EFFECT OF ADDITION AGENTS ON THE PROPERTIES OF ALUMINUM DEPOSITED FROM AN ALUMINUM CHLORIDE-SODIUM CHLORIDE MELT

by

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I. INTRODUCTION

The corrosion problem facing industry for centuries is very serious. Corrosion takes on many forms, some of which are beneficial, but most of which are a source of constant trouble. Many different methods have been used to inhibit or delay the corrosion of metals, but serious problems of importance still exist.

Corrosion of a metal may be delayed or inhibited by coating the metal with another that is not as susceptible to corrosive action, such as aluminum plating on steel. The process is essentially the passing of an electric current through an electrolytic bath of the salt of the metal to be deposited as the protective coating. A bar of aluminum is used as one electrode. The film thus deposited acts as a new surface and corrodes at a rate characteristic of its own physical properties.

Scientists from many countries have made many attempts to solve the problem of the electrodeposition of aluminum from various systems. The electrolytes investigated have included organic solutions, aqueous inorganic solutions, nonaqueous inorganic liquid solutions, and molten salt baths. Most of the research has been conducted with nonaqueous inorganic liquid solutions and molten salt baths. Aluminum halides have been utilized

with some success, but these baths absorb moisture from the air and aluminum deposits therefrom are very susceptible to corrosion.

The purpose of this investigation was to study the effect of addition agents on the electrodeposition of aluminum when added to the fused bath of aluminum chloride in sodium chloride.

II. LITERATURE REVIEW

Although aluminum has been known as a metal since about 1809, it did not achieve any significance until 1886[18]. 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 a fused salt bath containing aluminum chloride. 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, a brief account of some of the properties of aluminum electrodeposits, and the effects of addition agents on electrodeposits.

History of Aluminum

To trace the story of aluminum it is not necessary to go back very far, since aluminum is a recent development. 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 the uses for it[18].

Discovery of Aluminum. Aluminum was first recognized as a metal in the middle of the eighteenth century[18]. It was 1809, however, before an attempt to separate it from its oxide was made by Sir Humphrey Davy[15]. This attempt was made by passing an electric current from a voltaic pile through a fused bath of iron and aluminum oxide. The product was an alloy, from which aluminum could not be separated. Davy abandoned his study at this point, but he had contributed to the meager knowledge of the metal the important discovery that the aluminum oxide could be reduced.

Oersted[55] produced the first metallic aluminum in 1824 by gently heating potassium amalgam with aluminum chloride and then distilling off the mercury, leaving a small lump of aluminum metal under potassium chloride.

Wohler[80] repeated Oersted's experiment in 1827, but was unable to reproduce the results. By using metallic potassium instead of the amalgam, he produced aluminum as a metallic powder. In further experiments in 1844, Wohler produced enough aluminum metal to begin the study of its properties[81].

In 1854, Deville[16] improved on Wohler's method by substituting sodium for potassium. In the presence of sodium chloride, a double salt - $NaCl \cdot AlCl_3$ - was formed with the excess aluminum chloride. This salt acted as a flux, thus allowing the small particles of metal to coalesce. Deville set up the first plant for manufacturing aluminum in Nanterre, France, and produced about 60 pounds of the metal at about 27 dollars per pound. In 1866, Castner[10] developed a cheaper method of producing sodium which eventually led to the production of 500 pounds of aluminum per day at about four dollars per pound. In three years of operation, approximately 250,000 pounds of aluminum were produced by the Deville-Castner method.

Gurbau[28] patented a process in 1888 in which aluminum fluoride was employed as the source of aluminum and using sodium as the reducing agent. Pure granular aluminum fluoride was heated to 600 °C and dropped into molten sodium. The sodium fluoride produced in the reaction formed a slag under which the aluminum collected. He claimed that the aluminum that was produced was very pure and the sodium was used more efficiently.

Hall's and Heroult's Discovery. Charles Martin Hall and Paul L. T. Heroult, each working separately in the United States and France[18], respectively, discovered an electrolyte from which molten aluminum could be obtained.

Hall's Discovery. Hall[18] reasoned that it would be possible to electrolyze alumina in solution with a fused salt which would dissolved the alumina in substantial quantities. The extremely high melting point of pure alumina, 2050 °C, was too high for electrolysis. Hall found that cryolite, Na_3AlF_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. It is interesting to note that Hall's process will work because the specific gravity of molten cryolite at 1000 °C (2.09) is less than that of molten aluminum at the same temperature (2.29)[19]. This is an inversion of the densities at 20 °C, where that of cryolite is 2.90 and that of aluminum is 2.70.

Heroult's Discovery. Heroult[18] was granted a French patent on April 23, 1886, for electrolyzing alumina in a bath of cryolite. His success 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 Kilizni converted their alloy furnaces to the alumina-cryolite process and began to produce aluminum.

Present Production Methods. The modern method of producing aluminum[19], 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 an ore, bauxite[19]. Bauxite is primarily a hydrated aluminum oxide with impurities of iron oxide, silicon dioxide, and titanium oxide. On a percentage basis, bauxite comprises 50 to 60 per cent aluminum oxide, 25 to 32 per cent

chemically combined water, 2 to 14 per cent silicon dioxide, 2 to 10 per cent iron oxide, and 2 to 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 hammermills 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:

$$(Al(OH)_3 + NaOH = NaAlO_2 + H_2O.$$

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:

$$NaAlO_2 + 2\ H_2O = Al(OH)_3 + NaOH.$$

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

$$Al(OH)_3 + \text{heat} = Al_2O_3 + 3\ H_2O.$$

The Electrolytic Cell Construction. The cell used for the electrolytic production of aluminum[19] 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 cells are thirty feet long, eight feet wide, and one and one-half feet deep; the amperage for cells using multiple electrodes ranges between 8000 and 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 plate. 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 above. 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 buss-bars 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 Soderberg[71] about the year 1920. The electrode[19] 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[19] 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 1-1/2 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.

