to determine if these compounds would furnish aluminum ions for electrodeposition.

## II. LITERATURE REVIEW

Although aluminum has been known as a metal since about 1809, it did not achieve any significant importance until 1886.<sup>(10)</sup> Since that time, the cost of manufacturing has gradually been cut to the point where aluminum is used as a commonplace metal of construction.

A review of the literature has been prepared as the basis of a research project on the electrodeposition of aluminum from liquid organic mixtures. This review comprises a brief history of aluminum, a discussion on the corrosion of aluminum, a discussion of methods of applying aluminum coatings to metals, a review of previous work performed on the electrodeposition of aluminum and a brief account of some of the properties of aluminum electrodeposits.

### History of Aluminum

A study of the history of aluminum reveals that after the difficulties encountered by those attempting to find a means of producing aluminum cheaply had been overcome there ensued a great effort to introduce the new metal to the general public as well as to find new uses for it.<sup>(10)</sup>

Hall's and Heroult's Discovery. Charles Martin Hall and Paul L. T. Heroult, each working separately in the United States and

France, (10) respectively, discovered an electrolyte from which molten aluminum could be obtained.

Hall's Discovery. Hall (10) reasoned that it would be possible to electrolyze alumina in solution with a fused salt which would dissolve the alumina in substantial quantities. The extremely high melting point of pure alumina was 2050 °C and too high for electrolysis. Hall found that cryolite,  $\text{Na}_3\text{AlF}_6$ , was a suitable solvent and, on February 23, 1886, he produced globules of aluminum by electrolyzing a solution of alumina in molten cryolite. The advantages of cryolite were its low melting point of 1000 °C and its high stability as compared to that of alumina. In addition, the specific gravity of the electrolyte was low enough at 900 to 1000 °C to allow the aluminum to settle to the bottom of the cell and be protected by the solution.

Heroult's Discovery. Heroult (10) was granted a French patent on April 23, 1886 for electrolyzing alumina in a bath of cryolite. His process was so similar to Hall's that priority of invention was given to Hall, and Heroult did not obtain a patent in this country. It seems possible that Heroult did not realize the importance of his discovery, for he patented and began to commercialize an entirely different process about a year later. Only aluminum alloys could be produced by this new process. Pure alumina was fused

electrothermally in a carbon-lined crucible and a copper-aluminum alloy was obtained by electrolyzing the solution through the use of a carbon anode and a layer of molten copper as the cathode.

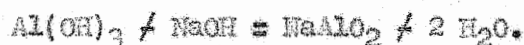
Several years later, Heroult and Kiliiani converted their alloy furnaces to the alumina-cryolite process and began to produce aluminum.

The Production of Aluminum. The modern method of producing aluminum<sup>(11)</sup> is fundamentally the same process as was conceived and developed by Charles M. Hall. Aluminum, like most metals, except those found free in nature, is produced by the reduction of its oxide. Whereas most metals are purified after production, aluminum is produced from purified raw materials. The study of aluminum production has been confined to the raw materials, the electrolytic cell construction, and the operation of the electrolytic cell.

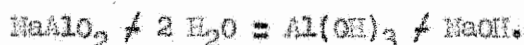
Raw Materials. Practically all of the aluminum obtained commercially in the United States comes from one ore, bauxite.<sup>(11)</sup> Bauxite is primarily a hydrated aluminum oxide with impurities of iron oxide, silicon oxide, and titanium oxide. On a percentage basis, bauxite comprises 50-60 per cent aluminum oxide, 25-32 per cent chemically combined water, 2-14 per cent silicon oxide, 2-10 per cent iron oxide, and 2-3 per cent titanium oxide. Ore used in the manufacture of

aluminum in the United States comes from South America, the West Indies, and Arkansas. Bauxite is mined either by open-pit or underground mining.

The Bayer process is one of the most common methods for refining bauxite. The washed and dried bauxite from the mines is broken up in hammer mills and crushers, powdered, mixed with a hot solution of sodium hydroxide, and pumped into large pressure digesters. Sodium aluminate solution is formed as the caustic soda dissolves the aluminum hydroxide out of the bauxite:



The impurities remain in solid form and are removed by pumping the solution through filter presses. The sodium aluminate filtrate is pumped to precipitating tanks and allowed to cool. The aluminum hydroxide settles as fine crystals, is removed and washed free of caustic soda:



The hydrated aluminum oxide is charged to rotary kilns and heated white hot to drive off the chemically combined water:



The Electrolytic Cell. The cell used for the electrolytic production of aluminum<sup>(11)</sup> is a rectangular or circular steel box with a carbon lining 6 to 10 inches thick. The steel plate is from 1 to 2 inches thick and it usually makes direct contact with the carbon lining and thus conducts the



current to the carbon cathode. The size of the cell and the electrolyte cavity vary as the amperage which it will use; the amperage for cells using multiple electrodes ranges between 8000 to 30,000 amperes.

The carbon lining of the cell must have adequate electrical conductivity to carry the current to the aluminum as well as sufficient strength to stay in place. If the lining becomes overheated or stressed during operation, loose particles of carbon may float in the bath and cause partial short circuits between anodes and the metal. Cracks in the lining may result in leakage of the aluminum through the carbon blocks with subsequent contamination from the steel shell.

Two types of linings are used by the aluminum industry. One is made by ramming a hot mixture of pulverized coke with tar and pitch into a steel shell and then baking the whole in a furnace at 600 to 800 °C. The other method is to use carbon blocks which have been preformed and baked in the same manner as the electrodes are made and a mixture of tar, pitch, and ground coke cements them together.

The carbon anodes are made from a mixture of carbon, tar, and pitch by either molding or extrusion. They are baked at about 1000 °C or more. Petroleum or low-ash anthracite coke are used for anodes to avoid contamination of the aluminum by silica and iron oxide in the ordinary coke.

The anodes hang from two or more aluminum or copper busbars supported above the cell and are held by aluminum or copper rods which carry current to the anodes; the rods serve also as a means of lowering the anodes as they are consumed. Care must be taken to keep the anodes adjusted properly to insure evenly distributed current among them.

The continuous self-baking electrode was invented by C. W. Soderberg<sup>(48)</sup> about the year 1920. The electrode<sup>(11)</sup> has a metal electrode shell which is filled with the electrode paste. As the paste drops or is forced down through the mantle, it is gradually heated and baked until it becomes a solid electrode before it is fed into the electrolyte. An aluminum shell is used in the manufacture of aluminum.

Operation of the Electrolytic Cell. A cell in operation<sup>(11)</sup> contains three layers: a lower layer of molten aluminum which varies in thickness from a fraction of an inch to about five inches; an intermediate layer 6 to 12 inches deep of fused electrolyte consisting of molten cryolite in which is dissolved 2 to 5 per cent alumina; and an upper crust of solidified electrolyte through which the anodes project to within 2 to 4 inches from the surface of the molten aluminum.

Agitation of the electrolyte is provided by bubbles of carbon dioxide and carbon monoxide given off at the anodes, and by the effect of the magnetic field produced by the flow

of large currents through the cell. This agitation is important since the specific gravity of alumina is 4 as compared to 2.095 for cryolite and 2.29 for molten aluminum. Without agitation, the alumina would sink to the bottom of the cell when it was added instead of being dissolved by the cryolite. With agitation, it takes from  $1\frac{1}{2}$  to 9 minutes for 200-mesh alumina to dissolve completely in fused cryolite, depending on the saturation and temperature of the electrolyte and the character of the alumina.

During operation of the cell, the alumina content is decreased in direct proportion to the aluminum produced. The "anode effect" occurs when the concentration of the alumina is decreased to less than about two per cent, and the effect is a warning to the operator that it is time to break the electrolyte crust and add more alumina. With this addition, the "anode effect" disappears and electrolysis continues until the "effect" is again noticeable.

It is thought that the "anode effect" is caused by an increase in anode potential when the alumina concentration decreases. This increase causes energy in the form of heat to be liberated at the anode thus increasing the proportion of carbon monoxide in the gas formed at the anode. As the amount of gas around the anode increases, there is less contact between it and the electrolyte. The electrical resistance

increases and, if the current is kept constant, there is a sharp rise in voltage across the cell, from 6 to 7 volts up to 30 or even 60 volts.

Usually, 30 to 100 cells are connected in series to require from 200 to 600 line volts. This is done to make the generation of electricity economical since each cell requires a large current and a small voltage. It is not economical to generate electricity at low voltages.

To produce one pound of aluminum requires from 10 to 12 kilowatt hours of electricity and about 0.6 to 0.8 pound of anode. As the aluminum accumulates, it is removed about every 2 or 3 days either by tapping the cell or by ladling off the electrolyte and then the molten aluminum. The aluminum from many cells is combined and remelted to insure uniformity of composition and finished ingots are cast from this metal.

#### The Corrosion of Aluminum

Aluminum has a great many applications where metals and metallic coatings which are resistant to oxidation and corrosion are required for handling certain types of chemicals. A few generalizations may be given before some specific properties of aluminum are mentioned.

Generalizations. At least five generalizations may be made with regard to the behavior of aluminum in contact with other chemicals. (29) They are:

1. Neutral solutions are less corrosive to aluminum than are acidic or basic solutions.
2. In the presence of an electrolyte, the electrical contact of aluminum with heavy metals, such as copper, iron, nickel, lead, etc., produces galvanic corrosion of aluminum.
3. Aluminum is more resistant generally to the action of oxidizing substances than to that of reducing substances.
4. The halogen salts of the alkali metals are more active in producing attack on aluminum than are most other neutral salts of these metals, and
5. The simultaneous presence of dissolved heavy metal compounds and halogen salts is likely to cause severe attack on the aluminum.

Atmospheric Corrosion. Aluminum has a high affinity for oxygen, quickly forming a protective oxide film upon exposure to an oxygen-bearing atmosphere. (29) The film is estimated to be approximately  $5 \times 10^{-7}$  inch thick and it prevents further attack unless removed or penetrated by chemical or mechanical means. It is this characteristic that furnishes aluminum and its alloys their resistance to corrosion.

The heavily polluted industrial atmospheres, particularly in the moist climates, lead to considerable corrosion of aluminum. (49) Although gases such as carbon dioxide and hydrogen sulfide have very little effect on aluminum, the metal is attacked by moist sulfur dioxide and moist chlorine. The atmosphere along the sea coasts is not especially harmful unless direct contact is made between aluminum and the salt spray.

Atmospheric corrosion of aluminum and its alloys is generally not excessive. (29) When conditions are extremely severe, it is advisable to use a common alloy of the magnesium-silicon type, a clad high copper or zinc-bearing alloy or a protective coating of paint.

Aluminum is highly resistant to corrosion at high temperatures (26) in dry atmospheres containing such gases as air, oxygen, nitrogen, carbon dioxide and hydrogen; it is not resistant to halogens or their compounds. A highly protective film forms on the surface of aluminum when it is exposed to certain gases.

Above 700 °F, internal oxidation of certain aluminum alloys may occur upon exposure of the metal to atmospheres containing both oxygen and water vapor. This phenomenon takes place particularly with aluminum-base alloys containing appreciable amounts of magnesium.

Steam creates a protective white film on aluminum alloys which is highly protective up to 250 °C. Above this temperature, under some conditions, aluminum oxide and hydrogen are formed by the reaction between aluminum and steam.

Aluminum is one of the most effective elements<sup>(2)</sup> used in alloying steel to reduce the rate of scaling. Formation of the oxide retards further attack on the underlying metal.

Approximately ten per cent aluminum is required as an alloying element with steel and this amount tends to cause embrittlement.<sup>(47)</sup> For many applications, calorized coatings have been used quite successfully. Such surfaces are particularly resistant to sulfur dioxide and find wide use in the oil industry at temperatures up to 1000 °C. Diffused-aluminum coatings do not protect iron from ordinary atmospheric or aqueous corrosion.

Chemical Corrosion. A desirable property of aluminum and its alloys is its resistance to attack from many chemicals.<sup>(35)</sup> Many strong mineral acids, alkalies, and acid-salt solutions quickly penetrate the oxide film and attack aluminum, forming a salt and liberating hydrogen. Unprotected aluminum alloys should not be used with such solutions. Specific examples pertaining to chemical corrosion will be given in a discussion on chemical resistance.

Types of Corrosion. When aluminum and its alloys are not immune to corrosion under a specific set of conditions, control of the type of corrosive attack becomes important.<sup>(29)</sup> It is desirable that corrosion be of the pitting type since this type has the least effect on the mechanical properties. On the other hand, intergranular corrosion can cause premature failure due to the stress by rapidly reducing the effective cross-sectional area of the metal.

Practically all types of corrosion prevalent in aluminum alloys, other than chemical attack, are caused by galvanic action. The conditions necessary for such an attack are at least two areas of different potentials connected by an electrolyte. Water, contaminated with chlorides or salts, is generally the electrolyte. The areas of different potentials can be dissimilar metals or alloys, concentration of constituents of the solution, inclusions or similar non-homogeneous material.

In galvanic action, the current flows from the anodic to the cathodic areas. Aluminum is dissolved at the anode but immediately reacts to form aluminum hydroxide which precipitates around the anodic area. Hydrogen is evolved at the cathode which is not attacked.

When intergranular corrosion occurs, the attack takes place in the impoverished zones adjacent to the grain boundaries which are anodic to both the matrix and the precipitate. This attack quickly penetrates the metal resulting in a serious loss of mechanical properties. This type of attack is known as interfragmentary corrosion when present in an unrecrystallized structure, which is often predominant in large extruded sections.

Alloys which have a high copper content are susceptible to intergranular attack when subjected to a slow quenching rate, a delayed quench and, with some alloys, heating to the critical



temperatures after quenching. When the foregoing conditions prevail, excessive precipitation results as the metal cools.

A few of the very high strength alloys, particularly those of high zinc content, are occasionally susceptible to stress-corrosion cracking which is the fracture of metal under the combined effect of high stress and corrosion. The use of small amounts of specific elements, (14) such as titanium, silicon, vanadium and molybdenum, and the control of the precipitation processes has alleviated this difficulty.

Chemical Resistance. The following discussion is concerned with the behavior of aluminum with certain chemicals (29) and of some of the inhibitors (13) which are used to decrease corrosion of aluminum and its alloys.

Concentrated nitric acid, 95 per cent by weight, does not attack high purity aluminum. The rate of attack is low for concentrations above 80 per cent or below 5 per cent, but the attack is considered excessive for concentrations between 5 and 70 per cent by weight.

The attack by sulfuric acid is greater than with nitric acid, but high purity aluminum is used with solutions containing up to 5 per cent sulfuric acid. High purity alloys have been used with solutions of up to 15 per cent sulfuric acid. Fuming sulfuric acid has a low rate of attack, but any appreciable amounts of water or water vapor causes serious attack.

Hydrochloric acid, hydrofluoric acid and hydrobromic acid solutions readily attack the aluminum alloys. Perchloric acid is decidedly corrosive to aluminum alloys. Phosphoric acid solutions used to clean and etch aluminum surfaces and, therefore, should not be used in lengthy contact with aluminum.

All strengths of boric acid solutions have very limited effects on aluminum. Weak solutions, less than 5 per cent, of chromic acid have little effect on aluminum; the rate of attack is excessive for concentrations above 10 per cent.

Simple organic acids, such as acetic, citric, lactic, and tartaric acids, in conjunction with a slight amount of water, have little or no effect on aluminum. Fatty acids likewise have a low rate of attack. However, the attack may be increased in the total absence of water. Simple acids that contain a halogen radical, and such acids as formic and oxalic are too corrosive for most applications.

Strong caustic solutions rapidly attack aluminum. Weak solutions, containing chemical inhibitors, have a low rate of attack. Ammoniacal solutions have little effect on aluminum after building up a protective surface film. Calcium hydroxide and calcium chloride, in the presence of water, are highly corrosive to aluminum unless an inhibitor is used.

Salts composed of strong acid radicals, except the halogens, and weak base radicals have very little effect on aluminum. The halogen-bearing salts, such as ammonium chloride, are very corrosive

unless used in conjunction with an inhibitor. Ammonium nitrate and ammonium sulfate are used satisfactorily with aluminum.

Salts composed of weak acid radicals and strong base radicals, which hydrolyze forming pseudo-alkaline solutions, should not be used with aluminum unless suitable corrosion inhibitors, such as sodium or potassium chromate or sodium silicate, are employed.

Neutral salts, and solutions of neutral salts, have little effect on aluminum if heavy-metal salts are absent. However, solutions containing strong halogen salts are corrosive to aluminum, especially when heavy metal salts are present, unless a corrosion inhibitor is used. Neutral nitrates and sulfates are mild inhibitors of corrosion.

When aqueous solutions, or liquids containing small amounts of water, are contaminated with heavy metals or their salts and in contact with aluminum, a severe pitting type of corrosion may occur. Aluminum, being anodic, that is electronegative, to practically all of the heavy metals will replace them from their compounds. The replaced metals will be deposited upon the aluminum surface causing galvanic action. Small pits are formed on the surface and eventually become holes and the aluminum must be replaced. Frequent cleaning or the addition of corrosion inhibitors will minimize the degree of attack.

Corrosion Inhibitors. Inhibitors for aluminum corrosion behave differently in various acids, according to Eldridge and Mears. (13)

Chromates are effective in phosphoric acid but not in hydrochloric acid. Nitrogen compounds and steel pickling inhibitors are usually effective inhibitors for aluminum in hydrochloric acid but are less efficient for aluminum in other acids such as phosphoric acid. No inhibitor is needed for nitric acid at concentrations of 70 per cent or more. Very small chromate additions are effective in dilute solutions under 20 per cent nitric acid. No very satisfactory inhibitors for aluminum in sulfuric acid are known.

No very satisfactory inhibitors for sodium hydroxide or potassium hydroxide are available although agar agar, gum arabic, glucose, and gelatin are stated<sup>(13)</sup> to be reasonably effective. Silicates and fluosilicates are very effective in alkali carbonate or phosphate solutions. However, large concentrations of inhibitors are required at temperatures near the boiling points of these solutions. Sodium disilicate is effective in sodium hypochlorite solutions and is reported to be effective in chlorine water. If the chromates are not present in sufficient amounts, they will cause pitting.

Borates and phosphates are used as inhibitors in ethylene glycol solutions. Chromates have been successfully used in alcohol solutions. Tricresyl phosphates are most effective in preventing perforations in aluminum cans containing gasoline with a synthetic sump-water or sea-salt solution.

Underground Corrosion. The principal metallic coating used for protection of steels and iron against soil corrosion is hot-dipped zinc. Both the composition and concentration of the chemical constituents of the soils have an effect on the corrosive action towards metals.<sup>(8)</sup> Contact of soil particles with a metal surface gives rise to oxygen concentration cells; areas deficient in oxygen become anodic and the areas high in oxygen become cathodic, leading to galvanic corrosion.<sup>(17)</sup>

The use of aluminum for electrical grounds has proved satisfactory provided that no electric current is passed through them.<sup>(18)</sup> When an electromotive force is applied, rapid oxidation occurs and corrosion cannot be prevented. Gypsum formations yield soils which are least resistant to current and most liable to cause corrosion of the metal. Cathodic resistance is increased by a continuously regenerated corroding system<sup>(18)</sup> established when aluminum metal is in contact with soil containing alkali or alkaline earth metal cations. These metal cations form a base at the cathode by combining with the hydroxide liberated by evolution of hydrogen. The base attacks the aluminum and aluminate is formed. The aluminate is hydrolyzed with the formation of oxide and regeneration of the base which again attacks the metal.

The best protection<sup>(44)</sup> of steel pipes from subsoil corrosion is given by magnesium alloys containing 6 and 0.4 per cent of aluminum and manganese, respectively; or 3, 1, and 0.3 per cent of aluminum, zinc, and manganese, respectively.

Methods for Testing the Corrosion of Aluminum. The corrosion of aluminum by the atmosphere is tested by exposing thin sheets of the metal or its alloys to the atmosphere for different periods of time; the rate of corrosion is measured by the change in the tensile properties of the metals. (8)

Soil corrosion tests consist in burying a number of aluminum specimens in the soil of particular interest so that sets can be removed at the end of successive intervals of time, one, three, five, and ten years, etc., to determine the rate of corrosion and probable life of the material. The loss in weight and depth of pitting are measured, the depth of pitting being measured from a small protected area on the sample.

The salt spray test is useful as a means of comparing the quality of different samples of a given material but it is not reliable as a test for evaluating the corrosion resistance of different metals. The sample to be tested is subjected to continuous spray of 20 per cent sodium chloride, or 3.5 per cent sodium chloride, solution in a box of suitable material, such as glass, rubber, wood, or soap-stone. The time of exposure may be chosen for best results since no standard exposure periods have been designated.

Intermittent immersion corrosion tests are operated by having the samples hung from a shaft which is turned by a motor controlled by a timing device. The specimens are lowered into the corrosive solution and then withdrawn for a period of time sufficient to dry

the sample; the process is repeated for an indefinite number of times, depending on the metal and size of the specimen. Various corrosive solutions have been used, such as 2 per cent ammonium chloride, 20 per cent sodium chloride, and 0.5 per cent each of malic acid and sodium chloride. Solutions are used at room temperatures, 35 and 60 °C, while the humidity of the atmosphere is usually controlled to obtain comparable rates of drying of the specimens.

The procedure for the accelerated corrosion test of sheet aluminum materials<sup>(53)</sup> is to cut a sample 1 x 5 inches and pretreat it at 95 °C for one minute in an etching solution containing 50 milliliters of 70 per cent nitric acid and 5 milliliters of 48 per cent hydrofluoric acid per liter of aqueous solution. After rinsing and drying, the pretreated specimen is totally immersed in the corrosion test medium which consists of 57 grams of U. S. P. sodium chloride and 10 milliliters of 30 per cent hydrogen peroxide dissolved in water to make a liter of solution. The usual exposure period is six hours at a temperature of 30 °C. The corroded specimen is then cross-sectioned and examined, metallographically, at magnifications of 100 and 500 to determine the type and extent of attack, which may be either interdendritic, interfragmentary, or pitting in nature.

### Aluminum Coatings on Other Metals

Aluminum is used extensively as a protective coating for other metals, particularly on iron and steel. Aluminum coatings are used for protecting the base metals from corrosion at high temperatures and from oxidation. Aluminum may be coated on the base metals by calorizing, spraying, hot rolling, painting, thermal evaporation, cathodic sputtering, and electrodeposition; these methods are discussed in order.

Calorizing. Calorizing is a trade name for processing alloying carbon or alloy steel with aluminum by diffusion. The depth of penetration ranges from 0.005 to 0.040 inch.<sup>(45)</sup> The alloyed surface usually contains about 25 per cent aluminum. Three methods of calorizing are by revolving retort, packing, and dipping.

Revolving Retort Method of Calorizing. The revolving retort method used prior to 1935<sup>(45)</sup> was to pack the article to be coated in a mixture comprising finely divided aluminum, alumina, and a material such as ammonium chloride in the amount of one per cent to facilitate the coating.<sup>(12)</sup> The packed article was sealed gastight in a heated revolving retort for 4 to 6 hours at 1550 to 1700 °F.<sup>(45)</sup> The surface obtained was an aluminum-iron alloy about 0.001 to 0.006 inch deep and containing about 60 per cent aluminum. However, the surface was brittle and weak, and these characteristics led to the modern method.



The new method<sup>(45)</sup> follows the old method with 12 to 48 hours of heat treatment of the coated article at temperatures of 1500 to 1800 °F. The aluminum is diffused to a depth of 0.025 to 0.040 inch, thereby decreasing the aluminum content of the surface to 25 per cent. The resulting surface is not only heat and corrosion resistant but it exhibits toughness and ductility.

Pack Calorizing. In pack calorizing, the article to be coated is packed with the powdered aluminum compound and sealed in an atmosphere of hydrogen in a stationary box.<sup>(45)</sup> It is then heated for 6 to 24 hours at 1500 to 1800 °F. The high temperature is maintained to prevent the coalescing of the small particles of aluminum and alumina and to cause diffusion of the aluminum into the base metal surfaces.<sup>(12)</sup> This process is used particularly for articles which would be damaged by tumbling about in a rotating retort.<sup>(45)</sup> Copper may also be coated by calorizing.<sup>(12)</sup>

Dip Calorizing. When dip calorizing is used, the article to be dipped is cleaned by using a flux, ammoniated zinc chloride or a concentrated solution of boric acid or borax, to remove the oxide coating.<sup>(7)</sup> After dipping it in molten aluminum, the article is heated to cause diffusion of the aluminum. The difficulty of obtaining an adherent coating is attributed to the formation of a film of aluminum oxide at the iron-aluminum interface in the dipping operation.

Spraying. The aluminum, usually in the form of a wire, is heated electrically or by a gas flame and then dispersed by gas pressure to the surface of the base metal.<sup>(12)</sup> Since the aluminum coating is quite porous, the surface does not resist corrosion but does offer protection against oxidation. The coating is usually from 0.004 to 0.012 inch in thickness and it does not adhere as well as those applied by other methods.<sup>(45)</sup>

Hot Rolling. Aluminum may be applied to iron<sup>(12)</sup> by heating thin sheets of aluminum and sheet iron to about 300 to 400 °C and passing them through rolls together while the aluminum strip is kept under tension. The combined metals are subjected to a second rolling to give the desired thickness and perfect the union of the metals. The result is a uniform coating of the iron with aluminum which is not alloyed to it and thus retains its ductility. This method combines the corrosion resistance of the aluminum with the strength of iron at reasonably low cost.

Painting. Although aluminum paint is a combination of several materials, the aluminum is the ingredient which acts as a corrosion inhibitor when applied to base metals.<sup>(12)</sup> Aluminum bronze powder is mixed with a vehicle such as varnish, lacquers, bronzing liquids, or bodied oils to make the paint. The powder is made from pure aluminum sheets which are stamped into small clippings and then hammered into thin foil-like pieces. The pieces become harder as they are cold-worked and break into tiny flakes to which a lubricant is added

to prevent adherence of the flakes together. A polishing process in which more lubricant, such as stearic acid, is used with revolving brushes which rub the flakes against the sides of a drum and each other to give the flakes maximum brightness.

The high durability of aluminum paint<sup>(12)</sup> is traced to a unique property of aluminum, which is its high opacity to light. Another characteristic which is desirable in a corrosion resistant paint is its moisture resistance. Tests made by the Forest Products Laboratory showed that three coats of aluminum paint made with spar varnish had a moisture-proofing efficiency of 94 per cent. The aluminum paint can be applied by brushing or spraying on the surface to be coated.

Thermal Evaporation. Thermal evaporation<sup>(22)</sup> is a physical method of coating a surface with a thin film. A thin film is defined as "a structure essentially fragmentary, without the ordered arrangement of crystal lattices which are characteristic of massive metal". The production of a thin film involves three essential stages: (1) the production of the gaseous phase of metal; (2) the distribution of the metallic gaseous phase; and (3) condensation.

Evaporation can be accomplished by heating a metal wire in an electric furnace in a vacuum. If the vacuum is sufficiently high,  $1 \times 10^{-4}$  millimeters of mercury, the atoms move in a straight path. Any residue of gas in the so-called vacuum will distribute the metal vapors according to the diffusion law. The physical condition and adherence of the deposit is affected by the presence of gases as well

as the distance between the evaporating source and the receiving surface, and the temperature. To obtain good adherence of the metal atoms, their mean free path should be greater than the longest path between the source of evaporation and the receiving surface. A number of sources is arranged geometrically to give the desired uniformity of thickness to the coating. This process is used for coating mirrors as large as 48 inches in diameter.

Cathodic Sputtering. Cathodic sputtering<sup>(22)</sup> is the dislodging of the cathode material by high-speed positive gaseous ions. Subatmospheric pressures from  $1 \times 10^{-6}$  to 3 millimeters are used. The processes are still unexplained and it is not known whether the particles emitted are atomic or molecular in size. Aluminum is one of the most difficult of metals to sputter, irrespective of the gas employed in the sputtering chamber, such as hydrogen, helium, nitrogen, oxygen, or argon. The apparatus comprises two bell jars, the upper of which holds the electrode of the metal to be sputtered in a gas-tight connection. This electrode is connected with the negative pole. The aluminum compensating electrode is sealed into the lower bell jar and connected with the positive pole. During the sputtering, the article to be coated is placed between anode and cathode and is heated either by a gas discharge or glow current to a temperature not lower than that of the eutectic alloy of the two metals involved.

Cathode sputtering results in a thin film which is useful for astronomical mirrors. These coatings do not oxidize normally and they are of remarkable chemical purity and stability.

### Electrodeposition of Aluminum

Methods for the electrodeposition of aluminum so far investigated have not all been successful. The methods studied for electroplating of aluminum may be classified into four systems: from aqueous solutions; from nonaqueous organic liquid solutions; from nonaqueous inorganic liquid solutions; and from fused salts mixtures.

Previous Work with Inorganic Salts and Solutions. Many investigations of electrodeposition of aluminum have been from nonaqueous inorganic solutions and fused salts baths. Aluminum halides, especially aluminum chloride, are the most frequently used solutes. Because the aluminum chloride is one of the strongest peptizing agents for aluminum oxide and its hydrate, the articles plated with aluminum from aluminum chloride are subject to severe corrosion. For this reason, use of other aluminum salts as solutes appears to be more promising.

Aqueous Solutions. Tucker and Thompson<sup>(51)</sup> claimed to have produced a suitable method for the electrodeposition of aluminum by carrying on the electrolysis in an aluminum chloride paste in which the cathode rotated at 20,000 revolutions per minute. P. Marino<sup>(24)</sup> obtained a patent for electrolyzing

an aqueous solution of sodium pyrophosphate to which had been added 10 per cent phosphoric acid and from 5 to 10 per cent sulfanilic acid; G. Marino<sup>(25)</sup> patented a process using an aqueous ammonia solution of aluminum tartrate, paratartrate and oxalate. Both used aluminum anodes.

Fused Salt Bath. Considerable work has been done in an attempt to electrodeposit aluminum from aluminum-alkali halide mixtures. Wade and his coworkers<sup>(52)</sup> employed a system of 20 mole per cent sodium chloride, 14 mole per cent potassium chloride, and 66 mole per cent aluminum chloride in a study of deposition and decomposition potentials of a number of chlorides. Platinum was used as the reference electrode and aluminum was found to deposit a smooth surface at a potential of -2.02 volts and at a current density of 15 amperes per square decimeter. Dendritic aluminum was deposited at a potential of -2.17 volts and the same current density.

Wade prepared a sample of each deposit type of aluminum for study. The smooth surface was deposited by impressing -2.09 volts on the cathode for one hour at 1.25 amperes per square decimeter. The deposit was easily removed by scraping the surface of the cathode with a dull blade. A dendrite aluminum deposit was made at a potential of -2.2 volts at the same current density. This deposit also was removed easily. Examination of the deposits by x-ray comparison with pure aluminum confirmed their identity as the pure metal.

Plotnikov et al<sup>(31)</sup> claim to have produced a satisfactory surface of aluminum on copper from a bath containing aluminum chloride and sodium chloride in a 2 to 1 ratio at 200 to 250 °C. Cathode current density was one ampere per square decimeter.

Previous Work with Organic Salts and Solutions. The aluminum halides are soluble in many solvents, as seen from the wide application of Friedel-Craft reactions. Meerwein<sup>(27)</sup> has shown that many weak electrolytes are increased in strength by the formation of complex ions. The existence of conductivity has been attributed to the formation of solute-solvent complexes by Hein and Schramm.<sup>(27)</sup> Consideration of all of these facts indicates a possible means of solving the problem of electroplating aluminum from organic solvents.

Single Solvents. The literature reports the electrochemical study of aluminum halides in many solvents, including: various alkyl halides, e. g. ethyl chloride, ethyl bromide, ethyl iodide, and ethyl thiocyanate; aromatic hydrocarbons, e. g. benzene, toluene, and xylene; nitroderivatives of aromatic hydrocarbons, e. g. nitrobenzene; heterocyclic compounds, e. g. pyridine; ethers, e. g. ethyl ether; polyhydric alcohols, e. g. cellosolve, and glycerine; aldehydes, e. g. valeraldehydes, benzaldehyde, crotonaldehyde, and cinnamaldehyde; ketones, e. g. acetone, methyl acetone, and acetophenone; acids, e. g. formic acid, acetic acid, etc. Of these, more detailed information can be found and will be summarized for ethyl bromide, benzene, and nitrobenzene.

The following data on the electrochemical properties of various aluminum salts in single solvents have been found in the literature.

Ethyl Bromide as a Solvent. For the aluminum bromide-ethyl bromide system, the specific conductivity increases with the concentration of  $\text{AlBr}_3$  within the range 46.3 to 72.34 per cent. <sup>(19)</sup> The maximum specific conductivity is obtained at the mole ratio of 0.64 to 0.66,  $\text{AlBr}_3$  to  $\text{C}_2\text{H}_5\text{Br}$ .

The decomposition potential of aluminum bromide in ethyl bromide is 0.98 volts. <sup>(19)</sup> At various current densities, the lower constant value is 0.74 volts; 1.76 volts is the value calculated from thermochemical data. <sup>(16)</sup> The upper decomposition potentials for 5, 30, and 55 weight percentages of  $\text{AlBr}_3$  are 3.25, 2.10, and 2.05 volts, respectively.

The current-voltage relation for the system aluminum bromide-ethyl bromide consists of two straight lines crossing the abscissa at 0.8 and 2.4 volts for white and black aluminum deposits, respectively. <sup>(21)</sup>

For the ternary system of alkali halide-aluminum bromide-ethyl bromide, the specific conductivity is increased by the addition of either a metal bromide or chloride, where the metal is lithium, sodium, potassium, or silver, also rubidium in the case of bromine. <sup>(28,35,40)</sup>



For the metal bromide-aluminum bromide-ethyl bromide system, (35) the conductivity increases with the concentration of the bromide of a metal in the first group in the periodic system and decreases with dilution. For different metal salts, the conductivity decreases in the following order: silver, lithium, copper, potassium, and rubidium.

For the lithium bromide-aluminum bromide-ethyl bromide system, (35) maximum specific conductivity is  $12.78 \times 10^{-3}$  ohm<sup>-1</sup> at 18 °C for the ratio of 0.839, LiBr to AlBr<sub>3</sub>. This value was obtained by holding the molar ratio of AlBr<sub>3</sub> to C<sub>2</sub>H<sub>5</sub>Br equal to 0.289 while the ratio of LiBr to AlBr<sub>3</sub> was varied between 0.617 and 0.905.

For the sodium bromide-aluminum bromide-ethyl bromide system, (40) the specific conductivity of solution increases as the sodium bromide concentration increases. The increase in conductivity is greater for solutions with greater aluminum bromide concentrations. Addition of 0.5 gram mole of NaBr per gram mole of AlBr<sub>3</sub> to a solution with a ratio of AlBr<sub>3</sub> to C<sub>2</sub>H<sub>5</sub>Br of 0.27 raises the conductivity five times. The increase is tenfold for solutions containing less aluminum bromide.

For the metal chloride-aluminum bromide-ethyl bromide system, (39) where the metal is lithium, sodium, or potassium, the increase in conductivity is more rapid for the metals of greater atomic weight.

The increase in conductivity with temperature was noted in the case of lithium chloride and sodium chloride only. (28)

During electrolysis of the systems metal chloride-aluminum bromide-ethyl bromide with a platinum anode, a reddish-yellow coloration was observed in the anode region. This coloration was absent when aluminum and silver anodes were used. (28)

For the potassium iodide-aluminum bromide-ethyl bromide system, (19) the increase in conductivity depends on the concentration of aluminum bromide in the solution to which potassium iodide is added. The conductivity, upon addition of potassium iodide, increases with aluminum bromide up to a molar ratio of 0.3 for  $\text{AlBr}_3$  to  $\text{C}_2\text{H}_5\text{Br}$ . The conductivity, for ratios of  $\text{AlBr}_3$  to  $\text{C}_2\text{H}_5\text{Br}$  above 0.42, decreases with increasing concentration of aluminum bromide when potassium iodide is added.

In each ternary system, (35) when the metal added as chloride is lithium, sodium, potassium, or rubidium, a deposit of aluminum forms on the cathode; but when it is silver, silver is deposited on the cathode.

The decomposition potentials (35) for lithium bromide, rubidium bromide, and silver bromide were 2.0, 1.66, and 1.3 volts, respectively. A decomposition potential of 1.68 volts is obtained for the following two systems: (40) (A) 2.51 mole per cent  $\text{NaBr}$ , 28.49 mole per cent  $\text{AlBr}_3$ , and 68.97 mole per cent  $\text{C}_2\text{H}_5\text{Br}$ ; (B) 6.9 mole per cent  $\text{NaBr}$ , 36.8 mole per cent  $\text{AlBr}_3$ , and 56.3 mole per cent  $\text{C}_2\text{H}_5\text{Br}$ .

With the sodium chloride-aluminum bromide-ethyl bromide system, <sup>(21)</sup> the addition of salt to the aluminum bromide and ethyl bromide causes the disappearance of the decomposition potential of 0.80 volts. Addition in large amounts causes an increase of the greatest decomposition potential from 2.4 to 4.05-4.25 volts for the molar ratio of 1 to 1, NaCl to  $\text{AlBr}_3$ .

Current-voltage curves <sup>(21)</sup> show a decomposition potential of 2.0 volts when  $x$  is 0.5 or less, where  $x$  represents moles of NaCl in a solution of one mole of  $\text{AlBr}_3$  and ten moles of  $\text{C}_2\text{H}_5\text{Br}$ , a decomposition potential of 2.0 to 4.0 volts when  $x$  is 0.6 to 0.9, and a decomposition potential of 4.0 volts when  $x$  is 1.0. These data show that at small values of  $x$ , only aluminum bromide is decomposed; at medium values of  $x$ , both aluminum bromide and sodium chloride are decomposed; and at high values of  $x$ , only the decomposition of sodium chloride takes place.

For the systems aluminum bromide-sodium bromide-ethyl bromide and aluminum bromide-potassium bromide-ethyl bromide, <sup>(56)</sup> only the alkali salt is decomposed at a 1 to 1 mole ratio of  $\text{AlBr}_3$  to  $\text{MBr}$ , where  $M$  is sodium or potassium; only aluminum bromide decomposes at mole ratios of  $\text{MBr}$  to  $\text{AlBr}_3$  which are much less than one.

For the aluminum bromide-potassium iodide-ethyl bromide system, <sup>(19)</sup> the decomposition potential is 1.28 volts. Electrolysis results in electrodeposition of aluminum on the cathode and liberation of iodine at the anode.

Ethyl Iodide as a Solvent. Upon investigation of the solubility <sup>(15)</sup> of alkali halides in an aluminum bromide-ethyl iodide solution, the literature states that the solubilities of the alkali halides increase with the concentration of aluminum bromide in the solution. For a definite aluminum bromide concentration, the solubility of halides decreases in the following order: lithium, sodium, and potassium.

Conductivity <sup>(20)</sup> is affected by the addition of salts at different molar ratios of aluminum bromide to ethyl iodide. For a molar ratio of 0.23 to 0.24, the addition of halides decreases the conductivity. For a molar ratio of 0.44 to 0.46, the addition of chlorides or bromides raises the conductivity but iodides lower it. For a molar ratio of 0.67 to 0.71, the conductivity rises in all cases except for the addition of potassium iodide.

The decomposition potential <sup>(20)</sup> is 1.26 to 1.29 volts for the aluminum bromide-ethyl iodide-alkali halide system regardless of which halide is used. Electrolysis of these systems results in aluminum crystals which adhere to the electrode poorly.

Ethyl Thiocyanate as a Solvent. The specific conductivity of thiocyanate solutions<sup>(1)</sup> is similar to the absolute values and in the character of the curves to that of ethyl bromide and ethyl iodide for the systems: aluminum bromide-ethyl thiocyanate, potassium bromide-aluminum bromide-ethyl thiocyanate, potassium iodide-aluminum bromide-ethyl thiocyanate, and potassium thiocyanate-aluminum bromide-ethyl thiocyanate. There is closer similarity in the properties of ethyl thiocyanate and ethyl iodide than of ethyl thiocyanate and ethyl bromide.

Benzene as a Solvent. The specific conductivity<sup>(39)</sup> of aluminum bromide or aluminum chloride in benzene rises with dilution and with increasing concentration of the metal halide, where the metal is potassium, rubidium, lithium, and the halide is chlorine or bromine, and falls with increasing aluminum halide.

When ammonium halides are added to the system of aluminum bromide-benzene<sup>(39)</sup> within the mole ratio range 0.15 to 0.36, several effects are obtained. Increase in the concentration of ammonium halides increases the specific conductivity. The specific conductivity decreases in the order of chlorine, bromine, and iodine. Within the range of 18 to 50 °C, the conductivity increases with temperature and the function is linear. The maximum conductivity of all three systems occurs when the mole ratio of  $\text{NH}_4\text{X}$  to  $\text{AlBr}_3$  is 1 to 2, where X is chlorine, bromine, or iodine.

The maximum specific conductivity for the sodium iodide-aluminum bromide-benzene system occurs at 0.5 mole of NaI and 1.0 mole of  $\text{AlBr}_3$ .<sup>(36)</sup>

The maximum specific conductivity<sup>(32)</sup> of lithium bromide in benzene solutions of aluminum bromide is  $5.72 \times 10^{-3} \text{ ohm}^{-1}$ . The specific conductivity<sup>(40)</sup> of the system of ratios 51.5, 41.5, and 7.0 for  $\text{C}_6\text{H}_6$ ,  $\text{AlBr}_3$ , and KBr, respectively, is  $5.72 \times 10^{-3} \text{ ohm}^{-1}$ .

The decomposition potentials<sup>(39)</sup> for the systems ammonium halide-aluminum bromide-benzene are 1.95 volts when the halide is chlorine, 2.00 volts when the halide is bromine, but no constant value is obtained when the halide is iodine. The decomposition potential<sup>(32)</sup> for the system lithium bromide-aluminum bromide-benzene is 1.60 volts.

For the sodium iodide-aluminum bromide-benzene system, the decomposition potential shows two discontinuities at 1.08 and 1.78 volts as determined by Plotnikov.<sup>(36)</sup> But Yakubson<sup>(56)</sup> gave two values at 1.1 to 1.2 and 1.9 to 2.0 volts. The former value is said to correspond to the decomposition potential of aluminum iodide and the latter value to aluminum bromide.

Toluene and Xylene as Solvents. The maximum conductivity<sup>(32)</sup> of the system lithium bromide-aluminum bromide-toluene is  $5.28 \times 10^{-3} \text{ ohm}^{-1}$ . With increase in the concentration of bromides of lithium, copper, and silver, the conductivity increases

and changes abruptly when the molar ratio corresponds to complexes of the compositions  $\text{LiBr} \cdot 2\text{AlBr}_3$ ,  $\text{CuBr} \cdot 2\text{AlBr}_3$ , and  $\text{AgBr} \cdot 2\text{AlBr}_3$ .

The decomposition potentials<sup>(56)</sup> of the system sodium iodide-aluminum bromide-toluene is 1.1 to 1.2 and 1.9 to 2.0 volts, corresponding to the decomposition of aluminum iodide and aluminum bromide, respectively.

The specific conductivities<sup>(42)</sup> of both the aluminum bromide-xylene system and the ternary systems aluminum bromide-xylene with potassium bromide, sodium bromide, ammonium bromide, potassium chloride, sodium chloride, ammonium chloride, ammonium iodide varies with time.

The decomposition potential<sup>(42)</sup> of aluminum bromide-xylene solutions, as well as the ternary system with alkali halides is 1.64 to 1.68 volts, which corresponds with the values calculated by the Thomson equation. Dense and shiny deposits of aluminum were obtained from xylene solutions of aluminum bromide containing additions of potassium chloride, sodium chloride, or ammonium iodide. Best deposits were obtained with the addition of ammonium iodide. During electrolysis of the aluminum bromide-xylene with the addition of potassium chloride and using an anode of silumin, pure metallic aluminum was deposited on a copper cathode.

Nitrobenzene as a Solvent. The specific conductivity<sup>(33)</sup> of aluminum chloride in nitrobenzene increases with the concentration of aluminum chloride, with a maximum conductivity of  $146.1 \times 10^{-5} \text{ ohm}^{-1}$  at 14 per cent  $\text{AlCl}_3$ . There is a similar increase in conductivity<sup>(43)</sup> with aluminum bromide solutions, with maximum specific conductivity at 18 per cent  $\text{AlBr}_3$ .

The addition of metal halides<sup>(38)</sup> increases the specific conductivity of the solution of aluminum chloride or aluminum bromide in nitrobenzene to a maximum at the molar ratio of 1 to 1 for  $\text{AlCl}_3$  to  $\text{MX}$ , where M is ammonia, potassium, rubidium, and lithium; and X is chlorine, bromine, and iodine. Aluminum bromide may be substituted for the aluminum chloride. Each specific conductivity-concentration curve of aluminum bromide in nitrobenzene shows a maximum.<sup>(30)</sup> At  $50^\circ \text{C}$ , the specific conductivity of a 28.3 per cent  $\text{AlBr}_3$  solution is  $252 \times 10^{-5} \text{ ohm}^{-1}$ . The molar conductivity<sup>(33)</sup> of aluminum chloride in nitrobenzene increases with dilution and reaches a limit of  $45 \text{ ohms}^{-1}$ .

Upon electrolysis of alkali halides mixed with aluminum halide in nitrobenzene solution, Mezheni,<sup>(28)</sup> in 1938, reported that alkali metal is deposited at the cathode and Plotnikov and Barmashenko,<sup>(43)</sup> in 1941, reported that halogen deposits at the anode. Plotnikov and Podovian,<sup>(33)</sup> in 1933, reported



that the decomposition potential is five volts for a potassium deposit at a copper cathode. For sodium deposits, the decomposition potential is 4.5 volts.

Upon electrolysis of an aluminum bromide-potassium bromide-nitrobenzene system with platinum electrodes, Plotnikov and Podovian, <sup>(34)</sup> in 1934, reported that metallic aluminum is deposited on the cathode and bromine on the anode. The decomposition potential is 2.12 volts. These results do not agree with those given in the foregoing paragraph; however, the work was performed by different men and at different times.

Mixed Solvents. All of the mixed solvents containing nitrobenzene and forming solutions with alkali halides and aluminum halides give alkali metal deposits upon electrolysis. <sup>(28,33,46)</sup>

Comparative Study of the Conductivity of Various Solvents.

The conductivity of aluminum halide solutions <sup>(55)</sup> made by dissolving it in different solvents depends on its reaction with the solvents. In the cases of crotonaldehyde, benzaldehyde, and cinnamaldehyde, aluminum bromide solvates in these solutions are salt-like so that molar conductivity increases with dilution. The aluminum chloride-ketone addition products are not salt-like, and the molar conductivity of aluminum chloride solutions in acetone, iso-propyl acetone and methyl acetone is small.

The conductivity of aluminum halide solution in ethyl bromide, or ethyl bromide and benzene, always increases with time. (54)

According to Wertyporoch, (54) the addition of some higher cyclic hydrocarbons to an aluminum halide solution sometimes increases the specific conductivity of the solution. For example, the conductivity of aluminum bromide in ethyl bromide is increased by the addition of benzene, the increase being greater with time. The increase is due to the greater ability of the higher cyclic hydrocarbons to form addition compounds. The behavior of naphthalene is similar, but the increased conductivity with 2-methyl butene-2 is due to polymerization.

The addition of polar compounds (32) to the aluminum halide solutions causes an increase in the conductivity of the solution due to the formation of complex associated compounds. For example, the cryoscopic investigation of the complexes  $\text{LiBr} \cdot 2\text{AlBr}_3$ ,  $\text{AgBr} \cdot 2\text{AlBr}_3$ , and  $\text{CuBr} \cdot 2\text{AlBr}_3$  in benzene shows that they are very much associated and the degree of association increases with concentration.

The addition of nonpolar compounds (16) to solutions of aluminum halide lowers the specific conductivity of the solutions. Compounds such as stannous bromide, stannous chloride, and carbon tetrachloride do not form complexes with aluminum salts and probably decompose the complexes already existing between the aluminum halide and the solvent. They increase the

viscosity of the solution. Even a slightly polar compound such as arsenous bromide<sup>(36)</sup> causes a decrease in specific conductivity. For example, at the molar ratios of 5.8 for  $\text{AsBr}_3$  to  $\text{AlBr}_3$  and 0.19 for  $\text{AlBr}_3$  to  $\text{C}_2\text{H}_5\text{Br}$ , the specific conductivity is  $1.03 \times 10^{-4}$  ohm<sup>-1</sup>. It is about three times less than the conductivity for the same solution of aluminum bromide in ethyl bromide but in the absence of arsenous bromide.

The conductivities of aluminum halide solutions in diethyl ether<sup>(40)</sup> are greater than those in ethyl bromide; those in benzene are greater than those in nitrobenzene.