Electrolytic Refining of Aluminum. The aluminum produced by the Hall process is seldom less than 97 per cent pure. Hoopes[31] developed a process in 1921, for refining aluminum electrolytically to produce a metal that is 99.99 per cent pure. The aluminum to be refined is alloyed with copper and silicon and rests in the bottom of a cell under a layer of a fused mixture of cryolite, aluminum fluoride, and barium fluorides, nearly saturated with alumina at a temperature of 900 to 1100 °C. A thick crust, which is rich in alumina, solidifies on the walls of the cell, insulating it electrically and thermally. The aluminum cathode floats on this bath, and contact is made by graphite electrodes. The aluminum is covered with a frozen crust of the bath, except where the electrodes dip into it. The cells operate at from five to seven volts and about 20,000 amperes.

Corrosion of Aluminum

Aluminum has many applications where metals and metallic coating 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[52]. 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 alumina 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-bearing atmosphere[52]. The oxide film is estimated to be approximately 5×10^{-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[72]. 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[52]. 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[47] 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[4] used in alloying steel to reduce the rate of scaling. Formation of the oxide retards further attack on the underlying steel. Approximately ten per cent aluminum is required as an alloying element with steel and this amount tends to cause embrittlement[70]. 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 by many chemicals[60]. However, 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[52]. It is desirable that corrosion be of the non-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 require the presence of at least two areas of different potentials connected by an electrolyte. Water, contaminated with chlorides is generally the electrolyte. The areas of different potentials

can be dissimilar metals or alloys, concentrations of constituents of the solution, inclusions, or similar nonhomogeneous 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 predominate in large extruded sections.

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[22], 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[52] and of some of the inhibitors[21] 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

solution is 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, 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 to practically all of the heavy metals, will replace them from their compounds. The replaced metals will be deposited upon the aluminum surfaces 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[21]. 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 satisfactory inhibitors for aluminum in sulfuric acid are known.

No satisfactory inhibitors for sodium hydroxide or potassium hydroxide are available although agar agar, gum arabic, glucose, and gelatin are stated[47] to be reasonably effective. Silicates and fluosilicates are effective in alkali carbonate or phosphate solutions. However, "substantial concentrations" of inhibitors are required at temperatures near the boiling points of these solutions. Sodium disilicate prevents attack of sodium hypochlorite solutions on aluminum. 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 inhibit corrosion in alcoholic solutions. Tricresyl phosphates prevent 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 toward metals[9]. 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[27].

Aluminum used for electrical grounds does not corrode, provided that no electric current is passed through it[34]. 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[34] 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.

Steel plates are protected from subsoil corrosion 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(64).

Methods of 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(9).

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 soapstone. 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[78] is to cut a sample 1 by 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[66].

The alloyed surface usually contains about 25 per cent aluminum. Three methods of calorizing are revolving retort, packing, and dipping.

Revolving Retort Method of Calorizing. The revolving retort method used prior to 1935[66] 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[20]. The packed article was sealed gastight in a heated revolving retort for 4 to 6 hours at 1550 to 1770 °F[66]. 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[66] 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[66]. 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[20]. This process is used particularly for articles which would be damaged by tumbling about in a rotating retort[66]. Copper may also be coated by calorizing[20].

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[8]. 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[20]. 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[66].

Hot Rolling. Aluminum may be applied to iron by heating thin sheets of aluminum and sheet iron 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[20]. 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.

Thermal Evaporation. Thermal evaporation[39] 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, 1×10^{-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 of the coating. This process is used for coating mirrors as large as 48 inches in diameter.

Cathodic Sputtering. Cathodic sputtering[39] is the dislodging of the cathode material by high-speed positive gaseous ions. Subatmospheric pressures from 1×10^{-6} to 3 millimeters are used. The processes are still unexplained and it is not known whether the particles emitted are monatomic or polyatomic 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 the 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.

Fused Salt Electrolysis

The electrochemistry of fused salts presents many problems that are not involved in the use of aqueous solutions. The temperature is a very critical property when dealing with molten salts, while it is of only minor importance with aqueous solutions[1]. Chemical side reactions and corrosion problems are much more prevalent when molten salts are used as electrolytes.

Conductivity. Molten salts are good conductors of electricity[1]. Conductivity increases almost linearly with increase in temperature except at a very high temperature where conductivity lags behing temperature increase. In most cases, the effect of temperature increase can be accounted for by the decrease produced in the viscosity of the melt.

The conductivity of fused salt mixtures falls below the calculated values according to the law of mixtures and in some cases falls below the conductivity values of any of the pure components.

Measurements of conductivity of fused salts may usually be accomplished by regular methods. Mantzell[42], and Yamoyuti and Siskdo[82], published methods of measuring conductivities of fused salts and fused salt mixtures.

Faraday's Laws and Fused Salts. Richards and Stull[68], and Lorenz and Helfenstein[40], have defended the application of Faraday's laws to electrolysis of fused salts. However, the causes of low current efficiency of aqueous solutions are accented in molten salt baths. Velocity of diffusion and of chemical reaction are both much greater. Therefore, unless anodic and cathodic products are carefully isolated from one another, from the action of the electrolyte, and from the air, the yields will be much less than those calculated by Faraday's laws.