Decomposition Potential Studies. The magnitude of electromotive force and the order of metals is different for various solvents.<sup>(39)</sup> Upon electrolysis of the alkali halide-aluminum halide-nitrobenzene system, the alkali deposits on the cathode. Electrolysis of the alkali halide-aluminum halide-benzene system or the alkali halide-aluminum halide-ethyl halide system results in a metallic aluminum deposit on the cathode, provided the concentration of alkali salts is low as compared to that of the aluminum salts. Among the three solvents, benzene, toluene, and xylene, the best results are obtained from using xylene.<sup>(32)</sup>

Addition of different solvents to solutions of aluminum halide-alkali halide may influence the direction of aluminum ions<sup>(54)</sup> during electrolysis. Approximately equal amounts of aluminum are transferred to the anode and cathode in the

electrolysis of solutions of aluminum bromide in ethyl bromide; when in hexaethyl benzene, most of the aluminum is combined in the negative portion of the complex ion and goes to the anode while most of the hexaethyl benzene goes to the cathode.

The magnitude of the decomposition potentials of different systems gives an insight into the strength of complexes and solvates in solutions and it can be used as an analytical tool. (57) Yakubson's data on particular systems are given in Table I.

The electrodeposition of aluminum-heavy metal alloys from halide solutions in benzene is easier than from aqueous solutions because the potentials of the metals are near the value for aluminum. (6) Aluminum alloy deposits of copper, zinc, cadmium, silver, tin, nickel, lead and mercury were obtained.

Except for the alkali metal salts, all other metal salts added to the aluminum halide salts solutions gave the corresponding metal on electrolysis with no aluminum deposits. Most of the heavy metals can be codeposited as an alloy with aluminum from aluminum halide organic baths. The better appearing alloy deposits are generally high in aluminum.

TABLE I

Decomposition Potentials of Some Systems  
Containing Aluminum Bromide

System Composition, moles			Decomposition Potential volts	
NaCl - AlBr <sub>3</sub> - C <sub>2</sub> H <sub>5</sub> Br				
0.5	1	10	2.0	
0.6-0.9	1	10	2.0	4.0
1.0	1	10		4.0
NaI - AlBr <sub>3</sub> - C <sub>6</sub> H <sub>6</sub> or C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>				
0.6	1	10 (C <sub>6</sub> H <sub>6</sub> )	1.1-1.2	
0.6	1	10	1.9-2.0	
KBr - AlBr <sub>3</sub> - C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>				
0.8	1	10	4.6-4.8	
NaBr - AlBr <sub>3</sub> - C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>				
0.7	1	10	4.3-4.4	
LiBr - AlBr <sub>3</sub> - C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>				
0.7	1	10	5.0	
0.7-1.0	1	10	3.8	5.0
LiCl - AlBr <sub>3</sub> - C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>				
0.6	1	3	3.75	
0.6	1	100	4.90	

Yakubson, S. I.: Decomposition Potentials of Aluminum Bromide with Halides of Lithium, Sodium and Potassium in Nonaqueous Solutions, *J. Phys. Chem. (U. S. S. R.)*, 21, 343-348 (1947); *G. A.*, 41, 6159 (1947).

Recent Developments in the Use of Organic Systems for Electrodeposition of Aluminum. The electrodeposition of aluminum from fused quaternary ammonium salts and nonaqueous solutions is reported by Wier and Hurley.<sup>(66)</sup> They prepared ethyl pyridinium bromide and chloride, butyl pyridinium chloride, benzyl pyridinium bromide and chloride, and ethylene dipyridinium dibromide and dichloride by reacting pyridine with alkyl and aryl halides. These compounds were used as electrolytes in the study of electrodeposition of metals, particularly aluminum.

Various metal chlorides were added to fused ethyl pyridinium bromide and metal deposits of silver, copper, bismuth, lead, tin, nickel, cobalt, cadmium, iron, zinc and aluminum were obtained upon electrolysis of their respective salts. Electrolytic experiments with fused benzyl pyridinium bromide as the solvent for some of the metal chlorides showed these solutions had a much lower conductivity than did the ethyl pyridinium bromide mixtures.

A phase diagram study was made of mixtures of aluminum chloride in fused ethyl pyridinium bromide and it was found that eutectics exist at approximate mole ratios of 1 : 2 and 2 : 1, aluminum chloride to ethyl pyridinium bromide; the melting points for these eutectics are 45 and -40 °C, respectively. Electrolyses showed the optimum composition for electrodeposition of aluminum to be that of the lower eutectic but satisfactory plates could be obtained over a range of 54 to 70 mole per cent aluminum chloride. These baths deteriorated,

by air oxidation, unless protected by an atmosphere of dry, nonoxidizing gas. Optimum conditions for aluminum plating on steel were a current density of 0.5 ampere per square decimeter for one hour at 125 °C. Only 2 to 3 volts was required for the electrolysis. Similar studies with fused mixtures of aluminum chloride in ethylene dipyridinium dibromide and dichloride showed that satisfactory deposits of aluminum could be obtained at the low-melting eutectic composition of four moles of aluminum chloride to one mole of the pyridinium salt.

Then a study was made <sup>(67)</sup> to determine what effect the addition of various organic solvents to a mixture of aluminum chloride and ethyl pyridinium bromide would have on the electrodeposit of aluminum. Among the solvents tested were pyridine, ethyl ether, benzene, hexane, carbon disulfide, chloroform, alkyl halides, and chlorobenzene; benzene proved to be the most satisfactory of these.

An excess of benzene was added to a mixture of aluminum halide and ethyl pyridinium bromide until the electrolyte layer was covered with a protective layer of benzene. The optimum condition for electrolysis of this bath was found to be a current density of about one ampere per square decimeter, and the composition range for satisfactory deposits was 50 to 63 per cent by weight of aluminum chloride. The potential required for plating was approximately one volt. The usual thickness of the deposit was 0.006 millimeters and, although plates of 0.025 millimeters could be obtained, the thinner coating was adequate for complete coverage. After 18 months of exposure to

rains and the atmosphere, only a few pinholes were observed on the exposed plated surfaces. As with the fused baths, these nonaqueous systems had to be protected from moisture and oxygen to prolong the life of the electrolyte. Although the other pyridinium salts in nonaqueous solutions could be used for electrodeposition of aluminum, they were not as satisfactory as the one described.

Some experiments were performed to study the effect of superimposing alternating on direct current. The platings obtained under these conditions were brighter, more adherent, and it was possible to increase the thickness to 0.030 millimeter without lowering the ductility. Higher current densities, as much as 100 per cent greater, could be used with the superimposed alternating current.

Electroforming Methods for Manufacture of Wave Guides. In a report by Safranek, Schickner and Faust<sup>(64)</sup> on electroforming methods for manufacture of wave guides, an account is given of further investigation of the system aluminum chloride, ethyl pyridinium bromide and toluene.

The principle bath used for the electroforming of wave guides was composed of 36 parts of ethyl pyridinium bromide-aluminum chloride fusion product dissolved in 64 parts, by volume, of toluene. This is a ratio of 49 to 51, respectively, by weight. Baths which were operated continuously for more than about 40 days, without replenishing, deteriorated so that the electroforms produced were defective in density and outer surface smoothness. To prevent this



deterioration, the specific gravity of the bath was maintained at 1.11 to 1.13 and the weight fraction of toluene at 0.47 to 0.48. These conditions were held constant by the replacement of 1.8 per cent of the volume with fresh bath every three days. The new bath added contained 1.2 per cent methyl tertiary butyl ether which resulted in a long-lasting smoothening of the deposits.

Plating Cell Operation. The largest cell used for electroforming of wave guides was a nine-liter container made of Pyrex glass. Four aluminum anodes were spaced in a circle of  $2\frac{1}{2}$ -inch radius around the cathode, which was a copper-coated low-melting alloy such as cadmium-nickel. The alloy contained one to two per cent nickel and had a melting point of about 600 °F. The cell was sealed to prevent loss of toluene vapor and a water-cooled condenser was used to return condensed toluene to the bath continuously.

When electroforming was accomplished with the use of direct current only, the plates were ductile and smooth but so highly stressed that they usually cracked in a short time.

The superimposition of alternating current on the direct current decreased the dislodgement of sludge particles from the anodes and this decrease resulted in smoother, less nodular aluminum plates. The best ranges for the cathode current density were found to be 8 to 12 amperes per square foot for the direct current and 10 to 20 amperes per square foot for the alternating current. For the anode, the best ranges of current density were 1 to 3 amperes per square

foot for the direct current and 10 to 12 amperes per square foot for the alternating current. The potential differences between the cathode and the anodes were 1.5 to 2 volts direct current and 1.5 to 2.5 volts alternating current. The bath temperature was maintained at 83 to 87 °F. Nitrogen, employed for agitation of the bath, was used at the rate of 6.5 to 3 cubic feet per hour.

Electroforming of wave guides produced the smooth and shiny inner surface which was desirable for satisfactory radar-wave transmission. It also produced a wave form of good ductility and strength which had a pore-free surface.

Electroformed aluminum shells, having wall thicknesses of 0.010 to 0.015 inch, were reinforced by spraying with 100-mesh aluminum powder. The spraying was accomplished with a Scherl oxygen-acetylene gun held five to six inches from the work. The shells were pretreated for spraying by degreasing with carbon tetrachloride, etching in a five per cent solution of sodium hydroxide, rinsing, dipping in a two per cent solution of nitric acid, rinsing and drying. After preheating the shells to 450 °F, the work was rotated at six revolutions per minute and sprayed with about 0.025 to 0.035 inch thickness of aluminum.

In another method of reinforcement of the electroformed aluminum shells, a coating of polyethylene was flame-sprayed onto the shell which was preheated to about 275 °F. This coating did not adhere well to the shells and it was slightly charred during the spraying.

The substitution of the following addition agents for methyl tertiary butyl ether also resulted in smooth deposits: dimethylaniline, di-*o*-tolylurea, diphenyl oxide, di-*o*-tolylthiourea, dichloroethylene, pyridine, quinoline, butyraldehyde and ethyl ether. Of these additives, only ethyl ether could be used without some slight degrading of the deposit such as treeing, porosity, nodularity, or cracking.

Several attempts were made to reduce the cost of operation of the bath containing ethyl pyridinium bromide, aluminum chloride and toluene. Commercial toluene, which had been dried over calcium sulfate, was used satisfactorily in place of chemically pure toluene. The substitution of commercial aluminum chloride for the resublimed compound was not satisfactory for making thick-walled electroforms, but it was expected to be usable for thinner coatings.

It was found that recycling of the nitrogen gas, used for agitation of the bath, might be feasible if all of the hydrogen halide vapors could be removed. An acid-absorbing tower containing sodium hydroxide pellets removed all but 0.0002 gram of hydrogen chloride per cubic foot of the nitrogen gas. It was not certain whether this small amount of hydrogen halide vapors or other impurities were the cause of nodularity on the electroforms. The substitution of carbon dioxide gas for nitrogen as the agitating medium resulted in powdery deposits of aluminum. Mechanical agitation did not prove satisfactory, since the action of the propeller tended to loosen sludge particles

from the anodes; the sludge particles made the deposits less ductile and not as smooth as those obtained with agitation by nitrogen gas.

#### Properties of the Aluminum Electrodeposit

Very little is written in the literature about the properties of aluminum electrodeposits. A number of claims have been made that smooth and adherent deposits may be obtained from a particular system. Many experiments have produced aluminum coatings which have varied from extremely poor to good in adherence. The surfaces have ranged from smooth and fine-grained to rough and dendritic formations of crystals. Some deposits obtained were very soft and could be scraped or rubbed off easily; others have been fairly hard.

It has been found that aluminum electrodeposits<sup>(15)</sup> obtained by the electrolysis of the fused salts aluminum chloride and sodium chloride, at temperatures from 130 to 210 °C and current densities from 0.002 to 0.2 amperes per square centimeter, are more finely crystalline at lower current densities and more compact at lower temperatures. Radiographic examination of the deposits showed irregular orientation in the crystal growth.

### III. EXPERIMENTAL

This section contains all of the information pertaining to the experimental research which was done in the laboratory and was governed, in part, by the information obtained from the records of previous work on the electrodeposition of aluminum.

#### Purpose of Investigation

The purpose of this research was to make an exploratory investigation of organic solutions containing the compounds aluminum bromide, aluminum stearate, aluminum basic acetate, aluminum phenoxide and nitrophenoxide, and aluminum acetylacetonate to determine if these compounds will furnish aluminum ions for electrodeposition.

#### Plan of Experimentation

The experimental work was conducted in the field of organic chemistry. Three requirements were the guide by which the search for a practical system to electrodeposit aluminum was conducted:

an organic compound to furnish aluminum ions for deposition;

an organic compound to furnish current-carrying ions, if necessary; and

an organic solvent which could dissolve the other two compounds.

Studies were made with regard to the solubilities, electrochemical properties, and physical properties of certain organic compounds which contain aluminum. An extensive investigation was conducted with these systems of organic compounds which indicated that they might be used successfully for the electrodeposition of aluminum.

Since this work was fundamental in nature, the greater portion of it was based on logical trial and error methods. Various systems were studied using these compounds as the basis for the investigations: aluminum bromide complex, duplication of a method reported in the literature; (3) aluminum stearate; aluminum basic acetate; aluminum phenoxide and aluminum nitrophenoxide; and aluminum acetylacetonate.

BROMIDE-COMPLEX SYSTEM

Initial experimental work was the duplication of some of the work reported by Blue and Mathers<sup>(3)</sup> on the aluminum bromide-ethyl bromide-benzene system.

Literature Review

Blue and Mathers<sup>(3)</sup> prepared an electroplating bath by warming 2.5 grams of aluminum foil with a few drops of bromine in a dry erlenmeyer flask equipped with a reflux condenser. The aluminum bromide thus formed catalyzed the reaction between ethyl bromide and aluminum when ten milliliters of ethyl bromide were added slowly over a period of 15 minutes followed by three 5-milliliter portions of ethyl bromide five minutes apart. The volume of the bath was increased by adding benzene and ethyl bromide alternately in five-milliliter portions to obtain any desired volume. The bath separated into two layers; the bottom layer was the electrolyte, and the benzene layer acted as a protection of the bath from atmospheric moisture.

This bath was electrolyzed at a current density of 1.25 amperes per square decimeter and an adherent deposit of aluminum was obtained on a copper cathode after ten hours. Other similar baths were electrolyzed at current densities of 0.90 to 2.80 amperes per square decimeter at 18 to 35 °C; the highest efficiencies obtained were 81.03 per cent for the anode and 64.40 per cent for the cathode at a current density of 0.9 amperes per square decimeter and at 18 °C.

The authors found that aluminum could be plated on platinum, copper, steel or cast iron but not on aluminum or magnesium cathodes.

Moisture was detrimental to the bath and caused evolution of hydrogen bromide gas. Some baths were operated successfully for as long as four months. Other solvents, including toluene, xylene, beta-tetra-hydronaphthalene and kerosene, were tried but benzene gave the best results. Several alkyl halides, including ethyl iodide, ethyl chloride, methyl chloride, and dichloroethane, were substituted for ethyl bromide but gave poor results.

Blue and Mathers concluded that the bath was best made by dissolving 30 grams of aluminum metal in one milliliter of bromine, 450 milliliters of ethyl bromide, and 250 milliliters of benzene. The bath probably contained ethyl and phenyl derivatives of aluminum bromide dissolved in ethyl bromide, benzene alkyl derivatives, and benzene.

In another paper, Blue and Mathers<sup>(4)</sup> claim that aluminum can be electrodeposited from a bath containing 20 grams of aluminum bromide, 20 grams of aluminum chloride, four grams of aluminum metal dissolved in 40 milliliters of ethyl bromide, 80 milliliters of benzene, and 40 milliliters of xylene. At a current density of 1.55 amperes per square decimeter and at 20 °C, the cathode efficiency is above 75 per cent and the anode efficiency is above 100 per cent. Hydrobromic acid or hydrochloric acid can be used in place of ethyl bromide but the results are not as good.



### Purpose of Investigation

The purpose of this investigation was to gain the experience of actually electrodepositing aluminum from an organic system.

### Materials

The following materials were used in the experiments with the aluminum bromide-ethyl bromide-benzene, aluminum bromide-butyl bromide-hexane and aluminum bromide-butyl bromide-iso-octane systems.

Aluminum Foil. Six inches square, 1/1000" thick. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of electrolytes.

Aluminum, Sheet. No. 3S-H14, 0.040" thick. Analysis: 0.6 % Si, 0.7 % Fe, 0.2 % Cu, 1.5 % Mn, 0.1 % Zn, 96.75 % Al, and 0.15 % others. Sample obtained from Reynolds Metals Co., Louisville, Ky. Used as anode material.

Benzene. Pure, B.P. 80-82 °C. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of electrolytes.

Butyl Bromide, Normal. C.P., B.P. 100-101°C, specific gravity 1.277. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of electrolytes.

Copper, Sheet. Twelve inches wide, 1/32" thick. Analyzed by Whaley<sup>(62)</sup> by means of electroanalysis and spectroscopy; average 100.06 % Cu; impurities of Fe, Si, Ca and Ag. Purchased from Economy Lumber Co., Christiansburg, Va. Used as cathode material.

Ethyl Bromide. Free from ether, B.P. 38-40 °C, highest purity. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of electrolytes.

Hexane. From petroleic ether, B.P. 65-67 °C. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of electrolytes.

Octane, Iso. Technical grade, B.P. 96-99 °C. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of electrolytes.

#### Apparatus

Apparatus used in experiments with the systems aluminum bromide-ethyl bromide-benzene, aluminum bromide-butyl bromide-hexane and aluminum bromide-butyl bromide-iso-octane was as follows:

Battery, Storage. Delco, Model 1724AN, 24-volt, 17 amp-hr at 5 hour rate. Manufactured by Delco-Remy Div., General Motors Corp., Anderson, Ind. Used as direct-current source.

Beaker. Berzelius, without spout, pyrex glass, 250-ml, 13 cm high. Sold by Eimer and Amend, New York 14, N. Y. Used as electrolytic cell.

Burner, Bunsen. Sold by Eimer and Amend, New York 14, N. Y. Used to warm reaction flask and contents.

Condenser, Liebig, Pyrex glass, 400 mm long. Sold by Eimer and Amend, New York 14, N. Y. Used as reflux condenser in preparation of electrolytes.

Cylinder, Graduated, Pyrex glass, 25-ml capacity. Sold by Eimer and Amend, New York 14, N. Y. Used for measuring reagents.

Flask, Distilling, Three-neck, pyrex glass, ground glass joints. Sold by Eimer and Amend, New York 14, N. Y. Used as reflux flask in preparation of electrolytes.

Funnel, Separatory, Globe-shaped, pyrex glass, with stopper and stopcock, 250-ml. Sold by Eimer and Amend, New York 14, N. Y. Used as reservoir for ethyl bromide.

Milliammeter, Direct current, 0-250 ma, U. S. N. type CAY-22065. Manufactured by Westinghouse Electric Co., Pittsburgh, Pa. Used to measure current.

Oven, Electric, Model OV-8, Ser. No. 8-270, 115 volts, 5 amp. Sold by Modern Electric Laboratory, Chicago, Ill. Used for drying equipment.

Thermometer, Mercury in glass, nitrogen filled, 0-300 °C. Sold by Eimer and Amend, New York 14, N. Y. Used to indicate temperature of reaction mass.

Voltmeter, Multiple-range, Model No. 489, No. 62580. Manufactured by Weston Electrical Instrument Corp., Newark, N. J. Used to measure cell voltage.

### Method of Procedure

Although the composition of the baths used varied from the ratios reported by Blue and Mathers, the general method of preparation, given by them, was followed.

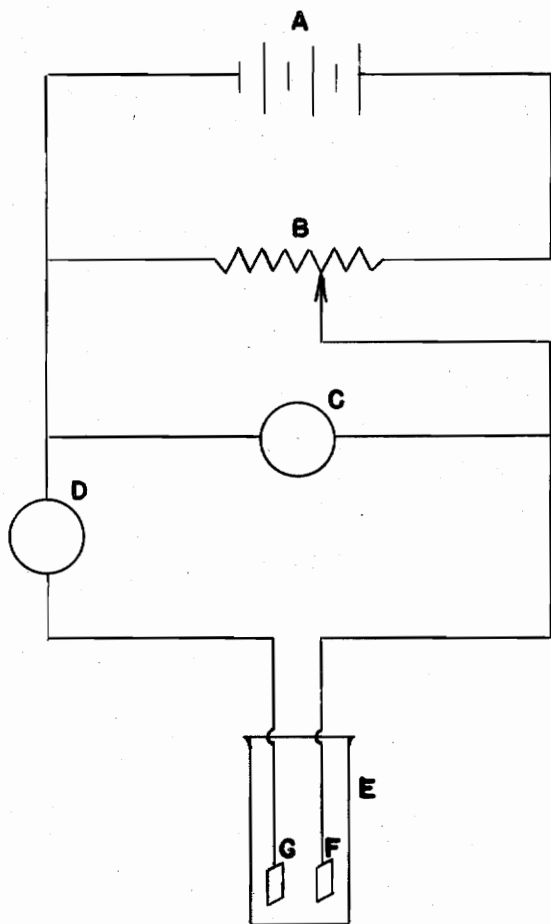
Preparation of the Electrolyte. The electrolyte was prepared by warming 5.087 grams of aluminum foil with a few drops of liquid bromine in a three-neck, round-bottom, one-liter flask. Two ground glass stoppers were fitted in the two outside necks and a water-cooled reflux condenser was fitted to the center neck of the flask. After allowing five minutes for the bromine to react completely, ten milliliters of ethyl bromide were added carefully. This mixture was warmed slightly to start the reaction and about five minutes were allowed for digestion. Twenty-five milliliters of benzene were added through the top of the condenser gradually over a period of 15 minutes. Fifteen milliliters of ethyl bromide were added five milliliters at a time at five-minute intervals. The electrolyte was increased in volume by adding five milliliters each of benzene and ethyl bromide every five minutes until the bath contained 70 and 110 milliliters total, respectively. Approximately 30 minutes were allowed for completion of the reaction before the electrolyte was poured into a tall 250-milliliter beaker to be electrolyzed.

Electrolysis of the Plating Bath. Electrolysis of the plating bath was begun after the 250-milliliter beaker was fitted with a cork stopper which mounted a 0 to 100 °C thermometer, a copper cathode,

and an aluminum anode; the electrodes were about one inch apart. In the first six experiments, voltages applied ranged from 0.6 to 4.1 volts, currents ranged from 45 to 118 milliamperes, and the current densities ranged from 0.379 to 0.9 amperes per square decimeter. The equipment and circuit used for the electrolysis is shown in Figure 1.

Variations of the Plating Bath. After six experiments, the composition of the electrolyte was varied. A solution was prepared from 4.75 grams of aluminum foil, 160 milliliters of butyl bromide, and 75 milliliters of hexane in a manner similar to that used for the original bath. An electromotive force of 4.5 volts and a current of 30 to 50 milliamperes was used for the electrolysis.

Another variation of the bath which was tested was one comprising 3.5 grams of aluminum foil, 165 milliliters of butyl bromide, and 85 milliliters of iso-octane. Two aluminum anodes and a copper cathode were used in the electrolysis; the voltage varied from 10 to 18 volts and the current was maintained at 90 milliamperes. The electrical circuit and the equipment were the same as that already mentioned.



**A - 24-VOLT STORAGE BATTERY**

**B - 112-OHM RHEOSTAT**

**C - MULTI-RANGE VOLTMETER**

**D - 0-250 M.A. MILLIAMMETER**

**E - 150-250 ML BEAKER**

**F - ALUMINUM ANODE**

**G - COPPER CATHODE**

**FIGURE I. SCHEMATIC DIAGRAM OF THE CIRCUIT FOR ALL ELECTROLYSES**

Data and Results

Data and results are given in Table II for the electrolyses of baths prepared from the following: 5.087 grams of aluminum foil, 110 milliliters of ethyl bromide, and 70 milliliters of benzene; 4.75 grams of aluminum foil, 160 milliliters of butyl bromide, and 75 milliliters of hexane; and 3.5 grams of aluminum foil, 165 milliliters of butyl bromide, and 85 milliliters of iso-octane.

The first two experiments were performed to establish the conditions under which a deposit of aluminum could be obtained. No weighings were made of the cathode before and after electrolysis and, therefore, no cathode efficiency could be calculated in Experiment 2.

TABLE II

Electrolyses of the Systems Aluminum Bromide, Ethyl Bromide and Benzene,

Aluminum Bromide, Butyl Bromide and Hexane, and Aluminum Bromide, Butyl Bromide and Iso-octane

Aluminum anodes and copper cathodes, 2.2 x 3.0 centimeters

No.	System	Time, hr	E.M.F., volts	Current, ma	C. D., a/dm <sup>2</sup>	Temp., °C	Results	Weight, gm	Cath. Eff., %
1.	AlBr <sub>3</sub> -C <sub>2</sub> H <sub>5</sub> Br-C <sub>6</sub> H <sub>6</sub>	10.75	2.4-4.1	118	0.895	23-30	No deposit	---	---
2.	AlBr <sub>3</sub> -C <sub>2</sub> H <sub>5</sub> Br-C <sub>6</sub> H <sub>6</sub>	10.17	2.2-2.9	70	0.540	25-29	Deposit	Not weighed	Unknown
3.	AlBr <sub>3</sub> -C <sub>2</sub> H <sub>5</sub> Br-C <sub>6</sub> H <sub>6</sub>	22.33	3.3-3.5	50	0.379	26-29	Deposit	0.0267	7.17
4.	AlBr <sub>3</sub> -C <sub>2</sub> H <sub>5</sub> Br-C <sub>6</sub> H <sub>6</sub>	24.25	2.8-3.6	50	0.379	26-28	Deposit	0.0652	16.05
5.	AlBr <sub>3</sub> -C <sub>2</sub> H <sub>5</sub> Br-C <sub>6</sub> H <sub>6</sub>	18.25	0.6-1.2	47	0.379	25-28	No deposit	---	---
6a.	AlBr <sub>3</sub> -C <sub>2</sub> H <sub>5</sub> Br-C <sub>6</sub> H <sub>6</sub>	5.75	1.2-1.3	70	0.569	27-29	No deposit	---	---
6b.	AlBr <sub>3</sub> -C <sub>2</sub> H <sub>5</sub> Br-C <sub>6</sub> H <sub>6</sub>	9.50	1.5-1.8	94	0.758	25	Deposit	0.0250	8.33
7.	AlBr <sub>3</sub> -C <sub>4</sub> H <sub>9</sub> Br-C <sub>6</sub> H <sub>14</sub>	0.75	4.5	30-50	0.606	30	No deposit	---	---
8.	AlBr <sub>3</sub> -C <sub>4</sub> H <sub>9</sub> Br-C <sub>8</sub> H <sub>18</sub>	0.92	10-18	90	1.397	30	No deposit	---	---



Sample Calculations

Calculations were made to determine the current densities being used and the cathode efficiencies obtained in the experiments with the systems aluminum bromide-ethyl bromide-benzene, aluminum bromide-butyl bromide-hexane and aluminum bromide-butyl bromide-iso-octane.

Current density: (Experiment 1)

$$C. D. = \frac{\text{Current in amperes}}{\text{Total area of cathode in square decimeters}}$$

$$C. D. = \frac{\text{amp} \times \text{cm}^2/\text{dm}^2}{\text{cm} \times \text{cm} \times \text{no. sides}} = \text{amp}/\text{dm}^2$$

$$C. D. = \frac{0.118 \times 100}{2.2 \times 3.0 \times 2} = 0.895 \text{ amp}/\text{dm}^2$$

Cathode efficiency: (Experiment 3)

$$C. E. = \frac{\text{Actual weight of deposit, in grams}}{\text{Theoretical weight of deposit obtainable, in grams}} \times 100$$

$$C. E. = \frac{\text{gm} \times \text{coul.}/\text{equiv.}}{\text{amp} \times \text{hr} \times \text{sec}/\text{hr} \times \text{gm}/\text{equiv.}} \times 100 = \text{per cent}$$

$$C. E. = \frac{0.0269 \times 96,500}{0.050 \times 22.33 \times 3600 \times 9} \times 100 = 7.17 \%$$

### Discussion of Results

In four of the experiments on electrodeposition of aluminum on a copper cathode from the bath aluminum bromide-ethyl bromide-benzene, the deposits of aluminum differed in character. These deposits will be discussed separately with regard to their weight per unit area of cathode surface, uniformity of distribution, appearance, adherence, and ability to be polished. An aluminum anode was used in all electrolyses.

Since no weights were recorded for the cathode before and after electrolysis, the weight distribution is not known for the deposit obtained in Experiment 2. The coating covered about one-third of the 13.2 square centimeters of surface and was distributed mainly on a single area of the cathode on the side adjacent to the aluminum anode. A current density of approximately 0.54 ampere per square decimeter was used during electrolysis. In appearance, the deposit was smooth, dull, and dark gray. The aluminum adhered very well and withstood tapping with a piece of steel and bending of the cathode several times without evidence of chipping. A dry buffing wheel did not brighten the plating but an application of silver polish gave it a dull polish.

The deposit obtained in Experiment 3 weighed 0.0267 gram and, since the total surface was 13.8 square centimeters, the amount of aluminum deposited was 0.00194 gram per square centimeter. Because the coating was distributed principally on one side of the cathode,

the covered area had an actual deposit of about 0.0038 gram per square centimeter. The current density was 0.379 ampere per square decimeter. A cathode efficiency of 7.17 per cent was obtained. On the surface adjacent to the anode, the deposit was quite uniform; only a scattered deposit was obtained around the edges of the opposite surface. The fresh deposit appeared to be finely crystalline, dull, medium gray, and smooth. The same tests were made for adherence of the aluminum and the surface was not injured by the tests. An application of silver polish removed the fine crystals from the surface and gave the aluminum a dull polish.

The aluminum deposited in Experiment 4 weighed 0.0652 gram and amounted to about 0.0095 gram per square centimeter on the basis of actual surface covered. A cathode efficiency of 16.05 per cent was obtained. The deposit was fairly uniform on the side adjacent to the anode but scattered around the edges of the opposite side. The current density used was 0.379 ampere per square decimeter. The deposit was rough, dendritic, dull, dark gray or black. The adherence tests caused the aluminum plating to crack and chip from the copper. Silver polish lightened the color of the surface but did not give it any polish.

The deposit from Experiment 6b was obtained by using two aluminum anodes, each spaced equidistantly about one-half inch from the cathode. The current density was 0.758 ampere per square decimeter. The weight of deposit was 0.025 gram, or 0.0041 gram per square

centimeter of coated copper. A cathode efficiency of 8.33 per cent was obtained. Uniformity was poor on this sample and the copper could be seen through the deposit at numerous places. The aluminum varied from light to dark gray, was finely crystalline, and streaked by uneven thicknesses of the metal plate. The deposit adhered to the copper better than did that obtained in Experiment 4 but not as well as the first two obtained; some chipping of the surface occurred when the metal was bent. The aluminum could be polished slightly.

Although deposits of aluminum can be obtained from the system aluminum bromide-ethyl bromide-benzene, the plating is dull and extremely sensitive to the current density. The maximum cathode efficiency of 16.05 per cent is very low and would have to be improved if the process was used commercially.

During the comparatively short periods of electrolyses of the systems aluminum bromide-butyl bromide-hexane and aluminum bromide-butyl bromide-iso-octane, a porous brown crust-like deposit formed on both electrodes. Apparently, these variations of the original bath cannot be used for the electrodeposition of aluminum because of the organic changes which take place when current is passed through the electrolyte.

### Limitations

All of the electrolyses in Experiments 1 through 6 were performed with baths prepared from 5.067 grams of aluminum foil, 110 milliliters of ethyl bromide, and 70 milliliters of benzene.

Voltages varied from 0.6 to 4.1 volts and the current densities were 0.379 to 0.9 amperes per square decimeter.

Aluminum anodes and copper cathodes were used in all cases and they measured 2.2 x 3.0 centimeters.

Temperatures of the baths varied from 23 to 30 °C. The elapsed times for electrolyses ranged from 5.75 to 24.25 hours.

In Experiment 7, the only electrolyte tested was one containing 4.75 grams of aluminum foil, 75 milliliters of hexane, and 160 milliliters of butyl bromide.

The voltage applied was 4.5 volts and the current density was about 0.606 amperes per square decimeter.

The bath temperature was approximately 30 °C during the 0.75 hour of electrolysis.

In Experiment 8, the electrolyte was composed of 3.5 grams of aluminum foil, 85 milliliters of iso-octane, and 165 milliliters of butyl bromide.

An electromotive force of 10 to 18 volts and the current density of 1.397 amperes per square decimeter were employed. The bath temperature was about 30 °C during the 0.92 hour of electrolysis.

### Conclusions

From electrolysis experiments performed with baths prepared from 5.087 grams of aluminum foil, 110 milliliters of ethyl bromide, and 70 milliliters of benzene, it can be concluded that;

1. The electrolyte, aluminum bromide-ethyl bromide-benzene, becomes inactive if it is allowed to stand for 6 to 8 hours after its preparation.

2. From 5 to 6 hours of electrolysis was required to eliminate moisture from the fresh electrolyte, aluminum bromide-ethyl bromide-benzene. Hydrogen, from the decomposition of water, combined with bromine, as hydrogen bromide, and was evolved at the cathode.

3. The deposits obtained from electrolysis of the aluminum bromide-ethyl bromide-benzene indicated the bath has poor throwing power and the deposit is sensitive with regard to current density. A current density of 0.54 amperes per square decimeter for about ten hours gave the best electrodeposit of aluminum from these experiments.

4. The aluminum bromide-ethyl bromide-benzene electrolyte does not appear to be practicable for the electrodeposition of

aluminum because of its poor throwing power, its low cathode efficiency of 16.05 per cent or less, and the sensitiveness of the bath.

Electrolysis experiments performed with a bath prepared from 4.75 grams of aluminum foil, 160 milliliters of butyl bromide and 75 milliliters of hexane and a bath prepared from 3.5 grams of aluminum foil, 165 milliliters of butyl bromide, and 85 milliliters of iso-octane led to the conclusion that:

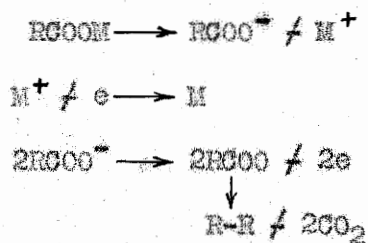
5. These baths cannot be used at current densities of 0.606 and 1.397 amperes per square decimeter, respectively, for the electrodeposition of aluminum since electrolysis causes organic changes which result in the formation of a porous brown crust-like deposit on the electrodes.

STEARATE SYSTEMS

From the literature, (50) information with regard to the ionization of alkali metal salts of fatty acids in aqueous solutions was obtained. It was expected that aluminum salts of fatty acids might, in some liquid, nonaqueous organic system as yet unknown, ionize in a similar manner so that metallic aluminum would be electrodeposited on a base metal cathode surface. Aluminum stearate was chosen as representative of aluminum salts of the fatty acid series because it is a common and stable compound of high molecular weight.

Literature Review

In reviewing the literature for possible compounds which could furnish aluminum ions for the electrodeposition of aluminum, the following reactions, attributed to Kolbe by Taylor, (50) were noted:



where M is usually an alkali metal and R represents any alkyl group. The ionization takes place in an aqueous solution.



These ions from the ionization of the alkali metal salts<sup>(59)</sup> carry electric current but may react with the solvent, with any nonionized molecules of the alkali metal salt present in the solution, or with each other. When an aqueous solution containing an alkali salt of this type is electrolyzed, the metal cation is discharged at the cathode. The products at the cathode are an alkali hydroxide and hydrogen gas if no substance capable of reduction is present. When a cathodic depolarizer is present, the hydrogen is not evolved at the electrode but is used up as a reducing agent.

Aluminum stearate is a compound of the type given by the formula  $R\text{COOAl}$  and it was hoped that the aluminum ions could be electrodeposited on a cathode surface upon electrolysis of some liquid, nonaqueous organic system containing this salt.

#### Purpose of Investigation

It was the purpose of this portion of the investigation to use aluminum stearate as a source of aluminum ions, to find a solvent for this compound and to determine what compounds could be used as additives to improve the current-carrying ability, if necessary, in their mutual solvent or combination of solvents.

Materials

The following materials were used in the experiments with aluminum stearate:

Acetic Acid, Glacial. Technical, Lot No. 82646.

Obtained from J. T. Baker Chemical Co., Phillipsburg, N. J.

Used as addition compound in conductivity tests.

Aluminum Phosphate. Purified. Obtained from Eimer and

Amend, New York 14, N. Y. Used as addition compound in con-

ductivity tests.

Aluminum Stearate. Technical. Purchased from Metasap

Chemical Co., Harrison, N. J. Used in preparation of electro-

lyte.

Ammonia. Dry gas. Prepared from reaction of ammonia

hydroxide and sodium hydroxide. Used as addition compound

in conductivity tests.

Ammonium Hydroxide. U.S.P., 26<sup>o</sup> Be. Obtained from

Eimer and Amend, New York 14, N. Y. Used in preparation of

ammonia gas.

Aniline. Tested purity. Obtained from Eimer and Amend,

New York 14, N. Y. Used as addition compound in conductivity

tests.

Calcium Chloride. Tested purity, calcined, porous, granu-

lar, 4 mesh, for drying tubes. Obtained from Eimer and Amend,

New York 14, N. Y. Used to dry ammonia gas.

Calcium Stearate. Technical. Obtained from Metasap Chemical Co., Harrison, N. J. Used as additive in conductivity tests.

Ethyl Phosphate. Practical. Obtained from Tennessee Eastman Corp., Kingsport, Tenn. Used as solvent for aluminium stearate electrolyte.

Lithium Stearate. Technical. Obtained from Metasap Chemical Co., Harrison, N. J. Used as additive in conductivity tests.

Platinum, Sheet. Chemically pure, 0.003" thick. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used for electrodes.

Potassium Iodide. U.S.P., crystals. Obtained from Eimer and Amend, New York 14, N. Y. Used as additive in conductivity tests.

Potassium Phosphate. Technical, dibasic. Obtained from J. T. Baker Chemical Co., Phillipsburg, N. J. Used as additive in conductivity tests.

Sodium Hydroxide. Tested purity, pellets. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of ammonia gas.

Sodium Iodate. Tested purity. Obtained from Eimer and Amend, New York 14, N. Y. Used as additive in conductivity tests.

Sodium Oxalate. Technical. Obtained from J. T. Baker Chemical Co., Phillipsburg, N. J. Used as addition compound in conductivity tests.

Sodium Phosphate. Technical, tertiary, anhydrous. Obtained from Eimer and Amend, New York 14, N. Y. Used as addition compound in conductivity tests.

Sodium Pyrophosphate, Anhydrous. C.P., Lot No. 8830. Obtained from J. T. Baker Chemical Co., Phillipsburg, N. J. Used as addition compound in conductivity tests.

Wire, Platinum. Chemically pure, 1/64" dia. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used as connecting wire to electrodes.

#### Apparatus

Apparatus used in the experiments with aluminum stearate was as follows:

Battery, Storage. Delco, Model 1724AN, 24-volt, 17 amp-hr at 5 hour rate. Manufactured by Delco-Remy Div., General Motors Corp., Anderson, Ind. Used as direct-current source.

Beaker. Griffin with spout, pyrex glass, 150-ml. Obtained from Eimer and Amend, New York 14, N. Y. Used as conductivity cell.

Milliammeter. Hickock, Model 209A, Serial No. 6-13232.

Obtained from Lafayette Concord Radio Corp., Atlanta, Ga.  
Manufactured by the Hickock Electrical Instrument Co.,  
10514 Dupont Ave., Cleveland 8, Ohio. Used to measure current.

Rheostat. Rex, No. 9-526-5F, 112-ohm, 2 amp, 16" long.

Manufactured by Rex Rheostat Co., Baldwin, L. I., N. Y. Used  
to vary voltage.

Stopper, Cork. Quality XXXX, #32. Obtained from Cork

Products Co., New York 16, N. Y. Used to position glass tub-  
ing and electrodes.

Thermometer. Mercury in glass, nitrogen-filled, 3-inch

immersion, 30-300 °F. Obtained from Eimer and Amend, New  
York 14, N. Y. Used to measure temperature of electrolyte.

Tubing, Glass. Pyrex, 6 mm O. D. Obtained from Eimer

and Amend, New York 14, N. Y. Used to position platinum  
electrodes.

Voltmeter. Multiple-range, Model No. 489, No. 62580.

Manufactured by Weston Electrical Instrument Corp., Newark,  
N. J. Used to measure cell voltage.

#### Method of Procedure

An investigation was made to find a solvent for aluminum stearate  
as the preliminary step to conductivity tests with various systems.

Solubility Tests. A series of experiments were undertaken to discover a solvent for aluminum stearate. At 26 °C, 20 milliliters each of kerosene, ethyl alcohol, xylene, o-toluidine, pyridine and ethyl phosphate were measured into separate test tubes and the aluminum stearate added a few grains at a time. After stoppering, the test tubes were shaken intermittently for about ten minutes and then observed to note the solubility of aluminum stearate.

Conductivity Tests. Conductivity tests were performed with the systems aluminum stearate, ethyl phosphate and addition compounds using a 150-milliliter beaker, and two platinum electrodes approximately 2.5 centimeters square and spaced one inch apart by glass tubing inserted in a cork stopper. All solutions tested were approximately 25 to 50 milliliters at 78 to 260 °F and the current and voltage were observed. A few crystals of sodium stearate were added to a solution of one-half gram of aluminum stearate in 50 milliliters of ethyl phosphate and the solution tested for conductivity. Calcium and strontium stearate crystals were added to the solution and the conductivity was tested. One-quarter gram of lithium stearate was dissolved in the solution and another test for conductivity was made.

Another series of compounds were tested using approximately 25 milliliters of ethyl phosphate and 0.2 gram of aluminum stearate. Portions of 0.05 gram of each compound were added to separate solutions of aluminum stearate in ethyl phosphate at about 260 °F;

the conductivity of each solution was tested. The compounds were: dipotassium phosphate, sodium iodate, sodium pyrophosphate, aluminum phosphate, and tertiary sodium phosphate.

Conductivity tests were performed with the system aluminum stearate, aniline and ethyl phosphate in weight ratios of 0.5 gram : 1 to 8 grams : 41.5 grams of the components, respectively. Sodium oxalate and ammonia gas were used as additives, also, to determine their effect on the conductivity of aluminum stearate in ethyl phosphate.

Decomposition Potential of the System Aluminum Stearate and Ethyl Phosphate. A test was made to determine the decomposition potential of a solution of 0.3 gram of aluminum stearate in 70 milliliters of ethyl phosphate. Platinum electrodes, measuring about 2.5 centimeters square, were immersed in the solution at 260 °F and held one-half inch apart by glass tubing inserted in a cork stopper. Three 24-volt storage batteries were used in series and the potential across the electrodes was adjusted from 10 to 60 volts by means of a rheostat. The current was observed on a milliammeter as the potential was increased.

Tests to Improve Conductivity of Aluminum Stearate in Ethyl Phosphate. Four experiments were performed to test the influence of adding other compounds to the solvent, ethyl phosphate, in the presence of aluminum stearate. The compounds added were: ammonia gas, stearic acid, lithium stearate, and glacial acetic acid. The

same electrode arrangement and source of potential, as in the foregoing experiments, were used. With the potential set at 10, 20, 30, 40, and 50 volts, the corresponding currents were recorded.

#### Data and Results

The results of solubility tests at 26 °C showed that aluminum stearate is practically insoluble in kerosene, ethyl alcohol, xylene, o-toluidine, and pyridine but it is somewhat soluble in ethyl phosphate. The maximum solubility in ethyl phosphate is about 0.7 gram per 100 milliliters.

The results of conductivity tests with systems of aluminum stearate, ethyl phosphate and addition compounds are given in Table III.

No electrolyses were performed with these systems.

#### Discussion of Results

The group of solvents chosen for solubility tests with aluminum stearate represent various types of organic compounds, including hydrocarbons, alcohols, amines and esters.

The maximum current of 0.8 milliamperes, obtained with a potential of 60 volts on platinum electrodes in a solution of 0.3 gram of aluminum stearate and 70 milliliters of ethyl phosphate, was so small it was assumed that such a combination would be impractical for electrodeposition of aluminum.



TABLE III

Conductivity of the System of Aluminum Stearate and Ethyl Phosphate  
with Various Addition Compounds

Platinum electrodes, 2.5 x 2.5 centimeters, one inch apart

Addition Compounds	Weight Ratio,			Temperature, °F	E.M.F., volts	Current, ma
	Al(C <sub>17</sub> H <sub>35</sub> COO) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> PO <sub>4</sub>	Add'n Cmpd.			
None	0.5	51.8	0.05	260	24	0
C <sub>17</sub> H <sub>35</sub> COONa	0.5	51.8	0.05	260	24	0
Ca(C <sub>17</sub> H <sub>35</sub> COO) <sub>2</sub>	0.5	51.8	0.25	260	48	0
Sr(C <sub>17</sub> H <sub>35</sub> COO) <sub>2</sub>	0.5	51.8	0.25	260	48	0
K <sub>2</sub> HPO <sub>4</sub>	0.2	25.9	0.05	260	20	0
KI	0.2	25.9	0.05	260	20	0
NaIO <sub>3</sub>	0.2	25.9	0.05	260	20	0
Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	0.2	25.9	0.05	260	20	0
Na <sub>3</sub> PO <sub>4</sub>	0.2	25.9	0.05	260	20	0
AlPO <sub>4</sub>	0.2	25.9	0.05	260	20	0
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	0.5	41.5	1.00	200	2-6	0
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	0.5	41.5	2.00	158	2-6	0
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	0.5	41.5	3.00	151	2-6	0
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	0.5	41.5	8.00	126	2-6	0
Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	0.2	41.5	0.10	152	2-6	0
NH <sub>3</sub>	0.3	51.8	sat'd	78	2-6	0
C <sub>17</sub> H <sub>35</sub> COOLi	0.5	51.8	0.25	260	48	2
C <sub>17</sub> H <sub>35</sub> COOH	0.2	74.6	0.4	200	10	0.12
					20	0.27
					30	0.40
					40	0.53
					50	0.67
C <sub>17</sub> H <sub>35</sub> COOH	0.2	74.6	0.4	200	10	0.66
C <sub>17</sub> H <sub>35</sub> COOLi			0.2		20	1.37
					30	2.02
					40	2.68
					50	3.40
C <sub>17</sub> H <sub>35</sub> COOH	0.2	74.6	0.4	200	10	0.77
C <sub>17</sub> H <sub>35</sub> COOLi			0.4		20	1.58
					30	2.40
					40	3.30
					50	4.08
C <sub>17</sub> H <sub>35</sub> COOH	0.2	74.6	0.4	200	10	1.00
C <sub>17</sub> H <sub>35</sub> COOLi			0.6		20	2.00
					30	3.20
					40	4.25
					50	5.25
None	0.2	74.6	0.4	200	10	0.95
			0.8		20	2.05
					30	3.30
					40	4.40
					50	5.30
None	0.2	74.6		75	10	0.08
					20	0.18
					30	0.28
					40	0.37
					50	0.48
CH <sub>3</sub> COOH (glacial)	0.2	74.6	10.5	75	10	0.18
					20	0.40
					30	0.62
					40	0.83
					50	1.03
CH <sub>3</sub> COOH (glacial)	0.2	74.6	21.0	75	10	0.22
					20	0.45
					30	0.67
					40	0.89
					50	1.11
CH <sub>3</sub> COOH (glacial)	0.2	74.6	31.5	75	10	0.21
					20	0.42
					30	0.63
					40	0.84
					50	1.04

In attempts to improve the conductivity of a solution of aluminum stearate in ethyl phosphate, it was thought that other metallic stearates, such as calcium, sodium, strontium, and lithium, might dissolve in the solvent and ionize to carry the bath current. Also, glacial acetic acid and stearic acid were added as typical, but widely separated, members of the fatty-acid group. Liquid ammonia has been used as a solvent in other electroplating baths;<sup>(27)</sup> it was hoped that ammonia gas might aid conductivity in this case by forming a complex ion with aluminum, thus increasing ionization of the aluminum stearate by weakening its bonds. The potassium and sodium inorganic compounds, as given in Table III, page 88, were added because alkali metal salts frequently ionize in aqueous, and sometimes nonaqueous, solutions and conduct current.