The chief causes of low cathode efficiency are: volatility of the electrolyte due to the high temperature, diffusion of the anode products, formation of metal fog, and action of the atmosphere[40].

Metal Fog. Lorenz[40] noticed a property of molten salts that tends to decrease current efficiency and cause deviation from Faraday's laws. If a metal, such as zinc or lead, is melted under one of its fused salts, such as lead chloride or zinc chloride, the salt will be unaffected at low temperatures, but at higher temperatures the molten metal seems to volatilize and form an equilibrium mixture with the fused salt. This phenomenon may also be produced by adding a small amount of the reducing agent to the bath. While the amount of

metal included in the bath is not great, it tends to adversely affect the yield, since the metal in the "fog" form is not susceptible to chemical attack. It is believed that these fogs are colloidal in nature, but the forces that regulate their actions are not thoroughly understood.

Voltage in Fused Salts. In aqueous solutions, the electromotive force of cells depends upon the concentration of the electrolyte(74). With pure fused salts, concentration does not enter the picture, and, therefore, the primary electromotive force depends only on the nature of the electrodes, electrolyte, and the temperature. In pure fused salts, the electromotive force and the decomposition potential are essentially the same. In a mixture of salts, the electromotive force depends upon the concentration of the salt corresponding to the metal used as the cathode.

Anode Effect. In the electrolysis of fused salts, it frequently happens that the voltage rises suddenly and the amperage decreases, and a hissing sound is heard from the cathode(37). The anode appears to glow owing to the formation of innumerable little spark discharges. This phenomenon is known as the anode effect.

During the normal course of electrolysis, gas bubbles are constantly escaping at the anode in a smooth and regular order.

When the anode effect occurs the gases form a film around the anode which holds the molten electrolyte away from the surface. The anode effect is particularly noted with high current densities. It may be made to disappear by removal of the gas layer, which may be done by stirring, raising the anode, or reversing the current.

Concentration Polarization. At high current densities, the voltage does not increase linearly with the current density[1]. This phenomenon is due to the exhaustion of ions near the cathode in aqueous solutions and can be extended to explain the same phenomenon in fused salts, if the idea of ions is extended to include fused salts. Temkin[73] and Walden[77] have shown both experimentally and mathematically that ionisation should be extended to molten salts.

Electrochemistry of Aluminum

Some information as to the behavior of aluminum salts and ions in the presence of an electric current was available. Consideration was also given to the ability of aluminum to resist corrosion.

Electroplating on Aluminum. For over thirty years, the electrodeposition of other metals onto aluminum surfaces has

remained one of the concerns of the electroplating industry. During this time, many processes have been patented, but only in recent years have satisfactory methods been established[49].

Satisfactory plating on aluminum has been produced largely by two methods[49]. One consists of electrochemical oxidation of the aluminum and plating upon the oxide film, while the second involves the use of a sodium zincate dip. This dip imparts a zinc film to the aluminum, which subsequently may be plated with other metals.

Aluminum as an Anode. Aluminum has a high affinity for oxygen, quickly forming a protective oxide film upon exposure to an oxygen-bearing atmosphere[52]. While this film is ordinarily only about 5×10^{-7} inch thick, it effectively prevents further attack unless removed or penetrated by chemical or mechanical action. Advantage has been taken of this phenomenon in the finishing of aluminum[67]. The various oxide finishes are obtained by treating the aluminum to be coated anodically in various electrolytes in such a manner that a thin, inert, and durable aluminum oxide coating is obtained on the metal surface. The film formed is very hard and offers excellent abrasion and corrosion protection to the underlying metal. Some of these films are clear and transparent,

while others are colored in varying degrees of brown, gray, and silver.

The method of anodic film formation is not complicated. In anodizing, the aluminum is made the anode, and electrolytes capable of yielding oxygen on electrolysis are used. Examples of electrolytes include chromic, sulfuric, phosphoric, and boric acid[67].

While advantage has been taken of this anodizing principle for decoration and protection of aluminum, it must be remembered that this property can also be extremely disadvantageous[67]. In attempts to electrodeposit aluminum onto other metals, it is helpful to use an aluminum anode so that a source of aluminum, other than the electrolyte, will be present to supply the metal ions. Since an aluminum oxide coating will not conduct electricity, great care must be taken to insure that the electrolyte employed will not release oxygen at the anode upon electrolysis[52]. An aluminum anode must be highly polished before being placed into service to remove the oxide coating that it might have picked up from the atmosphere. The affinity of aluminum for oxygen is so great, in fact, that the surface reactivity of the metal may be greatly reduced after only seconds exposure to oxygen.

Electrodeposition of Aluminum

Electrodeposition of aluminum is one of the more difficult problems of the electroplating industry and, so far, not many of the methods investigated have been successful. The first article describing attempts to solve this problem was published in 1802[53]. The systems studied for electroplating aluminum may be divided as follows: from aqueous solutions; from nonaqueous inorganic liquid solutions; and from fused salt mixtures.

Electrodeposition of Aluminum from Organic Baths. The aluminum halides are soluble in many solvents, as seen from the wide applications of Friedel-Craft reactions. Meerwein[54] has shown that many weak electrolytes are increased in strength by the formation of complex ions. Consideration of this fact indicates a possible means of solving the problem of electroplating aluminum from organic solvents.

Mueller and his associates[53] were unsuccessful in depositing aluminum from a solution of anhydrous pyridine and aluminum tribromide, but did deposit it from solutions of aluminum bromide dissolved in ethyl bromide. Baraham and Taft[87] studied the electrodeposition of aluminum from liquid ammonia solutions and found that the same general factors influenced the deposition of metals as from aqueous solutions. Aluminum could not be readily deposited from liquid ammonia.