The maximum current of 5.3 milliamperes at 50 volts was obtained with platinum electrodes 2.5 centimeters square and one-half inch apart when a bath comprising 0.2 gram of aluminum stearate, 0.4 gram of stearic acid, 0.8 gram of lithium stearate and 74.6 grams of ethyl phosphate was electrolyzed. This current was so small that 46 hours would be required, theoretically, to deposit a coating of aluminum 0.001 inch thick on a base metal cathode surface. Commercial operation would be impractical under these circumstances. This time required to electrodeposit 0.001 inch thickness of

aluminum, under the foregoing conditions, was calculated in the following manner:

Rate of aluminum deposition:

Current density = 0.00039 amp/sq cm

Cathode efficiency assumed to be 100 per cent

$$\frac{\frac{\text{amp}}{\text{sq cm}} \times \frac{\text{sec}}{\text{hr}} \times \frac{\text{gm Al}}{\text{equiv.}}}{\frac{\text{coulombs}}{\text{equiv.}}} = \text{gm Al/hr-sq cm}$$

$$\frac{\frac{0.0053}{13.5} \times 3600 \times 9}{96,500} = 1.32 \times 10^{-4} \text{ gm Al/hr-sq cm}$$

Theoretical time required to plate 0.001 inch of aluminum:

$$\frac{\text{in.} \times \frac{\text{cm}}{\text{in.}} \times \frac{\text{gm Al}}{\text{cu cm}}}{\frac{\text{gm Al}}{\text{hr-sq cm}}} = \text{hours}$$

$$\frac{0.001 \times 2.54 \times 2.4}{0.000132} = 46.25 \text{ hours}$$

Limitations

Solubility tests were limited to the use of only a few grains of aluminum stearate in 20 milliliters each of kerosene, ethyl alcohol, xylene, o-toluidine, pyridine and ethyl phosphate at 26 °C.

Preliminary conductivity tests were performed using baths comprising 0.2 to 0.5 gram of aluminum stearate, 25.9 to 51.8 grams of ethyl phosphate, and 0.05 to 8 grams of the addition compounds. The compounds tested as additives were: sodium, calcium,

strontium and lithium stearates, dipotassium phosphate, sodium iodate, sodium pyrophosphate, tertiary sodium phosphate, aniline, aluminum phosphate, potassium iodide, ammonia gas, and sodium oxalate. The applied potentials varied from 2 to 48 volts and the bath temperatures were 78 to 260 °F.

Additional conductivity tests were performed using solutions of 0.2 gram of aluminum stearate, 70 milliliters of ethyl phosphate, and from 0.2 to about 30 grams of additives. The compounds tested as additives were: glacial acetic acid, stearic acid, and lithium stearate. The applied potentials were 6 to 50 volts and the bath temperatures were 75 to 260 °F.

### Conclusions

On the basis of experiments with the systems containing 0.2 to 0.5 gram of aluminum stearate, 25.9 to 74.6 grams of ethyl phosphate, and 0.05 to 31.5 grams of additives, it can be concluded that:

1. The solubility of aluminum stearate in kerosene, ethyl alcohol, xylene, o-toluidine and pyridine is apparently less than 0.005 gram per 100 milliliters at 26 °C.
2. The solubility of aluminum stearate in ethyl phosphate is about 0.7 gram per 100 milliliters of solvent at 260 °F.
3. The conductivity of a system containing 0.2 gram of aluminum stearate in 25.9 to 51.8 grams of ethyl phosphate was not improved by the addition of 0.05 to 8 grams of the following compounds: sodium, calcium and strontium stearates, dipotassium phosphate,

potassium iodide, sodium iodate, sodium pyrophosphate, tertiary sodium phosphate, aluminum phosphate, aniline, ammonia gas, and sodium oxalate.

4. The current-carrying ability of a system containing 0.2 gram of aluminum stearate in 74.6 grams of ethyl phosphate was increased from 0 to a maximum of 5.3 milliamperes at 50 volts by the addition of 0.4 gram of stearic acid, 0.2 to 0.8 gram of lithium stearate and 10.5 to 31.5 grams of glacial acetic acid.

5. The maximum conductivity of a system comprising 0.2 gram of aluminum stearate, 0.4 gram of stearic acid and 74.6 grams of ethyl phosphate was 0.67 milliamperes at 50 volts and 200 °F.

6. The maximum conductivity of a system comprising 0.2 gram of aluminum stearate, 31.5 grams of glacial acetic acid and 74.6 grams of ethyl phosphate was 1.04 milliamperes at 50 volts and 75 °F.

7. None of the baths prepared carried sufficient current for practical electrodeposition of aluminum. At the maximum of 5.3 milliamperes obtained at 50 volts and 200 °F with a system comprising 0.2 gram of aluminum stearate, 0.4 gram of stearic acid, 0.8 gram of lithium stearate and 74.6 grams of ethyl phosphate, about 46.25 hours would be required to electrodeposit aluminum 0.001 inch thick on a cathode surface.

8. Systems of aluminum stearate in ethyl phosphate do not appear to be practicable for the electrodeposition of aluminum because of the low solubility of aluminum stearate in ethyl phosphate and the low conductivity of the baths.

### ACETATE SYSTEM

Basic aluminum acetate was chosen as a salt of the fatty acids of lower molecular weight with which to continue the investigation of aluminum salts of fatty acids. An effort was made to determine if basic aluminum acetate will furnish aluminum ions for electro-deposition on a cathode surface from a liquid, nonaqueous organic system.

In the search for a suitable solvent for basic aluminum acetate, it was noted<sup>(3)</sup> that formamide had electrical characteristics and constants which are similar to those of water. Its dielectric constant is 84 as compared to 81 for water. It has been used as an ionizing solvent and for the electrodeposition of metal alloys of aluminum with iron, manganese, and zinc. Some binary salts ionize in formamide to a greater degree than they do in water. Thus, formamide was chosen for trial, as the solvent, with the expectation that it might dissolve and cause ionization of the basic aluminum acetate so that aluminum ions would be electrodeposited on a cathode surface.

### Literature Review

Blue and Mathers<sup>(3)</sup> obtained deposits of aluminum alloys from the electrolysis of metal chlorides dissolved in formamide. A thin deposit of aluminum-iron alloy was obtained from the electrolyte aluminum chloride-formamide which had been acidified with dry hydrogen

chloride gas. The iron was an impurity in the aluminum anode. Twelve hours were required to obtain a smooth, silvery-white, adherent deposit. A bath of the composition 0.5 gram of ferric chloride, 1.0 gram of aluminum chloride, and 30 milliliters of formamide gave thicker deposits of the alloy when electrolyzed for up to 30 hours at a current density of 1.5 amperes per square decimeter. The highest percentage of aluminum obtained in a deposit was 17.65 per cent. An alloy of zinc and aluminum was obtained in a deposit from a bath consisting of 0.5 gram of zinc chloride, 3.0 grams of aluminum chloride, and 30 milliliters of formamide by electrolysis at a current density of 0.9 ampere per square decimeter. Thin deposits were bright but thicker deposits were dark and spongy. Aluminum and manganese alloyed in a similar fashion from a bath comprising 2.0 grams of manganese chloride and 30 milliliters of formamide electrolyzed at 1.5 amperes per square decimeter using aluminum for the anode.

Formamide systems<sup>(3)</sup> have been used to obtain good deposits of copper from copper sulfate and copper chloride salts, lead from the chloride, zinc from the chloride and oxide, and tin from the chloride.

Although only aluminum alloys could be obtained from chloride-formamide baths, a system of another type of aluminum compound in formamide might electrodeposit aluminum.

### Purpose of Investigation

The purpose of this portion of the investigation was to determine if a bath containing basic aluminum acetate in an ionizing solvent, such as formamide, will yield aluminum on electrolysis.

### Materials

The following materials were used in the experiments with the acetate system:

Aluminum Acetate, Basic. Pure, powder. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of electrolyte and in solubility tests.

Aluminum, Sheet. No. 33-H14, 0.040" thick. Analysis: 0.6 % Si, 0.7 % Fe, 0.2 % Cu, 1.5 % Mn, 0.1 % Zn, 96.75 % Al, 0.15 % other. Sample obtained from Reynolds Metals Co., Louisville, Ky. Used as anode material.

Ammonium Hydroxide. U.S.P., 26 °Be. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of ammonia gas.

Benzene. Pure, B.P. 80-82 °C. Obtained from Eimer and Amend, New York, N. Y. Used in solubility tests.

Calcium Chloride. Tested purity, calcined, porous, granular. Obtained from Eimer and Amend, New York 14, N. Y. Used as drying agent for ammonia gas and the electrolyte.



Chloroform. U.S.P. Obtained from General Chem. Div., Allied Chem. and Dye Corp., New York, N. Y.

Copper, Sheet. Twelve inches wide, 1/32" thick. Analyzed by Whaley<sup>(65)</sup> by means of electroanalysis and spectroscopy; average 100.06 % Cu; impurities identified as traces of Fe, Si, Ca, and Ag. Obtained from Economy Lumber Co., Christiansburg, Va. Used for cathodes.

Dimethyl Glycol Monobutyl Ether. Purified. Obtained from Eimer and Amend, New York 14, N. Y. Used in solubility tests.

Ethyl Alcohol, Absolute. U.S.P. Sold only under Federal and State Gov. regulations. Obtainable from New York stock only. Used in solubility tests.

Ethyl Phosphate, Tri. Practical. Obtained from Tennessee Eastman Corp., Kingsport, Tenn. Used in solubility tests.

Formamide. C.P. Obtained from Eimer and Amend, New York 14, N. Y. Used as solvent for basic aluminum acetate.

Phosphorous Pentoxide, Anhydrous. Tested purity. Obtained from Eimer and Amend, New York 14, N. Y. Used as drying agent for formamide.

Sodium Hydroxide. Tested purity, pellets. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of ammonia gas.

Apparatus

Apparatus used in the experiments with formamide was as follows:

Battery, Storage. Delco, Model 1724AN, 24-volt, 17 amp-hr at 5 hour rate. Manufactured by Delco-Remy Div., General Motors Corp., Anderson, Ind. Used as direct-current source.

Beaker. Griffin, with spout, pyrex glass, 150-ml. Obtained from Eimer and Amend, New York 14, N. Y. Used as conductivity cell.

Beaker. Griffin, with spout, pyrex glass, 400-ml. Obtained from Eimer and Amend, New York 14, N. Y. Used with sulfuric acid to absorb excess ammonia gas.

Drying Tube. U-shape, with side tubes, 150-mm high. Obtained from Eimer and Amend, New York 14, N. Y. Used with calcium chloride for drying ammonia gas.

Flask, Distilling. Pyrex glass, 1-liter, three neck. Obtained from Eimer and Amend, New York 14, N. Y. Used as safety bottle.

Flask, Round Bottom. Pyrex glass, 500-ml, single neck. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of ammonia gas and to hold electrolyte for ammoniation.

Funnel. Buret filler, glass, 60 mm. Obtained from Eimer and Amend, New York 14, N. Y. Used for filtering.

Milliammeter. Hickock, Model 209A, Serial No. 6-13232.

Obtained from Lafayette Concord Radio Corp., Atlanta, Ga. Manufactured by the Hickock Electrical Instrument Co., Cleveland 8, Ohio. Used to measure cell current.

Rheostat. Rex, No. 9-526-5F, 112-ohm, 2 amp, 16" long.

Manufactured by Rex Rheostat Co., Baldwin, L. I., N. Y. Used to vary voltage.

Stopper, Cork. Quality XXXX, #32. Obtained from Cork

Products Co., New York 16, N. Y. Used to position glass tubing and electrodes.

Tubing, Glass. Pyrex, 6 mm O.D. Obtained from Eimer and

Amend, New York 14, N. Y. Used to position the electrodes.

Voltmeter. Multiple-range, Model No. 489, No. 62580.

Manufactured by Weston Electrical Instrument Corp., Newark, N. J. Used to measure cell voltage.

#### Method of Procedure

A group of solvents, representative of several types, was selected for solubility tests with basic aluminum acetate at 26 °C. The group included alcohols, hydrocarbons, substituted hydrocarbons, ethers, esters, and amines. About 0.1 gram of basic aluminum acetate was added to separate test tubes, each containing ten milliliters of absolute ethyl alcohol, benzene, chloroform, dimethyl glycol monobutyl

ether, ethyl phosphate, and formamide. After stoppering, the test tubes were shaken intermittently for approximately 15 minutes, allowed to stand, and observed for results.

To determine the solubility of basic aluminum acetate in formamide, about 70 milliliters of the solvent, at 25 °C, was measured into a 150-milliliter beaker and small portions of a five-gram sample of basic aluminum acetate were added gradually with stirring. At the first indication that the particles were not dissolving, the remainder of the basic aluminum acetate was weighed; by difference, the amount dissolved was computed.

Electrolytic work with the system basic aluminum acetate and formamide comprised three experiments; first, electrolysis of the system; second, electrolysis of the system after dry ammonia gas had been bubbled through it; and third, electrolysis of the system as in the first case but using formamide after it had been treated with anhydrous phosphoreous pentoxide.

For the first electrolysis, the bath was prepared by dissolving approximately 2.5 grams of basic aluminum acetate in 70 milliliters of formamide contained in a 150-milliliter beaker. A cork stopper for the beaker was used to support glass tubing which spaced an aluminum anode and copper cathode about one inch apart; each electrode measured approximately 2.5 centimeters square. An electromotive force of 8 to 18 volts was used for the electrolysis and the current, voltage, temperature and time were recorded.

The second electrolyte was prepared in a similar manner, but ammonia gas, generated by the reaction between 150 milliliters of ammonium hydroxide and about two grams of sodium hydroxide pellets, was bubbled through the bath for 20 minutes. The gas was passed through a calcium chloride filled drying tube before contacting the bath. This system was electrolyzed as before and the current, voltage, temperature and time were recorded. After 20 minutes, the solution was added to about five grams of calcium chloride in a 250-milliliter beaker for drying. After an attempt was made to filter the solution, it was discarded.

The third electrolysis was performed with a bath prepared by adding 140 milliliters of formamide to about ten grams of anhydrous phosphorous pentoxide in a 150-milliliter beaker, filtering the solution, and dissolving 4.9 grams of basic aluminum acetate in the filtrate. The solution was electrolyzed and data recorded as before.

#### Data and Results

Basic aluminum acetate was practically insoluble in benzene, absolute alcohol, dimethyl glycol monobutyl ether, chloroform, and ethyl phosphate; the solubility in these solvents was less than 0.05 gram per 100 milliliters. The solubility of basic aluminum acetate in formamide is about 3.5 grams per 100 milliliters at 26 °C.

In the three electrolyses of basic aluminum acetate in formamide, gas was evolved at both the aluminum anode and the copper cathode. Data and results of these electrolyses are given in Table IV.

A gray jelly-like precipitate formed in the first bath which contained 2.5 grams of basic aluminum acetate and 70 milliliters of formamide. This precipitate was not analyzed. The current dropped from 100 to 35 milliamperes during 11.33 hours of electrolysis.

The second electrolysis was discontinued after 20 minutes and then an attempt to dry the bath with calcium chloride resulted in the formation of an unidentified crystalline precipitate. This bath contained 2.5 grams of basic aluminum acetate in 70 milliliters of formamide plus dissolved dry ammonia gas.

The current dropped from 74 to 8 milliamperes during the electrolysis of the third bath which consisted of 4.9 grams of basic aluminum acetate in 140 milliliters of formamide that had been dried with ten grams of anhydrous phosphorous pentoxide.

#### Discussion of Results

During the three electrolyses of the systems of basic aluminum acetate in formamide, the presence of gases at both electrodes and the fact that evolution of the gases decreased with time indicated a possibility that water was decomposing. The formamide may have contained a small amount of moisture or the hydroxyl group in the

TABLE IV

Electrolyses of the Systems Basic Aluminum Acetate in Formamide and Basic Aluminum Acetate, Formamide and Ammonia at 25 °C

Aluminum anode, 2.5 x 2.5 centimeters

Copper cathode, 2.5 x 2.5 centimeters

Electrodes one inch apart

Expt. No.	System	Formulas	Composition, gm	Time, hr	E.M.F., volts	Current, ma	Results
1	Formamide Basic aluminum acetate	HCONH <sub>2</sub> AlOH(CH <sub>3</sub> COO) <sub>2</sub>	79.1 2.5	11.33	8-18	35-100	No Al
2	Formamide Basic aluminum acetate Ammonia gas	HCONH <sub>2</sub> AlOH(CH <sub>3</sub> COO) <sub>2</sub> NH <sub>3</sub>	79.1 2.5 sat'd	0.33	8-18	100	No Al
3	Formamide (dry) Basic aluminum acetate	HCONH <sub>2</sub> AlOH(CH <sub>3</sub> COO) <sub>2</sub>	158.2 4.9	0.91	18	8-74	No Al

basic aluminum acetate may have been decomposed. If the gases were oxygen and hydrogen at the anode and cathode, respectively, and their evolution had stopped eventually, the resultant drop in the current-carrying ability of the system would prohibit their use for electroplating of aluminum. From the final observations of current in the first and third experiments, calculations showed that 35 milliamperes for one hour could deposit a theoretical 0.00087 gram of aluminum per hour per square centimeter in the first case and the 8 milliamperes could deposit only 0.000199 gram of aluminum per hour per square centimeter in the third case. A minimum of 30 hours would be required to plate 0.001 inch of aluminum on a cathode in the latter instance. These values were calculated in the same manner as were those for the aluminum stearate systems, and are so small that commercial operation would be impractical.

The presence of an unidentified jelly-like precipitate in the first bath, after electrolysis, was evidence that the passage of current had caused some organic reaction to occur which would probably alter the composition of the system.

The second electrolyte which had been treated with dry ammonia gas was discarded when the addition of calcium chloride caused the formation of a crystalline precipitate.

Evolution of heat and increased viscosity accompanied the drying of formamide with anhydrous phosphorous pentoxide, probably due to a compound formation. Since the current drop in the third



electrolysis was about eight times as rapid as and the end current was approximately one-fourth the magnitude of that obtained in the first experiment, it is probable that the phosphorous pentoxide did remove, or tie up, some moisture from the bath.

#### Limitations

Limitations for the solubility, conductivity, and electrolysis tests with basic aluminum acetate and formamide were as follows:

The limitations of the solubility tests included the use of approximately 0.1 gram of basic aluminum acetate for each test in ten milliliters of the solvents absolute alcohol, benzene, dimethyl glycol monobutyl ether, ethyl phosphate, chloroform and formamide at 26 °C.

The limits of composition of three electrolytes tested were 2.5 grams of basic aluminum acetate in 70 milliliters of formamide; in addition, dry ammonia gas was bubbled through one bath for 20 minutes.

The limiting conditions for the electrolyses included the use of an aluminum anode and copper cathode, measuring 2.5 centimeters square and about one inch apart, with an applied potential difference of 8 to 18 volts at 25 °C. Times of electrolyses ranged from 0.33 to 11.33 hours.

### Conclusions

The solubility and conductivity tests with basic aluminum acetate and the electrolyses at 25 °C of baths prepared from 2.5 grams of basic aluminum acetate in 70 milliliters of formamide led to the following conclusions:

1. The solubility, at 26 °C, of basic aluminum acetate in benzene, absolute alcohol, dimethyl glycol monobutyl ether, ethyl phosphate, and chloroform is apparently less than 0.05 gram per 100 milliliters of solvent.

2. The solubility, at 25 °C, of basic aluminum acetate in formamide is approximately 3.5 grams per 100 milliliters.

3. With an aluminum anode and copper cathode measuring 2.5 centimeters square and spaced one inch apart, 100 milliamperes is the maximum current obtained from a system containing 2.5 grams of basic aluminum acetate and 70 milliliters of formamide with a potential of 18 volts across the electrodes.

4. Aluminum is not deposited during 11 hours of electrolysis of a bath containing 2.5 grams of basic aluminum acetate and 70 milliliters of formamide employing an aluminum anode and copper cathode.

5. It is unlikely that a system of basic aluminum acetate in formamide can be used for the electrodeposition of aluminum since gases are evolved at the aluminum anode and copper cathode and an organic reaction occurs during the passage of current, with formation of an unidentified precipitate in the electrolyte.

### PHENOXIDE SYSTEMS

Aluminum phenoxide and o-nitrophenoxide were chosen as representatives of another class of compounds which might furnish aluminum ions for electrodeposition. Phenol is acidic, soluble in organic solutions, and the hydrogen can be replaced by sodium to form a salt-like compound. (9) Aluminum phenoxide can be prepared and may be an ionized compound. If not highly ionized, aluminum phenoxide might be combined with the sodium phenoxide as a mixed electrolyte. The o-nitrophenoxide compound was investigated because the nitro group increases the acidity of the salt and it might tend to change the ion characteristics.

### Literature Review

Brockman (60) reports that electrolysis of alkaline aqueous solutions of phenolic salts results in regeneration of the free acid and evolution of oxygen at the anode. A neutral solution of potassium phenolate results in the formation of a compound  $C_{65}H_{48}O_{22}$  at the anode, which is soluble in alkaline solutions but insoluble in acids. A compound,  $C_{29}H_{20}O_8$ , is formed at the anode from electrolysis of neutral sodium phenolate solutions. These products were obtained at coke, graphite, and platinum anodes.

At a platinum cathode in acid solutions, Brockman (61) reports that Elba obtained p-aminophenol from electrolysis of p-nitrophenol

and o-nitrophenol; in addition, small amounts of an unknown blue compound were formed from the o-nitrophenol.

The preparation of aluminum phenoxide, or aluminum phenolate, has been reported by Cook. (9)

Preparation of Aluminum Phenoxide. A general method for preparing aluminum phenoxide is to heat 100 to 500 grams of phenol in a liter flask fitted with a return Liebig condenser. An air condenser is not sufficient since the tube becomes heated and allows the escape of phenol vapor. The addition of a little iodine reduces the temperature required for the reaction. The aluminum is added gradually in the form of strips, very slowly at first or the action may become too violent and most of the phenol will escape uncondensed. No heat is required once the action starts. A sharp heat is applied at completion of the reaction to evolve all of the hydrogen. The product is poured out on a plate, cooled and bottled.

Pure aluminum does not react with phenol but commercial aluminum, containing a small amount of carbon as impurity, reacts very nicely.

Properties of Aluminum Phenoxide. Aluminum phenoxide is a translucent, brittle solid, and gray or black. It melts at about 265 °C and decomposes at slightly higher temperatures. Its specific gravity is 1.23. It is soluble in hot toluene, benzene, xylene, in methyl, ethyl and amyl alcohols, but not if these contain small amounts of water. It is soluble in chloroform, carbon disulfide, aniline,

carbon tetrachloride, acetone, etc. It is probable that aluminum phenoxide reacts with all of these solvents. No method of purification was found by Cook.

#### Purpose of Investigation

The purpose of this portion of the investigation was to prepare the compounds aluminum phenoxide and o-nitrophenoxide and to determine their solubilities and conductivities, if warranted, in a group of various types of solvents. Sodium phenoxide or o-nitrophenoxide were added to any promising systems in an attempt to increase conductivity, and the baths were tested for the possibility of electrodepositing aluminum.

#### Materials

The following materials were used in the experiments with the aluminum and sodium phenoxide compounds:

Acetone. Tested purity, B.P. 55.5-57.5 °C. Obtained from Eimer and Amend, New York 14, N. Y. Used in solubility tests with aluminum phenoxide.

Aluminum Chloride. C.P., anhydrous. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of aluminum o-nitrophenoxide.

Aluminum Metal. Powdered. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparations.

Aluminum Metal. Foil, 1/1000" thick. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of aluminum phenoxide and o-nitrophenoxide.

Aluminum, Sheet. No. 3S-H14, 0.040" thick. Analysis: 0.6 % Si, 0.7 % Fe, 0.2 % Cu, 1.5 % Mn, 0.1 % Zn, 96.175 % Al, 0.15 % others. Obtained from Reynolds Metals Co., Louisville, Ky. Used as anode material.

Benzaldehyde. Practical. Obtained from Eimer and Amend, New York 14, N. Y. Used in solubility tests with aluminum phenoxide.

Benzene. Pure, B.P. 80-82 °C. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of aluminum o-nitrophenoxide.

Carbon, Activated. Obtained from Eimer and Amend, New York 14, N. Y. Used as catalyst in preparation of aluminum phenoxide.

Carbon Bisulfide. Technical. Obtained from Eimer and Amend, New York 14, N. Y. Used in solubility tests with aluminum phenoxide.

Chloroform. U.S.P. Obtained from Eimer and Amend, New York 14, N. Y. Used in solubility tests with aluminum phenoxide.

Copper, Sheet. Twelve inches wide, 1/32" thick. Analyzed by Whaley<sup>(65)</sup> by means of electroanalysis and spectroscopy;

average 100.06 % Cu; impurities identified as traces of Fe, Si, Ca, and Ag. Obtained from Economy Lumber Co., Christiansburg, Va. Used as cathode material.

Ethyl Phosphate, Tri. Practical. Obtained from Tennessee Eastman Corp., Kingsport, Tenn. Used in solubility tests.

Formaldehyde. C.P. Obtained from Eimer and Amend, New York 14, N. Y. Used in solubility tests with aluminum phenoxide.