When low melting organic compounds were used, Keyes and his co-workers[41] deposited aluminum on a copper cathode from an aluminum anode. Smooth aluminum coatings were obtained at room temperature from diethyl aluminum diiodide. These platings were done on a laboratory basis with the electrodes set only one centimeter apart. The current densities were low, being 0.02 ampere per square centimeter, while an electromotive force of 40 volts was used.

Blue and Mathers[41] found that aluminum in its pure form could not be deposited from solutions of aluminum chloride in formamide, but that alloys of aluminum with iron or zinc could be deposited in this electrolyte. They also found[41] that aluminum of high purity could be deposited easily in a bright, finely crystalline and adherent form from an electrolyte made by dissolving aluminum in ethyl bromide and benzene, with aluminum bromide as a starter or catalyst.

Gray and his associates[26] took out a patent which describes a method of plating with aluminum using aluminum anodes in an electrolyte comprising an aluminum salt of an aminobenzene-sulphonic acid.

The specific conductivity of solutions in ethyl thiocyanate[2] is similar in the absolute values and in the character of the curves to that of solutions in ethyl bromide and ethyl

iodide for the systems: aluminum bromide-ethyl thiocyanate, potassium bromide-aluminum 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.

For the aluminum bromide-ethyl bromide system, the specific conductivity increases with the concentration of aluminum bromide within the range 46.3 to 72.34 per cent[35]. 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[38].

The specific conductivity[58] of solutions of aluminum bromide or aluminum chloride in benzene rises with dilution and with increasing concentration of an added metal halide, where the metal is potassium, rubidium, lithium, and the halide is chlorine or bromine, and falls with increasing concentration of aluminum halide. When ammonium halides are added to the system of aluminum bromide-benzene within the mol 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.

Upon electrolysis of alkali halides mixed with aluminum halide in nitrobenzene solutions, Mezhenni[51], in 1938, reported that alkali metal is deposited at the cathode, and Plotnikov and Barmashenki[59], in 1941, reported that halogen deposits at the anode.

A new type of aluminum plating bath was developed by Couch and Brenner[14], consisting of an ethyl ether solution of anhydrous aluminum chloride and a metallic hydride. The concentration of aluminum chloride was varied from 1 to 4 molar, but optimum results were obtained with a 2 or 3 molar solution. Lithium hydride was added to make the bath 0.5 to 1.0 molar. The bath was operated at a current density of 5 amperes per square decimeter, and at "room temperature." At temperatures of 40 to 60 °C, no improvement in the deposit was observed. Deposits as thick as 0.5 millimeter were obtained. Anode and cathode efficiencies were about 100 per cent.

Anodes of aluminum 0.6 cubic centimeter in diameter were used. The effective life of the bath depended upon the conditions under which it was maintained. Occasional additions of lithium hydride were required to replace that decomposed by the moisture. Baths which had absorbed moisture required additions of aluminum chloride as well as lithium hydride for rejuvenation.

Baths prepared with commercial anhydrous ether, which probably contained some moisture and alcohol, operated as satisfactorily as baths which were prepared from ether carefully dried over sodium. The hydride precipitated a considerable amount of insoluble material, probably metallic impurities, which had to be removed by filtration. However, the solution did not require frequent filtration.

The smoothest deposits were obtained by the use of periodic reverse current. The reverse time for the best deposit was from 3 to 15 seconds with reverse current densities of 10 amperes per square decimeter. The plating time should be 10 seconds and the current density not over 4 amperes per square decimeter. The total cycle time should be 20 seconds.

Photographs of the aluminum deposits show that they have a definite columnar structure. Those made at low current densities have rather large crystals. As the current density was increased the crystals became smaller. It has the same columnar structure but is much finer grained than the deposit without periodic reverse current.

A number of different ethers were tried in place of ethyl ether in an attempt to develop a less volatile and less flammable bath, but none yielded as satisfactory deposits.

Not one of the ethers tried which contained more than one oxygen atom, gave a workable bath. The deposit obtained with the use of B,B'-dichloroethyl ether as an addition agent was the least ductile and would take only a slight bend without breaking. High current density, periodic reverse current, and B,B'-dichloroethyl ether in the bath increased the hardness of the deposits, which ranged from about 37 to 97 Vickers.

Watkins[89] studied the electrodeposition of aluminum from organic solutions of aluminum thiocyanate. Platinum electrodes were used with an area of 2 square inches. The organic solvents used were methanol, formamide, and pyridine. It was found that organic solutions of aluminum thiocyanate are poor electrolytes for the electrodeposition of aluminum.

Parker[84] investigated the electrodeposition of aluminum from organic solvents and an organic compound containing aluminum. Basic aluminum acetate in formamide was electrolyzed with formation of a dark unidentified precipitate in the bath. The following systems were also tried: aluminum o-nitrophenoxide, sodium o-nitrophenoxide, methyl alcohol, aluminum phenoxide, sodium o-nitrophenoxide, ethyl phosphate, aluminum phenoxide sodium phenoxide, ethyl phosphate, using a combination of either a platinum anode and copper cathode or aluminum anode and

copper cathode. No aluminum was obtained in 6 hours of electrolysis at 20 volts.

Electrodeposition of Aluminum from Aqueous Solutions. Tucker and Thompson[75] 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[43] 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; Q. Marino[44] patented a process using an aqueous ammonia solution of aluminum tartrate and oxalate. Both used aluminum anodes.

Electrodeposition of Aluminum from Sulfuric Acid Solutions. Hayford[29], attempting to confirm a patent by Williams[90], studied the solubility of aluminum sulfate in sulfur trioxide with the idea of electroplating aluminum from the solution. However, only 0.0880 weight per cent aluminum sulfate was soluble in sulfur trioxide at 40 °C, while the specific conductance was 0.000538 ohm per centimeter. The electrodeposition of alunium from this solution is impractical.

Electrodeposition of Aluminum from Fused Halide Baths. In 1808, Davy[15] tried to electrolyze molten alumina, but because of the weakness of the current available, he obtained no

aluminum. Bunsen[7] first obtained aluminum by electrolysis of a fused bath of sodium aluminum chloride contained in a partitioned, porcelain crucible and using carbon electrodes. At low temperatures, the aluminum was obtained as a gray powder, but by working at high temperatures, the aluminum was formed in small beads. Sodium chloride was used as a flux in this process. Deville[17] decomposed sodium aluminum chloride by electrolysis at about the same time. He used a porcelain crucible fitted inside a fireclay crucible. The fireclay cover was cut to admit a strip of platinum to serve as the cathode and a porous cell which contained the carbon anode. Chalilier[11] patented a similar process whereby an anode of carbon and alumina was used.

In 1924, S. Peacock[85] was granted a patent for another method of coating steel sheets. They were passed beneath the surface of a molten bath containing sodium and potassium aluminum fluorides at a temperature above 700 °C. An electric current was passed from the bath to the sheets. The aluminum compound was electrolyzed and aluminum deposited on the steel sheets. The aluminum coating was compacted by rollers and the coated sheets were cooled out of contact with the air.

Wade and coworkers[76] employed a system of 20 mol per cent sodium chloride, 14 mol per cent potassium chloride, and 66 mol per cent aluminum chloride in a study of deposition and

decomposition potentials of a number of chlorides. Platinum was used as the reference electrode. Aluminum was found to deposit as a smooth surface at a potential of 2.02 volts and at a current density of 1.25 amperes per square decimeter.

Fink and Solanki[23] investigated containers for electrolyzing a mixture of aluminum chloride and sodium chloride. The possibility of obtaining aluminum metal was also investigated. From a system of aluminum and sodium chloride, aluminum was obtained in crystalline form using a nickel crucible as cathode and a carbon rod as anode.

Plotnikov, et al[61], claim to have produced a satisfactory surface of aluminum on copper from a bath containing aluminum chloride and sodium chloride in a two to one ratio at 220 to 250 °C. Cathode current density was one ampere per square decimeter.

Wehrman and Yntema[79] studied the alkali-aluminum bromide series for deposition potentials of various metals. Aluminum bromide-potassium bromide had a decomposition potential of 1.61 volts which was more electronegative than that of any other metal studied. In the study of the addition of chlorides to the bromide series, a system of 66 mol per cent aluminum chloride, 20 mol per cent sodium bromide, and 14 mol per cent potassium bromide was investigated. The decomposition potential was

1.71 volts. Deposits of aluminum similar to those deposited from the chloride baths were found.

Chittum[12] patented a process for depositing aluminum on copper from a fused aluminum chloride-lithium chloride bath. A current density of 0.2 ampere per square centimeter was used. When the plating efficiency drops, the copper article is removed and cleaned. The bath consisted of 40.1 mol per cent lithium chloride and 59.9 mol per cent aluminum chloride. The melting point of such a mixture is 115 °C.

Plotnikov and Kolita[62] claimed that "a small addition" of calcium salts to a bath containing aluminum and sodium chloride improved the conductivity of the bath and the deposit.

Attempts to Improve Known Methods. A thorough investigation of the aluminum chloride-sodium chloride system has been made at the Aluminum Research Laboratories[13], and it has been shown that aluminum can be successfully electroplated onto various metals. For plating on steel articles, a bath of 75 per cent aluminum chloride, 20 per cent sodium chloride, and 5 per cent lithium chloride. For plating on copper, a melt of 80 per cent aluminum chloride and 20 per cent sodium chloride was used.

All ingredients of the plating baths should be of high quality in order to assure good plating. It is not necessary to use chemically pure ingredients except in cases where

exceptionally pure coatings are desired. The temperature should be maintained at 180 ± 5 °C while the optimum current density of 15 amperes per square foot should be used for 30 minutes.

Couch and Brenner[14] tried to find a stable addition agent which, when added to the melt of aluminum bromide and potassium bromide, would yield smoother deposits. Stannic chloride, chromic chloride, and lead chloride was found to give a smoothening effect. It was also found that the form in which the lead, tin, and chromium were added did not seem to matter; that is, lead oxide worked as well as lead chloride. Orlova and Lainer[56], while using a 3:1 aluminum-sodium chloride mol ratio, also announced plate improvement by using 0.2 weight per cent lead chloride.

Couch and Brenner[14] also developed a new plating bath. It consists of an ethyl ether solution of anhydrous aluminum chloride and lithium hydride. The hydride was added as lithium hydride or as lithium aluminum hydride in 0.5 to 1.0 molar concentrations. The bath was operated at room temperature and at 5 amperes per square decimeter. Deposits of 0.5 millimeter were obtained.

Additive Compounds in Electroplating Baths

The constituents of an electroplating bath, in its simplest form, must contain at least three components: a salt of the metal to be plated, a current carrier, and a solvent. Relatively few baths, however, have retained this simple make-up. In some cases, difficulties in operating the original bath created the need for extra constituents. Sometimes, fortuitous accidents gave platers the clue to helpful additions. Lately, the demands of the engineers for faster, brighter, finishes has increased the complexity of the plating bath. These additive compounds can be broken down into four groups commonly known in the field as wetting agents, addition salts, sequestering agents, and addition agents or brighteners.