Formamide. C.P. Obtained from Eimer and Amend, New York 14, N. Y. Used in solubility tests with aluminum phenoxide.

Iodine. Tested purity, crystals. Obtained from Eimer and Amend, New York 14, N. Y. Used to lower reaction temperature requirement in preparation of aluminum phenoxide.

Mercuric Chloride. Tested purity, crystals, Lot No. D173. Obtained from General Chemical Co., New York, N. Y. Used as catalyst in preparation of aluminum phenoxide and o-nitrophenoxide; used in water solution to activate aluminum foil.

Methyl Alcohol. Purified. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of sodium o-nitrophenoxide.

Oil, Motor. Essolube, S.A.E. 40. Obtained from Esso Service Station, Blacksburg, Virginia. Used for oil bath.

o-Nitrophenol. Technical. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of aluminum and sodium o-nitrophenoxide.

Phenol. Tested purity. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of aluminum and sodium phenoxide.

Platinum, Sheet. Chemically pure, 0.003" thick. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used for electrodes.

Potassium Hydroxide. Tested purity, Lot No. D345. Obtained from General Chemical Co., New York, N. Y. Used in preparation of aluminum o-nitrophenoxide.

Sodium Hydroxide. C.P., Lot No. 461988. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of sodium phenoxide and o-nitrophenoxide.

Stopper, Cork. Quality XXXX, #32. Obtained from Cork Products Co., New York 16, N. Y. Used to position glass tubing and electrodes.

Toluene. C.P. Obtained from Eimer and Amend, New York 14, N. Y. Used in solubility tests with aluminum phenoxide.

Tubing, Glass. Pyrex, 6 mm O.D. Obtained from Eimer and Amend, New York 14, N. Y. Used to position electrodes.

Wire, Platinum. Chemically pure, 1/64" dia. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used as connections to electrodes.

Xylene. Tested purity. Obtained from Eimer and Amend, New York 14, N. Y. Used in solubility tests with aluminum phenoxide.



Apparatus

Apparatus used in the experiments with aluminum and sodium phenoxides was as follows:

Battery, Storage. Delco, Model 1724AN, 24-volt, 17 amp-hr at 5 hour rate. Manufactured by Delco-Remy Div., General Motors Corp., Anderson, Ind. Used as direct-current source.

Beaker. Griffin, with spout, pyrex glass, 150-ml. Obtained from Eimer and Amend, New York 14, N. Y. Used as conductivity cell.

Beaker. Griffin, with spout, pyrex glass, 250-ml. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of compounds.

Beaker. Griffin, with spout, pyrex glass, 600-ml. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of compounds.

Beaker. Griffin, with spout, pyrex glass, 1-liter. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of compounds.

Condenser. Liebig, pyrex glass, 400 mm long. Obtained from Eimer and Amend, New York 14, N. Y. Used as reflux condenser in preparation of aluminum phenoxide and *o*-nitrophenoxide.

Crucible, Coor. Porcelain, size O, 17-ml capacity. Obtained from Eimer and Amend, New York 14, N. Y. Used in analyses of sodium phenoxide.

Dish, Crystallizing. Glass, 150-mm dia. Obtained from Eimer and Amend, New York 14, N. Y. Used for air drying of aluminum phenoxide.

Flask, Distilling. MCA, pyrex glass, 250-ml. Obtained from Eimer and Amend, New York 14, N. Y. Used for distilling off alcohol.

Flask, Distilling. MCA, pyrex glass, 1-liter. Obtained from Eimer and Amend, New York 14, N. Y. Used for distilling off alcohol.

Flask. Round bottom, pyrex glass, 1-liter. Obtained from Eimer and Amend, New York 14, N. Y. Used as reflux flask in preparation of aluminum phenoxide and o-nitrophenoxide.

Funnel, Buechner. Capacity, 150-ml. Obtained from Eimer and Amend, New York 14, N. Y. Used for filtering with suction.

Heater, Autemp. Volts A.C., 115. Obtained from Eimer and Amend, New York 14, N. Y. Used to heat water and oil baths.

Milliammeter. Direct current, 0-250 ma, U.S.N. type CAY-22065. Manufactured by Westinghouse Electric Co., Pittsburgh, Pa. Used to measure cell current.

Pan. Enamel, 3-qt capacity. Obtained from Brown Stores Co., Inc., Blacksburg, Va. Used for water and oil baths.

Rheostat. Rex, No. 9-526-5F, 112-ohm, 2 amp. 16" long. Manufactured by Rex Rheostat Co., Baldwin, L. I., N. Y. Used to vary voltage.

Test Tubes. Pyrex, 150-mm long, 16 mm O.D. Obtained from Eimer and Amend, New York 14, N. Y. Used in solubility tests.

Thermometer. Mercury in glass, nitrogen filled, -5 to 360 °C. Obtained from Eimer and Amend, New York 14, N. Y. Used to indicate temperature of reaction during preparation of compounds.

Voltmeter. Multiple-range, Model No. 489, No. 62580. Manufactured by Weston Electrical Instrument Corp., Newark, N. J. Used to measure cell voltage.

#### Method of Procedure

Experiments conducted in this section consisted of the preparation of aluminum o-nitrophenoxide, aluminum phenoxide, sodium o-nitrophenoxide and sodium phenoxide, with subsequent tests on their solubilities and conductivities in different combinations.

Preparation of Aluminum o-Nitrophenoxide. The preparation of aluminum o-nitrophenoxide consisted of dissolving 5.6 grams of potassium hydroxide in 20 milliliters of ethyl alcohol contained in a 250-milliliter beaker. In another beaker, 14 grams of o-nitrophenol was dissolved in 85 milliliters of benzene and added to the first solution. Filtering with suction removed the solid potassium o-nitrophenoxide which was washed with a little benzene. The solid was mixed with 380 milliliters of alcohol, containing 50 per cent each of methyl and ethyl alcohol, by volume, and then filtered to remove a few particles which did not dissolve. A total of 55 grams of aluminum chloride were dissolved in 290 milliliters of a similar mixture of

alcohols and this solution was added to the solution of potassium o-nitrophenoxide to precipitate the potassium chloride. The precipitate was removed by filtering with suction; the filtrate, in a one-liter distilling flask equipped with a water-cooled condenser, was heated by a water-bath to remove alcohol and leave 150 milliliters of viscous red solution. This solution was used in later experiments for the preparation of electrolytes, after its concentration was determined. The actual yield of aluminum o-nitrophenoxide crystals, determined by analysis, was 75 grams as compared to a theoretical yield of 225 grams, or an actual yield of 33.4 per cent.

Analysis of Aluminum o-Nitrophenoxide. Analysis of the aluminum o-nitrophenoxide was limited to the determination of the concentration of solid compound in the alcoholic solution. Ten milliliters of this solution was poured into an evaporating dish of known weight. The dish was heated over a water bath until the solution became viscous. After cooling, the dish and contents were placed in a vacuum desiccator for 35 hours at a pressure of five millimeters of mercury. The evaporating dish and dried aluminum o-nitrophenoxide were weighed and the weight of solid obtained by difference.

Preparation of Aluminum Phenoxide. The preparation of aluminum phenoxide was reported by Cook.<sup>(9)</sup> It consisted of heating 100 grams of phenol in a one-liter round bottom flask equipped with a water-cooled reflux condenser, by means of an oil bath, to a temperature of about 260 °F. A few small pieces of aluminum foil, a pinch of

powdered carbon, and 0.5 gram of mercuric chloride were added. Several crystals of iodine were added to lower the temperature requirement for the reaction. When the temperature was increased to 290 °F, digestion of the aluminum became evident; the oil bath was removed because the heat of reaction was sufficient to promote digestion. After seven grams of aluminum foil had been added slowly as the digestion proceeded, the reaction mixture began to solidify; increased heat was applied to complete the reaction. The product was dumped into a crystallizing dish and allowed to cool. A few pieces of unreacted aluminum foil were removed and the product bottled for later use in the preparation of electrolytes. A yield of 86 grams of aluminum phenoxide was obtained as compared to a theoretical yield of 79.3 grams, or an apparent yield of 108.5 per cent.

Preparation of Sodium o-Nitrophenoxide. The preparation of sodium o-nitrophenoxide was accomplished by dissolving ten grams of o-nitrophenol in 60 milliliters of methyl alcohol contained in a 150-milliliter beaker. This was mixed with a second solution of 2.9 grams of sodium hydroxide in 60 milliliters of methyl alcohol contained in a 250-milliliter beaker. The sodium o-nitrophenoxide was filtered with suction and washed with a small amount of alcohol. The product was a bright red-orange solid and it was bottled for later use in the preparation of electrolytes. A yield of 7.2 grams of sodium o-nitrophenoxide was obtained as compared to a theoretical yield of 11.6 grams, or an actual yield of 62 per cent.

Preparation of Sodium Phenoxide. The sodium phenoxide was prepared by dissolving 23.5 grams of phenol in 25 milliliters of absolute alcohol contained in a 150-milliliter beaker. This was mixed with another solution of ten grams of sodium hydroxide in 75 milliliters of absolute alcohol contained in a 250-milliliter beaker. The resulting solution was poured into a 250-milliliter distilling flask, which was equipped with a water-cooled condenser, and heated over a water-bath until only 56.3 milliliters remained in the flask. This solution was bottled for later use in the preparation of electrolytes, after its concentration was determined. A yield of 24.7 grams of sodium phenoxide crystals was obtained as compared to a theoretical yield of 29 grams, or an actual yield of 85 per cent.

Analysis of the Sodium Phenoxide. Analysis of the sodium phenoxide was limited to the determination of the concentration of the solid compound in the alcoholic solution. A sample of 6.3 milliliters of the solution was poured into a crucible of known weight and the alcohol evaporated by careful heating over a steam bath. The solid was dried by heating the crucible in an electric oven for two hours at 80 °C, and the weight of sodium phenoxide obtained by difference.

Solubility Tests Using Impure Aluminum Phenoxide. The solubility of the impure aluminum phenoxide was tested in eleven organic solvents. The solvents were: formamide, absolute alcohol, toluene, xylene, chloroform, acetone, formaldehyde, benzaldehyde, methyl alcohol,

and ethyl phosphate. In each case, 0.01 to 0.5 gram of the aluminum phenoxide was added to ten milliliters of solvent in a test tube at 20 °C, stoppered, shaken for several minutes to aid solution and observed. Each test tube and contents was heated by immersion in boiling water and again shaken and observed.

Conductivity of Aluminum o-Nitrophenoxide in Alcohol. The conductivity test was performed with a bath prepared by measuring 60 milliliters of the alcoholic solution of aluminum o-nitrophenoxide, which contained about 0.5 gram of solid per milliliter of solution, into a 150-milliliter beaker. A cork stopper was fitted with two glass tubes one-half inch apart. Platinum electrodes, each measuring 2.5 x 2.5 centimeters and spaced one-half inch apart by the glass tubes, were immersed into the solution. A potential of 18 volts was supplied from storage batteries through a variable resistor. Time and current were recorded.

Electrolysis of the System Aluminum o-Nitrophenoxide, Sodium o-Nitrophenoxide and Methyl Alcohol. The procedure followed in electrolysis of the system aluminum o-nitrophenoxide, sodium o-nitrophenoxide and methyl alcohol was to dissolve 30 milliliters of the alcoholic solution of aluminum o-nitrophenoxide, which contained about 0.5 gram of solid per milliliter of solution, in 30 milliliters of methyl alcohol nearly saturated with sodium o-nitrophenoxide and contained in a 150-milliliter beaker. Electrolysis was conducted at 8 to 18 volts potential using the same apparatus as for the conductivity test, but substituting a copper cathode for the platinum.

Electrolysis was discontinued after about 5.25 hours, the cathode washed with alcohol, and the black deposit on the top edge of the cathode was removed. Distilled water was added to the deposit in a test tube and the mixture was acidified with sulfuric acid. Ammonium hydroxide was added to precipitate aluminum hydroxide if any aluminum ions were present.

A new electrolyte was prepared in the same manner as the first one and electrolyzed with an aluminum anode and a copper cathode for 4.75 hours at 10 to 17 volts potential.

Solubility, Conductivity, and Electrolysis of Aluminum Phenoxide in Ethyl Phosphate. A preliminary solubility test was performed by adding a few grains of crushed aluminum phenoxide to five milliliters of ethyl phosphate in a test tube, stoppering and shaking it, and observing the effect.

One gram of aluminum phenoxide was added to 70 milliliters of ethyl phosphate in a 150-milliliter beaker and the solution was agitated with a mechanical stirrer. The solution was filtered into a clean 150-milliliter beaker and an electromotive force of 20 volts applied to a platinum anode and copper cathode, each measuring 2.5 centimeters square and one-half inch apart; the milliammeter was observed. A small amount of sodium nitrophenoxide was dissolved in the solution and the current observed again.

A new electrolyte was prepared by dissolving eight grams of aluminum phenoxide in 100 milliliters of ethyl phosphate in a



150-milliliter beaker. After decanting the solution to remove impurities which did not dissolve, a conductivity test was made employing platinum electrodes, measuring 2.5 centimeters square and one-half inch apart, at a potential of 54 volts. One-half gram of sodium o-nitrophenoxide was added and the conductivity tested at 55 volts. Electrolysis was carried out for 0.25 hour employing a platinum anode and copper cathode, each measuring 2.5 centimeters square and one-half inch apart, at a potential of 50 volts. Electrolysis of the same bath for one hour was carried out under similar conditions, except for the substitution of an aluminum anode for the platinum one. Observations of time, temperature, voltage and current were recorded.

Electrolysis of the System Aluminum Phenoxide, Sodium Phenoxide in Alcohol, and Ethyl Phosphate. An electrolyte was prepared by adding 12.6 milliliters of the alcoholic solution, containing 5.28 grams of sodium phenoxide, to a solution of eight grams of aluminum phenoxide in 100 milliliters of ethyl phosphate contained in a 150-milliliter beaker. No electrolysis was attempted because of the formation of an unidentified precipitate upon mixing.

A second electrolyte was prepared by dissolving seven grams of aluminum phenoxide in 100 milliliters of ethyl phosphate in a 150-milliliter beaker. To this solution, 0.2 gram of sodium phenoxide, from which the alcohol had been evaporated, was added. With 20 volts

applied across the electrodes, the amount of current was observed. Another 0.2 gram of sodium phenoxide was added and the current observed.

### Data and Results

Data and results are given in Tables V and VI for the solubility of aluminum phenoxide in various organic solvents and the electrolyses of the phenoxide systems, respectively.

After electrolysis of the bath containing 30 milliliters of the alcoholic solution of aluminum o-nitrophenoxide, 1.5 grams of sodium o-nitrophenoxide and 30 milliliters of methyl alcohol with a platinum anode and copper-cathode, a black deposit was found on the top edge of the cathode. An attempt was made to precipitate aluminum hydroxide from a sulfuric acid solution containing the deposit, by adding ammonium hydroxide, but no evidence of a precipitate was observed. The absence of a precipitate indicated that no aluminum was present in the deposit. When a similar system was electrolyzed with an aluminum anode and copper cathode, gas was evolved at the anode during the 4.75 hours, and an unidentified red-brown coating was easily washed from the cathode.

During electrolysis of the system containing one gram of aluminum phenoxide, 0.2 gram of sodium o-nitrophenoxide and 70 milliliters of ethyl phosphate with a platinum anode and copper cathode, gas was

TABLE V

Solubility of Aluminum Phenoxide in Various Organic Solvents

Solvent	Temperature, °C	Solubility, gm/100 ml	Temperature, °C	Solubility, gm/100 ml
Formamide	20	0.1	96	0.1
Absolute alcohol	20	< 0.1	78	< 0.1
Toluene	20	< 0.1	96	< 0.1
Xylene	20	< 0.1	96	0.1
Chloroform	20	< 0.1	61	< 0.1
Acetone	20	< 0.1	56	< 0.1
Formaldehyde	20	< 0.1	96	< 0.1
Benzaldehyde	20	< 0.1	96	< 0.1
Methyl alcohol	20	2.0	64	2.0
Ethyl phosphate	20	2.0	96	5.0

TABLE VI

Electrolyses of Phenoxide Systems

Electrodes, 2.5 x 2.5 centimeters, one inch apart

Expt. No.	System	Composition, gm	Electrodes	Time, hr	E.M.F., volts	Current, ma	Temp., °C	Results
1	Al(OOC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> ) <sub>3</sub> NaOC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> CH <sub>3</sub> OH	15 1.5 45	Pt anode Cu cathode	5.25	8-18	30-250	24	No Al
2	Al(OOC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> ) <sub>3</sub> NaOC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> CH <sub>3</sub> OH	15 1.5 45	Al anode Cu cathode	4.75	10-17	34-150	25	No Al
3	Al(OOC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> NaOC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> PO <sub>4</sub>	8 0.5 106.1	Pt anode Cu cathode Al anode Cu cathode	0.25 1.00	50 50	20-32 43-55	15.5 15.5	No Al No Al
4	Al(OOC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> NaOC <sub>6</sub> H <sub>5</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> PO <sub>4</sub>	8 0.4 106.1	Al anode Cu cathode	6.00	26-29	15	26	No Al

Al(OOC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)<sub>3</sub> = aluminum nitrophenoxide  
 NaOC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> = sodium nitrophenoxide  
 CH<sub>3</sub>OH = methyl alcohol

Al(OOC<sub>6</sub>H<sub>5</sub>)<sub>3</sub> = aluminum phenoxide  
 NaOC<sub>6</sub>H<sub>5</sub> = sodium phenoxide  
 (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>PO<sub>4</sub> = ethyl phosphate

evolved at the cathode and a brown coating formed on the anode.

When an aluminum anode and copper cathode were used, gas was evolved at the cathode and the aluminum anode darkened. No aluminum was visible on the cathode.

Gas was evolved at the copper cathode during electrolysis of the bath containing seven grams of aluminum phenoxide, 0.2 gram of sodium phenoxide and 100 milliliters of ethyl phosphate and no aluminum was visible on the cathode. An aluminum anode was used.

#### Discussion of Results

In searching for a solvent for aluminum phenoxide, an effort was made again to use several types of organic solvents; these included amines, alcohols, hydrocarbons, and aldehydes. Although Cook<sup>(9)</sup> reported that the aluminum compound was soluble in toluene, xylene, ethyl alcohol, chloroform, acetone and other solvents, the solubility tests performed in the course of this work did not verify his results. The only solvents tested which exhibited appreciable solubility of aluminum phenoxide were methyl alcohol and ethyl phosphate; solubility in the alcohol was about two grams per 100 milliliters at 20 to 64 °C, and in the ethyl phosphate it was about five grams per 100 milliliters at 96 °C.

Conductivity tests with the alcoholic solution of aluminum o-nitrophenoxide showed a rapid decrease in current from 150 to 10

milliamperes in about 11 minutes. This final current was insufficient for practical use in the electrodeposition of aluminum.

In Experiment 1, the current fluctuated as much as 100 milliamperes during a period of 15 minutes of electrolysis and varied between 30 and 250 milliamperes during the  $5\frac{1}{2}$  hours. Such a condition could not be tolerated in an electroplating bath because of the effect on the type of crystal formation.

In Experiment 2, it was assumed that the formation of a red-brown coating indicated the occurrence of an organic reaction during electrolysis, or the deposition of some complex organic cation. The gas evolved at the anode was probably oxygen from decomposition of water or one of the constituents of the solution.

In Experiment 3, gas at the cathode could have been hydrogen from decomposition of moisture in the ethyl phosphate or sodium o-nitrophenoxide. The brown deposit on the anode may have been a polymerization product from the aluminum phenoxide and/or the sodium o-nitrophenoxide.

In Experiment 4, the gas evolved at the cathode was probably hydrogen from decomposition of moisture in the ethyl phosphate or the phenoxides. The figure of 15 milliamperes was obtained from about ten minutes of electrolysis at 28 volts and may not be a true indication of a steady value for six hours. With electrodes one-half inch apart, a current of 15 milliamperes could deposit only about 0.00039 gram of aluminum per hour per square centimeter on a cathode;

this fact alone would preclude any practical use of the system for the electrodeposition of aluminum. An example of this calculation is given in the discussion section for the stearate systems, page 90.

### Limitations

The limitations for solubility, conductivity, and electrolysis tests with aluminum and sodium phenoxide compounds were as follows:

The aluminum o-nitrophenoxide was prepared and used, in all cases, as a 1 : 1 methyl-ethyl alcohol solution containing about 500 grams of aluminum o-nitrophenoxide per liter of solution.

The sodium phenoxide was prepared and used as an absolute alcohol solution containing about 440 grams of sodium phenoxide per liter of solution.

The solubility tests with aluminum phenoxide were made at 20 °C and at either 96 °C or the boiling point of the particular solvent, whichever was lower. Ten milliliters of solvent were used in each solubility test; the solvents included formamide, absolute alcohol, toluene, xylene, chloroform, acetone, formaldehyde, benzaldehyde, methyl alcohol, and ethyl phosphate.

All electrodes used in the conductivity and electrolysis tests measured 2.5 centimeters square and were spaced one-half inch apart.

A conductivity test with 60 milliliters of the 1 : 1 methyl-ethyl alcohol solution of aluminum o-nitrophenoxide was performed at 18 volts with platinum electrodes.

The system comprising 30 milliliters of the 1 : 1 methyl-ethyl alcohol solution of aluminum o-nitrophenoxide, 1.5 grams of sodium o-nitrophenoxide and 30 milliliters of methyl alcohol was electrolyzed for five hours between a platinum anode and a copper cathode at a potential of 18 volts.

The system comprising 30 milliliters of alcoholic aluminum o-nitrophenoxide, 1.5 grams of sodium o-nitrophenoxide and 30 milliliters of methyl alcohol was electrolyzed for 4.75 hours employing an aluminum anode and a copper cathode at a potential of 17 volts.

An electrolyte comprising eight grams of aluminum phenoxide, one-half gram of sodium o-nitrophenoxide and 100 milliliters of ethyl phosphate was electrolyzed for 15 minutes with a platinum anode and a copper cathode at a potential of 50 volts.

An electrolyte containing seven grams of aluminum phenoxide, 0.4 gram of sodium phenoxide and 100 milliliters of ethyl phosphate was electrolyzed for six hours employing an aluminum anode and copper cathode at a potential of 20 volts.

#### Conclusions

From the solubility, conductivity and electrolysis tests with aluminum phenoxide, aluminum o-nitrophenoxide, sodium phenoxide, and sodium o-nitrophenoxide and various electrolyte baths prepared with methyl alcohol and ethyl phosphate as solvents, it has been concluded that:



1. The solubility of aluminum phenoxide in formamide, absolute alcohol, toluene, xylene, chloroform, acetone, formaldehyde, and benzaldehyde is apparently less than 0.1 gram per 100 milliliters at 20 to 96 °C, or at their boiling points if less than 96 °C.

2. The solubility of aluminum phenoxide in methyl alcohol is approximately two grams per 100 milliliters at 20 and 64 °C.

3. The solubility of aluminum phenoxide in ethyl phosphate is about two grams per 100 milliliters at 20 °C, and about five grams per 100 milliliters at 96 °C.

4. No deposit of aluminum is obtained during five hours of electrolysis of a system comprising 30 milliliters of a 1 : 1 methyl-ethyl alcohol solution of aluminum o-nitrophenoxide, 1.5 grams of sodium o-nitrophenoxide and 30 milliliters of methyl alcohol at a potential of 18 volts between a platinum anode and a copper cathode, each measuring 2.5 centimeters square and spaced one-half inch apart.

5. When a system consisting of 30 milliliters of a 1 : 1 methyl-ethyl alcohol solution of aluminum o-nitrophenoxide, 1.5 grams of sodium o-nitrophenoxide and 30 milliliters of methyl alcohol is electrolyzed at a potential of 10 to 17 volts between an aluminum anode and copper cathode, each measuring 2.5 centimeters square and spaced one-half inch apart, gas is evolved at the anode. The ability of the bath to pass current is reduced to about 50 per cent of that noted with a platinum anode and copper cathode, under similar conditions. No aluminum is obtained during 4.75 hours of electrolysis.

6. No deposit of aluminum can be obtained from a one-hour electrolysis of a system containing eight grams of aluminum phenoxide, one-half gram of sodium o-nitrophenoxide and 100 milliliters of ethyl phosphate when a potential difference of 50 volts is applied to an aluminum anode and copper cathode, each measuring 2.5 centimeters square and spaced one-half inch apart.

7. An electrolyte containing eight grams of aluminum phenoxide, 5.28 grams of sodium phenoxide in about ten milliliters of absolute alcohol, and 100 milliliters of ethyl phosphate is not practical for use in the electrodeposition of aluminum because a heavy precipitate forms during preparation of the bath.