Wetting Agents. Wetting agents[63] are chemicals, usually organic in nature, which noticeably decreased the surface tension at the interface of the electrolyte and the electrodes. A wetting agent enables the solution to come into closer contact with the anodes and the work to be plated. Relatively small quantities, not exceeding three per cent, are added to the plating baths.

Addition Salts. Addition salts[83], generally, either stabilize the bath or increase the efficiency of the operating conditions, as for example, when an increase in the limiting

current density is permitted by sludge free dissolution of the anodes. Some addition salts in common use are: caustic soda in a cyanide zinc bath, to increase efficiency and anode corrosion, and boric acid in a nickel bath to act as a buffer.

Sequestering Agents. Sequestering agents[83] are virtual new-comers in the metal finishing field, and their use in this country is limited to cleaning and anodizing solutions. A sequestering agent is defined as a water-soluble ion exchanger. They serve to de-activate heavy metal and alkali earth ions by forming soluble, non-ionic compounds with them. Thus, heavy metallic impurities remain in solution, but are rendered harmless.

Addition Agents. Brightener or addition agents[25] are materials which are added to the plating bath, usually in small quantities, for the purpose of increasing the brightness, the smoothness of the deposit, or controlling its mechanical properties.

History of Addition Agents. Knowledge of where and when addition agents were first used is very limited. The use of addition agents has assumed new importance with the development in recent years of solutions for bright plating. Bright copper[50] was first observed in 1845 when wax molds were phosphorized in a solution of phosphorous in CS_2, then plated in

acid copper. For the next link in the chain, in 1870 glue was used in acid copper solutions during the electrolytic refining operation to give smoother deposits. The reason carbon disulfide was tried by early silver platers or glue was chosen to be added to acid copper baths will never be known.

In the early 1900's[30], new addition agents were used. A consultant, in 1902, while trying to check some difficulty in a nickel bath, had the solution stored in barrels while he checked the contacts. The glue sizing in the barrels dissolved somewhat in the nickel solution. Much to the consultant's surprise, the nickel bath now performed as never before.

Most of these addition agents were discovered by fortunate accidents. The use of casein in an acid copper bath had a similar beginning. A plater accidentally dropped his lunch bottle of milk in the copper tank, with excellent results. So, many platers used milk in their copper baths for years, until a chemist discovered that it was the casein in the milk that was causing all of the improvement.

Mathers[46], while testing glue as an addition agent for acid tin plating in 1918, had considerable difficulty with foaming. Realizing that certain phenolic or ring alcohols acted as foam controlling agents, he reached for a bottle of cresol handy

on a nearby shelf, and poured some into the bath. As a result of this lucky accident, today glue plus cresol is a standard addition agent for acid tin baths.

Types of Addition Agents. The types of addition agents used for improving electroplating deposits are: metallic salts, organic and inorganic crystalloids, and colloids.

Metallic Salts. Metallic salts[65] include such addition agents as cobalt or zinc salts in nickel baths, lead acetate in cyanide copper, or arsenic compounds in brass baths. In any alloy bath, each metallic salt may be considered an addition agent for the other. Thus, in a cadmium-zinc alloy bath, the cadmium may be considered a brightener for the zinc or vice versa.

Crystalloids. Crystalloids[69] used as brighteners are, for the most part, organic. These are salts, crystalline in form, which readily and completely dissolve in the solution. Tartaric acid, lactic acid, and sugar are typical organic crystalloids. Metaphosphoric acid is a commonly used inorganic crystalloid. The term crystalloid is used to indicate a structure opposed to that of colloids.

Colloids. Colloids[5] comprise by far the largest group of addition agents in use. The term colloid, as

here used, indicates a particle size division rather than a chemical class. Casein, glue, and gelatine are colloids frequently used as addition agents in plating baths.

Theories of How Addition Agents Actually Work

Addition agents are mainly used to obtain a brighter plate. "Brightness of metals is best defined in terms of percentage of light reflected from the surface. It is generally true that small metallic crystals reflect a higher percentage of light than large crystals"(69). Thus, any process limiting the growth of crystals at a cathode will tend to give brighter deposits. This, however, is only half the answer. There are many theories, but few facts explaining how addition agents act. Some of these theories will be discussed.

Reducing Menstruum Theory. Kern(36) postulated what is known as the "reducing menstruum" theory. According to Kern, the function of an addition agent is to maintain a reducing menstruum around the cathode. A reducing menstruum may be defined as a solvent film which tends to decrease the positive character of the ions in solution. Since the positively charged metallic ions are reduced at the cathode to a metal having no charge, any cathode film tending to make the change easier

should have a brightening effect. Therefore, a brightener must further this reducing process to be effective.

Kern supported the theory with a number of facts. He noticed that most brighteners were organic compounds, and that large numbers of these belonged to the same family, the benzene ring compounds. Also, the most effective brighteners were those benzene ring compounds containing hydroxyl and amine radicals fastened to the benzene ring, and the more amino and hydroxyl radicals it contained, the better the compound served as an addition agent. The more closely grouped these radicals appeared on the ring, the better was the addition agent.

The best reducing compounds of the ring series and those which more readily precipitate metals from their solutions, are those compounds containing the largest number of hydroxyl and amino radicals and those compounds in which these radicals are most closely grouped. Thus, it seems logical that the best reducing agents are also the best addition agents.

This theory is interesting to view in relation to the electromotive series of metals. Those metals which are above hydrogen in the series are strongly electronegative (tend to dissolve in the solution rather than deposit from it), and are thus not easily reduced. These metals (lead, tin, chromium, and zinc), tend to give rough deposits in the presence of free

acids and oxidizing agents. Metals below hydrogen in the series tend to give tougher deposits and are less easily affected by addition agents.

Adsorption Theory. Blum[6] publicized the adsorption theory. The theory postulates that: addition agents are colloids or form colloids in the solution as a whole or in the cathode film. These colloids to be effective must be positively charged and be attracted to the cathode by the current, and they must be adsorbed by the precipitating metal in such amounts as to cut down the size of the crystals formed.

The mechanism for cutting down the crystal's size is simple. The colloidal particles are adsorbed into the crystal lattices. There, they form a non-conducting blanket which prevents further growth of the particular crystals. Any metallic ions must now form new crystal nuclei in order to plate out. Thus, there is a constant interference of crystalline growth.

Effectiveness of the addition agent will vary with the speed of passage of the colloid toward the cathode and with the extent of the adsorption. The extent of adsorption depends on the nature of the colloid and the nature of the metal being plated.

The use of metallic addition agents can be explained by this theory. Cathode films are invariably more basic than the

rest of the solution. Even acid solutions sometimes have cathode films with an alkaline pH. It is possible that metallic compounds and some inorganic crystalloids, hydrolyze in the cathode film to form colloidal compounds. This is definitely shown to be true with amphoteric metals like aluminum.

Complex Ion Theory. Mathers[45] developed the complex ion theory. He postulated that the addition agents form complex cations in the bath by combining with the metal ion and in some cases the anion radical and water molecules. These complex cations are carried by the current and deposited on the cathode, interfere with normal crystal growth, and create a fine grained, bright deposit.

Mathers in postulating the theory took the following into account: analyses of deposits have shown them to contain many of the materials of the baths, complex cation such as gelatine plus zinc do exist, metals most easily affected by addition agents are often those which most easily form complexes, and there are several indications that the transfer of addition agents to the cathode and their deposition thereon is a phenomenon of an electrochemical nature rather than pure adsorption.

Hunt's Theory. The Hunt theory[32] states: The structure of the electrodeposited metal is determined by the ratio of the metal ion concentration to the concentration of the remaining

constituents of the film." If this ratio is high, coarse, crystalline deposits are obtained. A low ratio, showing high concentration of inert particles, produced interference with deposition and thus the formation of more nucleii. Hunt's theory is in a sense a corollary of both the adsorption and complex theories and gives additional rather than contradictory possibilities.

Surface Tension Theory. In 1919, Betts[69] evolved the surface tension theory. He states that each layer of metal, as it is built up at the cathode, obeys the laws of surface tension. According to this law, flat or extremely concave surfaces are at a more stable energy state than sharply curved or bent surfaces. Thus, there is always a tendency for the former to gain at the expense of the latter. The larger drops gain in size at the expense of the smaller drops, because larger drops have higher surface tensions. High surface tension metals, i.e., the strong, hard metals like copper, give the smoothest, brightest deposits. They do this because as each monomolecular layer deposits, it rearranges itself, the flat or most concave surfaces gaining at the expense of the bumps, nodules, trees, and other sharply curved projections. Weak, low surface tension metals like lead and tin give the roughest deposits, since there is little tendency toward the rearrangement. At high current densities,

however, there is less time for the play of surface phenomenon, resulting in treeing and rougher deposits.

According to this theory, addition agents serve to give brighter deposits by increasing the hardness and toughness of the metal, giving a deposit of extremely high surface tension.

Physical Properties of Anhydrous Aluminum Chloride

An attempt to correlate the physical properties of aluminum chloride is made here.

Molecular Structure. The structure[88] of anhydrous aluminum chloride purified by sublimation under high vacuum, has been found to be a colorless pseudo-hexagonal plate, composed of three individuals twinned together with rhombic symmetry. Further crystal structure study suggested that anhydrous aluminum chloride existed in two forms: (1) a yellowish modification, which is trigonal and isomorphous with chromic chloride, and (2) the white form which may be triclinic. Evidence in addition to crystal structure analysis points to existence of aluminum chloride as a double molecule.

Density, Melting Point, Boiling Point, and Molecular Weight of Aluminum Chloride. The density of solid aluminum chloride is 2.49 while the density of molten aluminum chloride at 190 °C is 1.33.

When anhydrous aluminum chloride is heated in small quantities, it volatilizes without melting. However, large quantities when rapidly heated melt and boil. The melting point is 193 °C at standard conditions. The boiling point is 183 °C at standard conditions.

It has been shown that in any solvent that combines with aluminum chloride, the aluminum chloride has a molecular weight corresponding to $AlCl_3$, whereas in an indifferent solvent such as carbon disulfide it has the doubled molecular weight. However, it has been concluded that the molecular state of anhydrous aluminum chloride is the dimer, Al_2Cl_6, when solid, liquid, or gas below 400 °C.

Conductivity of Anhydrous Aluminum Chloride. In the case of solid aluminum chloride, the conductivity increases with temperature from zero to a maximum at the melting point. On melting, the conductivity drops to absolute zero and slowly rises with an increase in temperature.

Thermal Analysis of $AlCl_3$-NaCl System. Thermal analysis was made for the whole region of concentrations for the system aluminum chloride and sodium chloride. This system showed a complex $AlCl_3 \cdot NaCl$ compound with a melting point of 152 °C. This system has two eutectics, at 152 and 108 °C. The equilibrium diagram is shown in Figure 1, page 68.