8. An electrolyte consisting of seven grams of aluminum phenoxide, 0.4 gram of sodium phenoxide, and 100 milliliters of ethyl phosphate will conduct only 15 milliamperes of current at 20 volts. At this current, only 0.00039 gram of aluminum per hour per square centimeter could be deposited, theoretically.

9. It does not appear that mixed electrolytes of aluminum phenoxide and sodium phenoxide, aluminum phenoxide and sodium o-nitrophenoxide, and aluminum o-nitrophenoxide and sodium o-nitrophenoxide can be used practicably for the electrodeposition of aluminum because of the organic reactions which occur during electrolysis.

### ACETYLACETONATE SYSTEMS

Another type of compound to be considered in these studies was the diketone derivatives. One of the simplest of these compounds is the derivative of acetylacetone,  $\text{CH}_3\text{COCH}_2\text{COCH}_3$ . Some metallic derivatives of acetylacetone, <sup>(60)</sup> such as the sodium compound, are salt-like. It was expected that a mixed electrolyte of aluminum acetylacetonate and sodium acetylacetonate might furnish aluminum ions for the electrodeposition of aluminum from liquid, nonaqueous organic solutions.

### Literature Review

No instances were found in which metal derivatives of acetylacetone were used in electrolysis experiments. However, methods for the preparation of aluminum acetylacetonate and sodium acetylacetonate have been reported.

Preparation of Aluminum Acetylacetonate. Young <sup>(58)</sup> has given a procedure for the preparation of aluminum acetylacetonate. To a solution of freshly distilled acetylacetone, six normal ammonium hydroxide was added, dropwise with stirring, to a suspension of six grams of aluminum sulfate in 60 milliliters of water until the mixture of the two solutions was neutral to litmus paper. The precipitate was filtered off, washed with water, and air dried.

The product was purified by subliming it at one millimeter pressure at about 156 °C. The sublimate was dissolved in the least possible benzene, and pure aluminum acetylacetonate was precipitated by the addition of petroleum ether. The product was filtered with suction, washed with petroleum ether and allowed to air dry. The yield of aluminum acetylacetonate was about 4.2 grams, or 81 per cent.

Aluminum acetylacetonate had a melting point of 194.6 °C, a boiling point of 314 to 315.6 °C, is insoluble in water but soluble in organic solvents.

Preparation of Sodium Acetylacetonate. Marchi <sup>(23)</sup> gives two methods for the preparation of sodium acetylacetonate. In the first method, very fine sodium was added to acetylacetone dissolved in ether. In the second method, the addition of sodium alcoholate solution to acetylacetone gave a white precipitate of sodium acetylacetonate which was insoluble in petroleum ether.

No definite information was found for the properties of sodium acetylacetonate. In general, alkali acetylacetonates are soluble in water and they char on heating.

#### Purpose of Investigation

The purpose of this portion of the investigation was to prepare aluminum acetylacetonate and sodium acetylacetonate for use as a mixed electrolyte, to test their solubilities in several types of organic solvents, to perform conductivity tests with their solutions,

and to electrolyze any promising systems to determine their ability to furnish aluminum ions for electrodeposition from liquid, nonaqueous organic solutions.

### Materials

The following materials were used in the experiments with aluminum and sodium acetylacetonates:

Acetylacetone. C.P. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of aluminum and sodium acetylacetonates.

Aluminum, Sheet. No. 3S-H14, 0.040" thick. Analysis: 0.6 % Si, 0.7 % Fe, 0.2 % Cu, 1.5 % Mn, 0.1 % Zn, 96.75 % Al, 0.15 % others. Sample obtained from Reynolds Metals Co., Louisville, Ky. Used as anode material.

Aluminum Sulfate. Tested purity, crystals. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of aluminum acetylacetonate.

Ammonium Hydroxide. Tested purity, 27 %. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of aluminum acetylacetonate.

Benzene. Pure, B.P. 80-82 °C. Obtained from Eimer and Amend, New York 14, N. Y. Used in solubility tests with aluminum and sodium acetylacetonates.

Copper, Sheet. Twelve inches wide, 1/32" thick. Analyzed by Whaley<sup>(65)</sup> by means of electroanalysis and spectroscopy: average 100.06 % Cu; impurities identified as traces of Fe, Si, Ca, and Ag. Obtained from Economy Lumber Co., Christiansburg, Va. Used as cathode material.

Dimethyl Glycol Monobutyl Ether. Purified. Obtained from Eimer and Amend, New York 14, N. Y. Used in solubility tests with aluminum and sodium acetylacetonates.

Ethyl Alcohol. U.S.F., 95 %. Sold only under Federal and State Gov. regulations. Obtainable from New York stock only. Used in solubility tests with aluminum and sodium acetylacetonates.

Ethyl Alcohol, Absolute. Sold only under Federal and State Gov. regulations. Obtainable from New York stock only. Used in solubility tests with aluminum and sodium acetylacetonates.

Ethyl Bromide. Free from ether, B.P. 38-40 °C, highest purity. Obtained from Eimer and Amend, New York 14, N. Y. Used in solubility tests with aluminum and sodium acetylacetonates.

Ethyl Phosphate, Tri. Practical. Obtained from Tennessee Eastman Corp., Kingsport, Tenn. Used in solubility tests with aluminum and sodium acetylacetonates.

Formamide. C.P. Obtained from Eimer and Amend, New York 14, N. Y. Used in solubility tests with aluminum and sodium acetylacetonates.

Nitric Acid. Tested purity, specific gravity 1.42. Obtained from Eimer and Amend, New York 14, N. Y. Used in analysis of aluminum and sodium acetylacetonates.

Oil, Paraffin. White, Lot No. F095. Obtained from General Chemical Div., Allied Chemical and Dye Corp., New York, N. Y. Used for bath in determination of the melting point of aluminum acetylacetonate.

Platinum, Sheet. Chemically pure, 0.003" thick. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used for electrodes.

Stopper, Cork. Quality XXXX, #32. Obtained from Cork Products Co., New York 16, N. Y. Used to position glass tubing and electrodes.

Sulfuric Acid. C.P., specific gravity 1.84. Obtained from General Chemical Div., Allied Chemical and Dye Corp., New York, N. Y. Used in analysis of aluminum and sodium acetylacetonates.

Toluene. C.P. Obtained from Eimer and Amend, New York 14, N. Y. Used in solubility tests with aluminum and sodium acetylacetonates.

Tubing, Glass. Pyrex, 6 mm O.D. Obtained from Eimer and Amend, New York 14, N. Y. Used to position electrodes.

Wire, Platinum. Chemically pure, 1/64" dia. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used as connections to electrodes.

Apparatus

Apparatus used in the experiments with aluminum and sodium acetylacetonates was as follows:

Battery, Storage. Delco, Model 1724AN, 24-volt, 17 amp-hr at 5 hour rate. Manufactured by Delco-Remy Div., General Motors Corp., Anderson, Ind. Used as direct-current source.

Beaker. Griffin, with spout, pyrex glass, 150-ml. Obtained from Eimer and Amend, New York 14, N. Y. Used as conductivity cell and in preparations of compounds.

Beaker. Griffin, with spout, pyrex glass, 250-ml. Obtained from Eimer and Amend, New York 14, N. Y. Used in preparation of compounds and analysis of the aluminum acetylacetonate.

Crucible, Coor. Porcelain, size 0, 17-ml capacity. Obtained from Eimer and Amend, New York 14, N. Y. Used in analysis of sodium acetylacetonate.

Crucible, Coor. Porcelain, size 2, 50-ml capacity. Obtained from Eimer and Amend, New York 14, N. Y. Used in analysis of aluminum acetylacetonate.

Desiccator. Diameter 200 mm. Obtained from E. H. Sargent and Co., Chicago, Ill. Used in analysis work.

Funnel, Buechner. Capacity 150-ml. Obtained from Eimer and Amend, New York 14, N. Y. Used for filtering with suction.



Heater, Autemp. Volts A.C., 115. Obtained from Eimer and Amend, New York 14, N. Y. Used to heat water and oil baths.

Milliammeter. Direct current, 0-250 ma, U.S.N. type CAY-22065. Manufactured by Westinghouse Electric Co., Pittsburgh, Pa. Used to measure cell current.

Oven, Electric. Model OV-8, Ser. No. 8-270, 115 volts, 5 amp. Obtained from Modern Electric Laboratory, Chicago, Ill. Used for drying equipment and compounds.

Rheostat. Rex, No. 9-526-5F, 112-ohm, 2 amp, 16" long. Manufactured by Rex Rheostat Co., Baldwin, L. I., N. Y. Used to vary voltage.

Test Tubes. Pyrex, 150-mm long, 16 mm O.D. Obtained from Eimer and Amend, New York 14, N. Y. Used in solubility tests with the aluminum and sodium acetylacetonates.

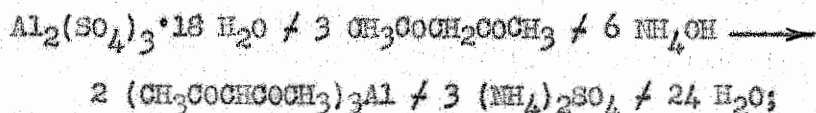
Thermometer. Mercury in glass, nitrogen filled, -5 to 360 °C. Obtained from Eimer and Amend, New York 14, N. Y. Used to indicate temperature of bath for determining melting point of aluminum acetylacetonate.

Voltmeter. Multiple-range, Model No. 489, No. 62580. Manufactured by Weston Electrical Instrument Corp., Newark, N. J. Used to measure cell voltage.

Method of Procedure

Aluminum acetylacetonate and sodium acetylacetonate were prepared according to the methods described by Young<sup>(58)</sup> and Marchi,<sup>(23)</sup> respectively. The quantities of the reactants used were calculated according to the reactions:

1. For aluminum acetylacetonate,



2. For sodium acetylacetonate,



Preparation of Aluminum Acetylacetonate. Six grams of aluminum sulfate were dissolved in 60 milliliters of water contained in a 250-milliliter beaker. To this solution, 2.71 grams of acetylacetonone were added and the mixture neutralized by adding six normal ammonium hydroxide dropwise; litmus paper was used as an indicator. A precipitate formed; it was filtered with suction, washed with distilled water, and dried in an oven at 100 °C. A yield of 2.89 grams of crude mixture was obtained as compared to a theoretical yield of 5.84 grams of aluminum acetylacetonate, or an actual yield of 50.5 per cent. The crude product was bottled for later use in the preparation of electrolytes after a sample was analyzed to determine its composition.

Analysis of the Crude Aluminum Acetylacetonate. A sample of 1.3020 grams of crude aluminum acetylacetonate was analyzed to determine

approximate composition. Preliminary solubility tests were made with the impure aluminum acetylacetonate and benzene was the only organic solvent, of those tested, which would dissolve the compound to any appreciable extent. The analysis was based on the assumption that the impure aluminum acetylacetonate probably contained unreacted aluminum sulfate, aluminum hydroxide, and aluminum acetylacetonate. The sample to be tested was weighed into a 250-milliliter beaker and about 200 milliliters of hot distilled water was added to dissolve the aluminum sulfate. The mixture was filtered and the solid portion put aside for further treatment. To the filtrate, one drop of phenolphthalein indicator was added as a check to insure that the solution was acid. A five per cent solution of barium chloride was added dropwise, with stirring, to the filtrate which had been heated to boiling. A total of nine milliliters of barium chloride was added to precipitate all of the barium sulfate. This mixture was heated to about 65 °C for 12 hours, with occasional addition of distilled water, to coagulate the barium sulfate. The solution was filtered through quantitative filter paper and washed with hot distilled water to dissolve all of the barium chloride. The filter paper was folded and heated slowly in a weighed crucible until the paper became white ash. The crucible was covered and heated at full flame for 15 minutes, allowed to cool, and then weighed. This weight of barium sulfate was converted, by calculations, to the equivalent of aluminum sulfate,  $Al_2(SO_4)_3$ .

The solid portion, remaining from the first filtration, was washed from the filter paper into a 250-milliliter beaker with 200 milliliters of benzene. After stirring to dissolve the aluminum acetylacetonate component, the aluminum hydroxide was separated by filtering on quantitative filter paper. The filter paper was folded, placed in a weighed crucible and ignited for two hours to oxidize the aluminum hydroxide to aluminum oxide. The crucible was cooled and weighed, and the weight of aluminum oxide converted by calculations, to the equivalent of aluminum hydroxide,  $\text{Al}(\text{OH})_3$ .

The benzene filtrate containing aluminum acetylacetonate was heated at about  $70^\circ\text{C}$  to evaporate all but 3 to 4 milliliters of solution. Upon standing, the remaining benzene evaporated leaving crystals of purified aluminum acetylacetonate. These crystals were weighed, crushed and used for the determination of the melting point.

A melting point tube was made from soft glass tubing, filled with the purified and powdered aluminum acetylacetonate, and attached to a thermometer so that the compound in the tube was adjacent to the bulb of the thermometer. The tube and thermometer were immersed to a depth of about one inch in a bath of white paraffin oil contained in a 250-milliliter beaker. The oil was heated rapidly, on a hotplate, to about  $150^\circ\text{C}$  and then slowly, at 1 to  $2^\circ\text{C}$  per minute, until the purified aluminum acetylacetonate began to melt.

Preparation of Sodium Acetylacetonate. Sodium etholate was prepared by reacting 1.62 grams of fine cut sodium with 29.6

milliliters of ethyl alcohol in a 150-milliliter beaker. Six grams of acetylacetone were added to the sodium etholate, with stirring, to precipitate sodium acetylacetonate. The product was filtered with suction and the filtrate treated with petroleum ether to precipitate the remaining sodium acetylacetonate. This additional amount was filtered, added to the other product, and dried in an oven at 90 °C. A yield of 3.61 grams of sodium acetylacetonate was obtained as compared to a theoretical yield of 7.32 grams, or an actual yield of 49.3 per cent. The product was bottled for later use in the preparation of electrolytes.

Analysis of the Sodium Acetylacetonate. The sodium acetylacetonate was analyzed for its sodium content by determination as sodium sulfate. One-half gram of the sodium acetylacetonate was weighed in a crucible which had been ignited to a constant weight. The contents of the crucible were ignited over a bunsen burner flame; the crucible was allowed to cool several times and a drop or two of concentrated nitric acid added to the contents, after cooling, to aid in the oxidation to sodium carbonate. Ignition was continued until the solid was completely white. Concentrated sulfuric acid was added to the sodium carbonate to convert it to sodium sulfate and ignition continued until the contents were dry; after cooling in a desiccator, the crucible and sodium sulfate were weighed. Ignition, cooling, and weighing were repeated until constant weight was attained.

The weights of sodium in the sodium acetylacetonate and in the sodium sulfate were calculated and compared.

Solubility Tests for Purified Aluminum and Sodium Acetylacetonates.

The solubility of each compound was tested by adding approximately 0.01 gram samples to five milliliters of each solvent contained in a separate test tube. The test tube was stoppered, shaken intermittently for about ten minutes and the result observed. The following seven solvents were tested; benzene, toluene, absolute alcohol, dimethyl glycol monobutyl ether, ethyl phosphate, formamide and ethyl bromide. After tests conducted at 25 °C, each test tube and contents, except for that containing the ethyl bromide, were warmed by partial immersion in a water-bath. The first three solvents were warmed to about 60 °C and the next three were warmed to about 95 °C. After warming, they were again stoppered, shaken for about ten minutes and the results observed.

Quantitative solubility tests for the purified aluminum and the sodium acetylacetonates were performed using ten milliliters of each solvent contained in separate test tubes. Weighed amounts of the acetylacetonates were tested, as before, at 25 °C.

Miscibility tests were performed at 25 °C with the following combinations, using two milliliters of each solution; crude aluminum acetylacetonate in benzene with sodium acetylacetonate in ethyl alcohol at concentrations of 10 and 20 grams per liter, respectively; crude aluminum acetylacetonate in toluene with sodium acetylacetonate in ethyl alcohol at concentrations of 10 and 20 grams per liter,

respectively; crude aluminum acetylacetonate in benzene with sodium acetylacetonate in ethyl phosphate at concentrations of 10 and 20 grams per liter, respectively; crude aluminum acetylacetonate in formamide with sodium acetylacetonate in dimethyl glycol monobutyl ether at concentrations of 1 and 40 grams per liter, respectively; crude aluminum acetylacetonate in toluene with sodium acetylacetonate in dimethyl glycol monobutyl ether at concentrations of 10 and 40 grams per liter, respectively; and crude aluminum acetylacetonate in toluene with sodium acetylacetonate in formamide at concentrations of 10 and 40 grams per liter, respectively.

Conductivity Tests Using Solutions of Aluminum and Sodium Acetylacetonates. The conductivities of four systems were tested using the circuit shown in Figure 1, page 69 and cell potentials of 10 to 30 volts. Platinum electrodes and the combination of a copper cathode and aluminum anode were used in these tests; all electrodes measured approximately 2.5 x 2.5 centimeters and were spaced one-half inch apart. The systems tested were; 0.3 gram of crude aluminum acetylacetonate in 43.9 grams of benzene; 0.3 gram of crude aluminum acetylacetonate in 43.9 grams of benzene and 0.4 gram of sodium acetylacetonate in 9.2 grams of dimethyl glycol monobutyl ether; 0.2 gram of crude aluminum acetylacetonate in 43.9 grams of benzene and 0.2 gram of sodium acetylacetonate in 7.9 grams of absolute alcohol; and 0.3 gram of crude aluminum acetylacetonate in 43.9 grams of benzene and 0.3 gram of sodium acetylacetonate in 21.3 grams of ethyl phosphate.

Data and Results

Data and results of the solubility, miscibility and conductivity tests with the acetylacetonates of aluminum and sodium are given in Tables VII, VIII, and IX.

Analysis of the crude aluminum acetylacetonate indicated a composition of 4.53 per cent aluminum sulfate, 46.90 per cent aluminum hydroxide, 43.20 per cent purified aluminum acetylacetonate, and about 5.47 per cent water, by difference. The percentage of aluminum sulfate, contained in 1.3020 grams of the crude aluminum acetylacetonate, was calculated from 0.1206 gram of barium sulfate separated during the analysis;

$$\frac{\text{Molecular weight aluminum sulfate}}{3 \times \text{Molecular weight barium sulfate}} \times \text{Weight barium sulfate, grams} = \text{grams aluminum sulfate}$$

$$\frac{342.12}{3 \times 233.44} \times 0.1206 = 0.059 \text{ gram aluminum sulfate}$$

$$\frac{\text{Weight aluminum sulfate, grams}}{\text{Weight crude sample, grams}} \times 100 = \text{per cent aluminum sulfate}$$

$$\frac{0.059}{1.3020} \times 100 = 4.53 \text{ per cent aluminum sulfate.}$$

The percentage of aluminum hydroxide, in the same 1.3020 grams of crude aluminum acetylacetonate, was calculated from 0.3989 gram of aluminum oxide obtained from the ignition of aluminum hydroxide which was separated during the analysis;



TABLE VII  
Solubility of the Acetylacetonates of Aluminum and Sodium in  
Certain Organic Solvents

Solvent	Temp., °C	Al(O <sub>2</sub> C <sub>5</sub> H <sub>7</sub> ) <sub>3</sub> , gm/100 ml	Temp., °C	Al(O <sub>2</sub> C <sub>5</sub> H <sub>7</sub> ) <sub>3</sub> , gm/100 ml	Temp., °C	NaO <sub>2</sub> C <sub>5</sub> H <sub>7</sub> , gm/100 ml	Temp., °C	NaO <sub>2</sub> C <sub>5</sub> H <sub>7</sub> , gm/100 ml
Benzene	25	> 11	60	< 0.1	25	< 0.01	60	< 0.01
Toluene	25	> 11	60	< 0.1	25	< 0.01	60	< 0.01
Absolute alcohol	25	< 0.01	60	< 0.01	25	2	—	—
Dimethyl glycol nonobutyl ether	25	< 0.1	95	< 0.1	25	4	—	—
Ethyl phosphate	25	< 0.01	95	< 0.1	25	2	—	—
Formamide	25	< 0.1	95	< 0.1	25	4	—	—
Ethyl bromide	25	< 0.01	—	—	25	< 0.01	—	—

Al(O<sub>2</sub>C<sub>5</sub>H<sub>7</sub>)<sub>3</sub> = aluminum acetylacetonate

NaO<sub>2</sub>C<sub>5</sub>H<sub>7</sub> = sodium acetylacetonate

TABLE VIII

Miscibility of Organic Solutions of the  
Acetylacetonates of Aluminum and Sodium at 25 °C

Solutions, 2 ml each	Formulas	Concentration,		Miscibility
		gm/l		
Impure aluminum acetylacetonate in benzene Sodium acetylacetonate in ethyl alcohol	Mixture <sup>a</sup> -C <sub>6</sub> H <sub>6</sub> Na <sub>2</sub> O <sub>5</sub> H <sub>7</sub> -C <sub>2</sub> H <sub>5</sub> OH	10		Miscible
		20		
Impure aluminum acetylacetonate in toluene Sodium acetylacetonate in ethyl alcohol	Mixture -C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> Na <sub>2</sub> O <sub>5</sub> H <sub>7</sub> -C <sub>2</sub> H <sub>5</sub> OH	10		Miscible
		20		
Impure aluminum acetylacetonate in benzene Sodium acetylacetonate in ethyl phosphate	Mixture -C <sub>6</sub> H <sub>6</sub> Na <sub>2</sub> O <sub>5</sub> H <sub>7</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> PO <sub>4</sub>	10		Miscible
		20		
Impure aluminum acetylacetonate in formamide Sodium acetylacetonate in dimethyl glycol monobutyl ether	Mixture -HCONH <sub>2</sub> Na <sub>2</sub> O <sub>5</sub> H <sub>7</sub> -CH <sub>2</sub> CHOH CH <sub>3</sub> CHOC <sub>4</sub> H <sub>9</sub>	1		Miscible
		40		
Impure aluminum acetylacetonate in toluene Sodium acetylacetonate in dimethyl glycol monobutyl ether	Mixture -C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> Na <sub>2</sub> O <sub>5</sub> H <sub>7</sub> -CH <sub>2</sub> CHOH CH <sub>3</sub> CHOC <sub>4</sub> H <sub>9</sub>	10		Miscible
		40		
Impure aluminum acetylacetonate in toluene Sodium acetylacetonate in formamide	Mixture -C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> NaO C H -HCONH <sub>2</sub>	10		Immiscible
		40		

<sup>a</sup> Composition of mixture: 4.53 % aluminum sulfate  
46.60 % aluminum hydroxide  
43.20 % aluminum acetylacetonate  
5.47 % water (by difference)

TABLE IX

Conductivity in Solutions of the Acetylacetonates

of Aluminum and Sodium at 25 °C

Electrodes, 2.5 x 2.5 centimeters, one-half inch apart

Electrolyte	Formulas	Composition,		E.M.F., volts	Current, ma	Electrodes
		gm	gm			
Benzene Impure aluminum acetylacetonate	$C_6H_6$ <sup>a</sup> Mixture	43.9		10	0	Pt cathode Pt anode
		0.3		30	0	
Benzene Impure aluminum acetylacetonate Dimethyl glycol monobutyl ether	$C_6H_6$ Mixture $CH_3CHOH$	43.9		10	0	Pt cathode Pt anode
		0.3 9.2		30	0	
Sodium acetylacetonate	$CH_3CHOC_4H_9$ $NaO_2C_5H_7$	0.4				
Benzene Impure aluminum acetylacetonate Absolute alcohol Sodium acetylacetonate	$C_6H_6$ Mixture $C_2H_5OH$ $NaO_2C_5H_7$	43.9		10	0	Cu cathode Al anode
		0.2		30	0	
		7.9 0.2				
Benzene Impure aluminum acetylacetonate Ethyl phosphate Sodium acetylacetonate	$C_6H_6$ Mixture $(C_2H_5)_3PO_4$ $NaO_2C_5H_7$	43.9		28	0	Cu cathode Al anode
		0.3 21.3 0.3				

<sup>a</sup> Composition of mixture: 4.53 % aluminum sulfate  
46.80 % aluminum hydroxide  
43.20 % aluminum acetylacetonate  
5.47 % water (by difference)

$$\frac{2 \times \text{Molecular weight aluminum hydroxide} \times \text{Weight aluminum oxide, grams}}{\text{Molecular weight aluminum oxide}}$$

= grams aluminum hydroxide

$$\frac{2 \times 78 \times 0.3989}{102} = 0.61 \text{ gram aluminum hydroxide}$$

$$\frac{\text{Weight aluminum hydroxide, grams} \times 100}{\text{Weight crude sample, grams}} = \text{per cent aluminum hydroxide}$$

$$\frac{0.61}{1.3020} \times 100 = 46.8 \text{ per cent aluminum hydroxide}$$

The percentage of purified aluminum acetylacetonate, in the 1.3020 grams of crude sample, was calculated from 0.5627 gram of pure crystals which were separated during the analysis:

$$\frac{\text{Weight purified aluminum acetylacetonate, grams} \times 100}{\text{Weight crude sample, grams}}$$

= per cent purified aluminum acetylacetonate

$$\frac{0.5627}{1.3020} \times 100 = 43.2 \text{ per cent purified aluminum acetylacetonate.}$$

The percentage of water, in the 1.3020 grams of crude sample, was calculated to be 5.47 per cent, by difference.

The purified aluminum acetylacetonate had a sharp melting point of 192.5 °C and a solubility, at 25 °C, of at least 11 grams per 100 milliliters of benzene.

From the analysis of 0.500 gram of sodium acetylacetonate, 0.2615 gram of sodium sulfate containing 0.0941 gram of sodium was obtained. This weight of sodium was calculated to be 18.8 per cent of the total weight of original sample. The theoretical amount of sodium in 0.500 gram of sodium acetylacetonate is 18.8 per cent.

### Discussion of Results

The investigation of the solubility of the acetylacetonates of aluminum and sodium was conducted with several types of solvents including hydrocarbons, alcohols, ethers, esters, amines, and halides. The results of these tests, given in Table VII, page , indicated that the salt-like sodium compound is most soluble in the polar-type solvents, such as formamide. The solubility in formamide was about four grams per 100 milliliters at 25 °C. The purified aluminum acetylacetonate was more soluble in the nonpolar solvents, such as benzene and toluene, to the extent of at least 11 grams per 100 milliliters at 25 °C. The purified aluminum acetylacetonate, at 25 °C, showed a solubility of less than 0.1 gram per 100 milliliters in an alcohol, ether, amine, and ester. Since mutual solvents were not discovered, tests were conducted to determine the miscibility of the solvents which contained the aluminum and sodium acetylacetonates. The benzene and toluene solutions of aluminum acetylacetonate were miscible, and formed clear single phase mixtures with solutions of sodium acetylacetonate in ethyl alcohol, ethyl phosphate, and dimethyl glycol monobutyl ether. Crude aluminum acetylacetonate in toluene was immiscible with sodium acetylacetonate dissolved in formamide and a precipitate formed on mixing the two solutions.

Although the analysis showed the crude aluminum acetylacetonate to be extremely impure, it could not be expected that current would be

carried by the purified crystals of aluminum acetylacetonate. Marchi<sup>(23)</sup> stated that the chelate compound formed by aluminum and acetylacetone is a nonelectrolyte, since the coordination number of aluminum is six, or two times that of its oxidation state valence of three. Complex cations are formed only when the coordination number is less than twice the value of the oxidation state.

The sharp melting point of 192.5 °C, obtained for the crystals of purified aluminum acetylacetonate which were separated during analysis of the impure compound, was an indication of purity. Young<sup>(58)</sup> reported a melting point of 194.5 °C for pure aluminum acetylacetonate.

Analysis of the 0.500 gram of sodium acetylacetonate showed that the actual sodium content of the sodium sulfate was within 0.1 per cent of the theoretical amount of sodium in the sample of sodium acetylacetonate.

None of the systems tested for conductivity, at a potential of 10 to 30 volts, gave any indication on a milliammeter that current was passing through the baths. The absence of any current-carrying ions made it impractical to use the acetylacetonates of aluminum and sodium as a mixed electrolyte for electrodeposition of aluminum.

### Limitations

The limitations for the solubility, miscibility and conductivity tests with the acetylacetonates of aluminum and sodium were as follows:

Solubility tests were made with the acetylacetonates of aluminum and sodium using ten milliliters of each solvent for each test at temperatures of 25, 60 and 95 °C. The solvents tested were: benzene, toluene, absolute alcohol, dimethyl glycol monobutyl ether, ethyl phosphate, formamide and ethyl bromide.

Miscibility tests, at 26 °C, were performed by mixing a two-milliliter solution of crude aluminum acetylacetonate in either benzene or toluene with a two-milliliter solution of sodium acetylacetonate in ethyl alcohol, ethyl phosphate, dimethyl glycol monobutyl ether, or formamide in a test tube.

Because of the similarity of benzene and toluene, only benzene solutions of crude aluminum acetylacetonate were used in the conductivity tests at 26 °C. To three solutions of 0.2 to 0.3 gram of crude aluminum acetylacetonate in 50 milliliters of benzene were added 0.4, 0.2, and 0.3 gram of sodium acetylacetonate dissolved in ten milliliters of dimethyl glycol monobutyl ether, ten milliliters of absolute alcohol and 20 milliliters of ethyl phosphate, respectively. Both platinum electrodes and the combination of a copper cathode and aluminum anode were used, in separate experiments, at 10 to 30 volts potential.

### Conclusions

From the results obtained in determinations of composition, solubility, miscibility and conductivity using the acetylacetonates of aluminum and sodium, it can be concluded that:

1. The solubility of purified aluminum acetylacetonate in benzene and toluene is at least 11 grams per 100 milliliters at 25 °C.

2. Purified aluminum acetylacetonate is practically insoluble, at 25 °C, in absolute alcohol, dimethyl glycol monobutyl ether, ethyl phosphate, formamide and ethyl bromide. The solubility is less than 0.1 gram per 100 milliliters.

3. The solubility of sodium acetylacetonate in absolute alcohol and ethyl phosphate is about two grams per 100 milliliters at 25 °C.

4. The solubility of sodium acetylacetonate in dimethyl glycol monobutyl ether and formamide is about four grams per 100 milliliters at 25 °C.

5. The solubility of sodium acetylacetonate in benzene, toluene, and ethyl bromide, at 25 °C, is less than 0.01 gram per 100 milliliters.

6. No current passes through the following solutions when a potential of 10 to 30 volts is applied to electrodes which measure 2.5 centimeters square and one-half inch apart; 0.3 gram of crude aluminum acetylacetonate in 43.9 grams of benzene, employing platinum electrodes; 0.3 gram of crude aluminum acetylacetonate in 43.9 grams of benzene and 0.4 gram of sodium acetylacetonate in 9.2 grams of



dimethyl glycol monobutyl ether, employing platinum electrodes; 0.2 gram of crude aluminum acetylacetonate in 43.9 grams of benzene and 0.2 gram of sodium acetylacetonate in 7.9 grams of absolute alcohol, employing platinum electrodes or a combination of a copper cathode and aluminum anode; and a solution of 0.3 gram of crude aluminum acetylacetonate in 43.9 grams of benzene and 0.3 gram of sodium acetylacetonate in 21.3 grams of ethyl phosphate, employing a copper cathode and aluminum anode.

7. The composition of the crude aluminum acetylacetonate was found to be approximately 4.53 per cent aluminum sulfate, 46.80 per cent aluminum hydroxide, 43.20 per cent aluminum acetylacetonate, and about 5.47 per cent water, by difference.

8. It was found that the purified aluminum acetylacetonate had a sharp melting point of  $192.5^{\circ}\text{C}$ , as compared to  $194.5^{\circ}\text{C}$  reported by Young. (58)

9. The composition of the sodium acetylacetonate was found to be  $100 \pm 0.1$  per cent sodium acetylacetonate.

10. The successful deposition of aluminum from solutions of aluminum acetylacetonate is improbable because of the limited solubility of the salt in typical organic solvents, other than benzene and toluene, and the lack of conductivity of its solutions in these solvents.

#### IV. DISCUSSION

Since each of the systems tested has been discussed individually, this section will be devoted to a general, qualitative review of the problem of electrodepositing aluminum.

##### Interest in Electroplated Aluminum

For over 100 years, men have sought a satisfactory method of electroplating aluminum on base metals, such as iron, steel and copper. Several reasons may be given for this great interest in aluminum coatings. Aluminum is one of the most abundant metals in the world and the cost of obtaining it has now been reduced so that it can compete with other materials of construction, as well as the metals used in electroplating. Aluminum is resistant to corrosion by many chemicals and to oxidation by the atmosphere. At high temperatures, aluminum diffuses into base metals to form alloys which are highly resistant to scaling from hot atmospheres. This ability to resist the effect of heat is an important consideration in the design of rocket and jet engine equipment.

##### Difficulties in Electroplating of Aluminum

A few of the reasons why no practical method has been found for the electrodeposition of aluminum are presented.

Aqueous systems or any system containing traces of moisture cannot be used; the electromotive force required to electrodeposit aluminum from a solution is greater than the decomposition potential of water. This means that any water present in an electroplating bath would be decomposed during operation of the cell, hydrogen gas would be evolved at the cathode before the aluminum deposition would start.

Another reason, which is closely related to the previous difficulty, is that some aluminum compounds, such as the halides and thiocyanate, tend to hydrolyze even in the presence of atmospheric moisture. Hydrolysis results in contamination of the bath with moisture and again, decomposition of the water occurs and hydrogen is liberated at the cathode. If equipment and atmospheric conditions could be properly designed to completely exclude moisture from a commercial process, the cost of operation and maintenance would probably be prohibitive as compared to other electroplating methods. However, the advantages of aluminum coatings would offset this additional expense to some extent.

A third difficulty which has been encountered is the great affinity which aluminum has for oxygen. Any dissolved or liberated oxygen in an electroplating bath, where an aluminum anode is present, tends to form a nonconducting layer of aluminum oxide on the anode. This layer increases the cell resistance and causes the current to decrease.

Types of Systems for Electrodeposition of Aluminum

Many of the methods tested for electrodeposition of aluminum have not been successful. The types of systems which have been investigated by others include aqueous solutions, nonaqueous inorganic solutions, fused salts mixtures and nonaqueous organic solutions.

Much of the work with aqueous solutions, nonaqueous inorganic solutions and fused salts mixtures has been with aluminum halides, and especially aluminum chloride. Aluminum chloride is a strong peptizing agent for aluminum oxide and, when aluminum is electrodeposited from a bath containing the halide, the aluminum chloride is occluded in the coating where it peptizes the oxide film which is formed on the aluminum. This reaction reduces the thickness of the deposit gradually until the base metal becomes subject to corrosion. When fused salts mixtures are used, the resulting deposit of aluminum is usually dendritic in nature as noted by Wade. (54)

Many investigations have been conducted with nonaqueous organic solutions. As with the other types of systems, considerable work has been carried out with aluminum halides as solutes. Many organic solvents have been employed in these studies; some of the types of solvents include: alkyl halides, aromatic hydrocarbons and their nitroderivatives, heterocyclic compounds, alcohols, and ketones.

Some systems have been discovered in which complex ions of aluminum not only furnish aluminum ions for electrodeposition but also

furnish those which carry the current. Blue and Mathers<sup>(3)</sup> deposited aluminum from a bath of this type containing aluminum bromide, ethyl bromide and benzene. Another bath, discovered by Wier,<sup>(66)</sup> also gave deposits of aluminum from complexes resulting from ionization of aluminum chloride in ethyl pyridinium bromide.

#### Systems of Aluminum Organic Salts in Organic Solvents

This research project has been directed toward a study of aluminum organic compounds in organic solvents. The requirements for a system to be used for the electrodeposition of aluminum are: a compound which will supply the aluminum ions to be electrodeposited; a compound to furnish the current-carrying ions, if necessary; and a solvent, or solvents, which will dissolve the other constituents of the system.

#### Discussion of Correlated Results

Four types of compounds were investigated in these studies: aluminum halides, aluminum salts of fatty acids, aluminum salts of phenolic compounds, and an aluminum salt of a diketone. Several types of solvents employed included: hydrocarbons, alcohols, ethers, amines, aldehydes, and esters. Various additives were tested but the principle ones were alkali salts and alkaline earth salts.

Work with the system aluminum bromide-ethyl bromide-benzene was performed for the purpose of observing some of the factors which contribute to the electrodeposition of aluminum on a base metal.

Although this bath contains an aluminum halide, it is not particularly sensitive to moisture because of the presence of a benzene layer above the electrolyte layer. The physical characteristics of an aluminum deposit obtained from this bath are closely related to the current density used during electrolysis. This system is quite unstable if not electrolyzed within a few hours of its preparation; vaporization of bromine from the bath causes a change which makes it inactive. However, if the system is electrolyzed soon after its preparation, it becomes stable and electrolysis can be interrupted without any serious effects on the bath.

The fact that an aluminum electrodeposit of fairly fine crystals and good adherence can be obtained from an organic system suggests that, eventually, an organic electrolyte may be found which will be practical for the commercial electrodeposition of aluminum.

In searching for a system it must be remembered that there are two possible sources of the aluminum ions to be deposited. One of the possibilities is the existence of the aluminum ion in the original electrolyte as the currentcarrier. Another possibility is that the ions may be supplied from the corrosion of an aluminum anode; these ions may replace those deposited from the electrolyte or they may be the depositing ions, themselves. With this in mind, several aluminum organic compounds were chosen for the investigation.

On the basis of the work with aluminum stearate, aluminum basic acetate, aluminum phenoxide, aluminum o-nitrophenoxide, and aluminum acetylacetonate, it is apparent that one of the greatest problems

confronting an investigator is that of finding solvents which will dissolve the aluminum organic compounds. Equally difficult is the problem of obtaining and improving the conductivity of organic solutions. In the event that a suitable solvent is found for a particular solute, other problems, such as the evolution of gases at the electrodes and the occurrence of complex organic reactions during electrolysis, may be insurmountable.

#### Limitations

The limitations of the study of each group of systems have been given in their respective sections of the thesis. Briefly, the overall limitations of the work are given here.

The following systems were partially investigated, that is, the whole range of compositions was not studied. The systems were: aluminum bromide-ethyl bromide-benzene, aluminum bromide-butyl bromide-hexane, aluminum bromide-butyl bromide-iso-octane, aluminum stearate-ethyl phosphate-addition compounds, basic aluminum acetate-formamide, basic aluminum acetate-formamide-ammonia gas, aluminum o-nitrophenoxide-sodium o-nitrophenoxide-methyl alcohol, aluminum phenoxide-sodium o-nitrophenoxide-ethyl phosphate, aluminum phenoxide-sodium phenoxide-ethyl phosphate, aluminum acetylacetonate-benzene, aluminum acetylacetonate-benzene-sodium acetylacetonate-dimethyl glycol monobutyl ether, aluminum acetylacetonate-benzene-sodium acetylacetonate-absolute alcohol, aluminum acetylacetonate-benzene-sodium acetylacetonate-ethyl phosphate.

The electromotive force applied was limited to that believed to be practical, and ranged from 0.6 to 55 volts.

Platinum electrodes, aluminum anodes, and copper cathodes were used in the conductivity and electrolysis tests; they measured 2.2 to 2.5 centimeters wide and 2.5 to 3.0 centimeters long. These tests were carried out with electrodes spaced either one-half or one inch apart.

Solubility tests were performed at 20 to 96 °C for the compounds aluminum stearate, basic aluminum acetate, aluminum phenoxide and o-nitrophenoxide, sodium phenoxide and o-nitrophenoxide, aluminum acetylacetonate and sodium acetylacetonate.

Conductivity tests for the various systems were performed at 24 to 127 °C.

All electrolyses were carried out at 23 to 30 °C, and the times ranged from 0.25 to 24.25 hours.

#### Recommendations

It is recommended that further investigation of a variety of aluminum organic compounds be made with particular emphasis on matching the polarity of the solutes and solvents. There is an attraction<sup>(63)</sup> between groups of similar polarity; this accounts for the solubility of polar solutes in polar solvents and of non-polar solutes in nonpolar solvents. An example of the latter case is the solubility of the nonpolar aluminum acetylacetonate in the



nonpolar solvent benzene. If a solute contains both polar and nonpolar groups, it is possible to use mixed solvents, one polar and one nonpolar, in an optimum ratio to give maximum solubility.

It is recommended that further investigation be made of complex compounds similar to the aluminum bromide complex, <sup>(3)</sup>  $\text{AlBr}_4^-$ . Aluminum cyanate may react with ethyl cyanate to form the complex ion  $\text{Al}(\text{CN})_4^-$ , or aluminum fluoborate may react with ethyl fluoborate to form the complex ion  $\text{Al}(\text{BF}_4)_4^-$ . Another possibility may be the reaction of an alkali metal ethyl, such as sodium ethyl, with aluminum triethyl to form the complex ion  $\text{Al}(\text{C}_2\text{H}_5)_4^-$ .

## V. CONCLUSIONS

From the exploratory investigation of organic systems using aluminum bromide, aluminum stearate, aluminum basic acetate, aluminum phenoxide and o-nitrophenoxide, and aluminum acetylacetonate, the following general conclusions can be drawn:

1. An aluminum deposit can be obtained from electrolysis, at 25 to 29 °C, of a bath containing 5.087 grams of aluminum foil, 110 milliliters of ethyl bromide and 70 milliliters of benzene, employing an aluminum anode and copper cathode and a current density of 0.379 to 0.758 amperes per square decimeter. Three disadvantages of this bath are: it requires care in preparation of the electrolyte and the disposal of evolved hydrogen bromide gas; it is sensitive to moisture; and the coatings obtained did not cover the cathode completely and uniformly.

2. Systems of aluminum stearate in ethyl phosphate do not appear to be practical for the electrodeposition of aluminum because of the low solubility of aluminum stearate in ethyl phosphate and the low conductivity of the baths.

3. It is unlikely that a system of basic aluminum acetate in formamide can be used for the electrodeposition of aluminum since gases are evolved at the aluminum anode and copper cathode and an organic reaction occurs during the passage of current with formation of an unidentified precipitate in the electrolyte.

4. It does not appear that systems of aluminum phenoxide and aluminum o-nitrophenoxide can be used practically for the electrodeposition of aluminum because of the complex organic reactions which occur upon electrolysis.

5. The successful deposition of aluminum from aluminum acetylacetonate solutions is improbable because of the limited solubility of the aluminum salt in many organic solvents and the lack of conductivity of these systems.

6. The evolution of gases at the electrodes and the occurrence of complex organic reactions, in many instances, complicates the problem of obtaining an electrodeposit of aluminum from organic systems.

## VI. SUMMARY

The purpose of this research was to make an exploratory investigation of organic solutions containing the compounds aluminum bromide, aluminum stearate, basic aluminum acetate, aluminum phenoxide, aluminum o-nitrophenoxide, and aluminum acetylacetonate to determine if these compounds will furnish aluminum ions for electrodeposition.

A review of the literature revealed that the ability of aluminum to resist corrosion by the atmosphere and many chemicals led to an extensive investigation of possible methods for electroplating aluminum on base metals.

All of the studies on the electrodeposition of aluminum may be classified into four systems: aqueous solutions, nonaqueous organic liquid solutions, nonaqueous inorganic liquid solutions, and fused salts mixtures. Aluminum halides, especially aluminum chloride and bromide, probably have been the most frequently used solutes. One of the disadvantages of using a system containing aluminum halides is that these compounds pick up moisture readily from the atmosphere, and electrolysis results in the decomposition of the water with evolution of hydrogen at the cathode instead of electrodepositing aluminum.

In the initial experiments, electrolyses were performed so that observations could be made of an aluminum deposit obtained from a

nonaqueous liquid organic system and the conditions for electro-deposition. Current densities of 0.379 to 0.9 amperes per square decimeter were employed with a bath containing 5.087 grams of aluminum foil, and 110 and 70 milliliters of ethyl bromide and benzene, respectively. The aluminum anode replenished the bath with aluminum which was electrodeposited on a copper cathode. Four deposits were obtained in these electrolyses but they indicated that this bath has poor throwing power and it is extremely sensitive to a change in current density.

The second series of experiments consisted of solubility tests with aluminum stearate in various organic solvents, and conductivity tests with the system aluminum stearate-ethyl phosphate-addition compounds. The addition of 0.4 gram of stearic acid and 0.6 gram of lithium stearate to a bath of 0.2 gram of aluminum stearate in 74.6 grams of ethyl phosphate resulted in the greatest increase in current obtained with any of the addition agents tested. Using platinum electrodes one inch apart, the current increased from 0 to 5.3 milliamperes at 50 volts potential. These experiments were discontinued because of the low solubility of aluminum stearate in typical organic solvents and insufficient current for practical use.

The third series of experiments consisted of solubility tests with basic aluminum acetate and electrolyses of the system basic aluminum acetate and formamide. Various types of organic solvents

were tested but only formamide dissolved the basic aluminum acetate. Electrolysis of a bath containing 2.5 grams of basic aluminum acetate and 79.1 grams of formamide for 11.33 hours resulted in the formation of an unidentified precipitate in the bath and around the aluminum anode and copper cathode. This work was discontinued since gases were evolved at both electrodes and the current decreased from 100 to 35 milliamperes during electrolysis.

In the fourth group of experiments, aluminum phenoxide, aluminum o-nitrophenoxide, sodium phenoxide, and sodium o-nitrophenoxide were prepared for use as mixed electrolytes. From the results of solubility tests with these compounds, the following systems were prepared and electrolyzed: 15 grams of aluminum o-nitrophenoxide, 1.5 grams of sodium o-nitrophenoxide, and 45 grams of methyl alcohol; 8 grams of aluminum phenoxide, 0.5 gram of sodium o-nitrophenoxide, and 106.1 grams of ethyl phosphate; 8 grams of aluminum phenoxide, 0.4 gram of sodium phenoxide, and 106.1 grams of ethyl phosphate. Using a combination of either a platinum anode and copper cathode or an aluminum anode and copper cathode, no aluminum was obtained in 1 to 6 hours of electrolysis at potentials of 8 to 50 volts. This work was discontinued because of evidence, in the form of heavy crust-like deposits on the electrodes, that the passage of current resulted in organic reactions.

The final group of experiments consisted of the preparation of the acetylacetonates of aluminum and sodium for use as a mixed

electrolyte, solubility tests in various types of organic solvents, and conductivity tests with several solutions. Conductivity tests at 10 to 30 volts potential across an aluminum anode and copper cathode, spaced one-half inch apart, showed no passage of current through three baths; each of the three solutions contained 0.2 to 0.3 gram of aluminum acetylacetonate in 43.9 grams of benzene and 0.4, 0.2, or 0.3 gram of sodium acetylacetonate in 9.2 grams of dimethyl glycol monobutyl ether, 7.9 grams of absolute alcohol, or 21.3 grams of ethyl phosphate, respectively. Since no current was observed in these tests, work with the acetylacetonates of aluminum and sodium was discontinued.

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VIII. ACKNOWLEDGMENTS

The author expresses his appreciation to the Air Materiel Command for the research fellowship under which this work was carried out, and to Dr. N. F. Murphy for his counsel during the actual research and writing of the thesis.

Appreciation is expressed to Professor D. S. Davis for his editorial reading of the thesis, to other members of the faculty for their criticisms, to Mr. T. Y. Chao for his assistance, and to Mrs. S. L. Parker for her part in making this work possible.

IX. VITA



On October 19, 1917, the author of this thesis was born in Hudson, Massachusetts and named Stewart Lincoln Parker. From 1920 to 1940, he lived in Fitchburg, Massachusetts where he attended the public schools and was graduated from Fitchburg High School in 1935. He attended Worcester Boys' Trade School, Worcester, Massachusetts, and was graduated as a machinist in 1938.

Prior to his service with the United States Army Air Force in 1944, the writer worked as a machinist for the Foster Grant Company in Leominster, Massachusetts, the U. S. N. Torpedo Station in Newport, Rhode Island and the General Electric Company in Fitchburg, Massachusetts. During nine months of active service, Private Parker received basic training, four months of radio-mechanic training and a 10,000-mile tour of the United States. He was released from active

duty to work as a toolmaker for the National Advisory Committee for Aeronautics at Langley Field, Virginia and was recalled for discharge in October, 1945. After eleven months more at Langley Field, he enrolled as a college student in September, 1946.

Technical training of the author includes one year of general engineering at the St. Helena Extension of the College of William and Mary in Norfolk, Virginia and four years of chemical engineering at the Virginia Polytechnic Institute in Blacksburg, Virginia. He was graduated with a Bachelor of Science degree in June, 1950 and with a Master of Science degree in June, 1952.

His extra-curricula activities have included memberships in the Engineers' Club, Debating Club, Glee Club, Cave Club, Civilian Senate, Student Chapter of the American Institute of Chemical Engineers and Phi Lambda Upsilon. He is registered as a professional chemical engineer with the Commonwealth of Virginia.

On June 28, 1947, he married Elizabeth Heartwell of McKenney, Virginia.