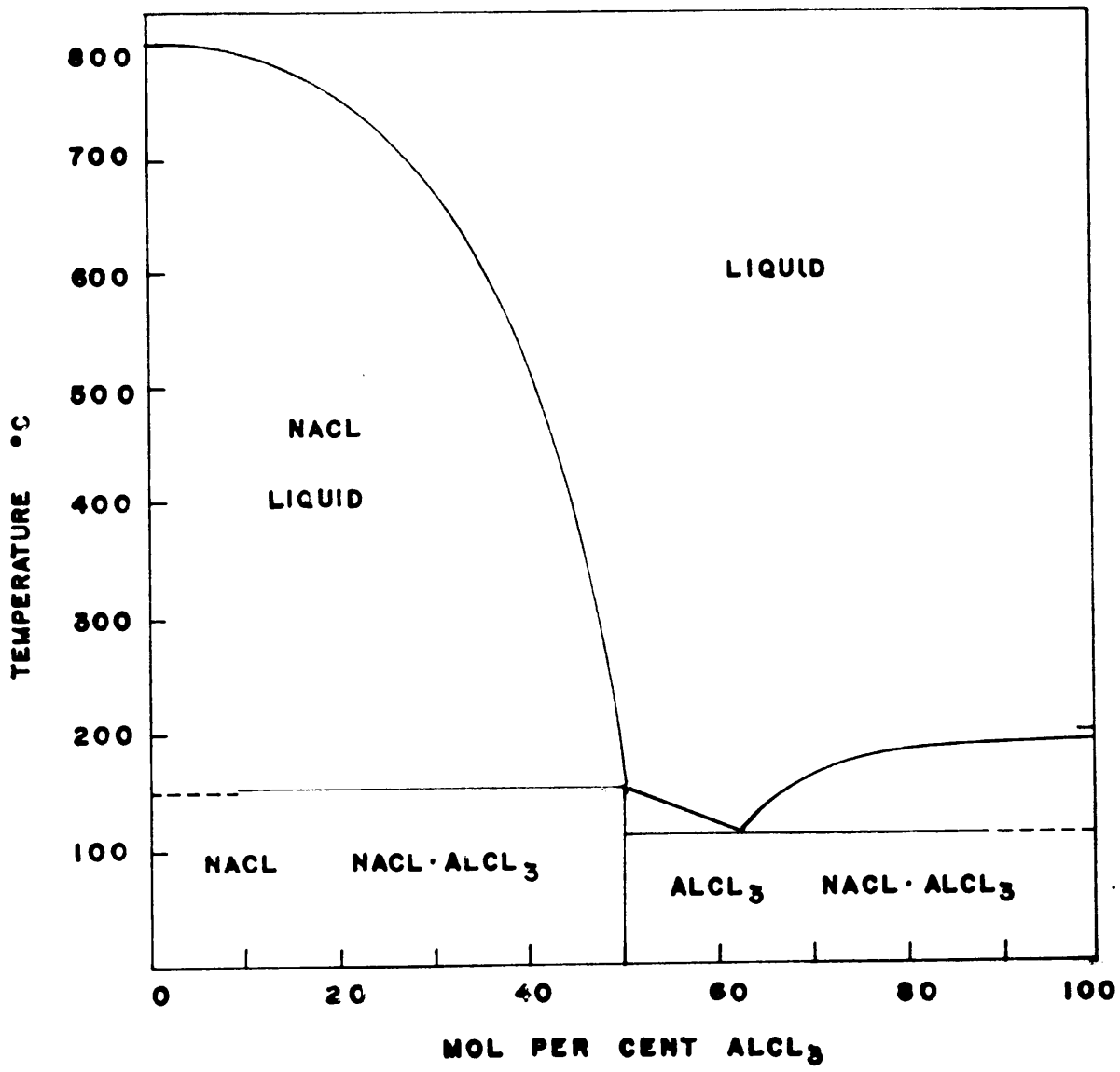

FIGURE 1. PHASE DIAGRAM FOR SYSTEM SODIUM CHLORIDE - ALUMINUM CHLORIDE

U. I. SHVARTSMAN: J. PHYS. CHEM. (U.S.S.R.) 14, 253 1940. C. A. 35, 1402 (1941).

III. EXPERIMENTAL

This section contains the information pertaining to the experimental work which was done in the laboratory to determine the effect of addition agents upon the electrodeposition of aluminum on copper from a fused halide bath. Study of the effect of addition agents on the properties of deposits on other metals (iron, aluminum, die-cast alloys, etc.) was deferred because of lack of time.

Purpose of Investigation

The purpose of this investigation was to study the effect of addition agents on the electrodeposition of aluminum when added to the fused bath of aluminum chloride in sodium chloride.

Plan of Experimentation

This investigation was carried out according to the following plan:

Literature Review. A literature review was conducted to obtain information concerning previous methods used in the electrodeposition of aluminum. Also, the review was made to

obtain information pertaining to the effects of addition agents on the electrodeposition of aluminum and other metals.

Construction of Apparatus. The apparatus to be used in this investigation consisted of a beaker fitted with a tight cover, through which the electrodes were introduced into the bath. The beaker was placed in an electric furnace capable of keeping the bath at a constant temperature during the experiments. An electrical circuit capable of delivering a variable direct current to the electrodes was assembled.

Experimental Procedure. The first series of tests was an attempt to electrodeposit aluminum from a fused salt bath of 75 per cent aluminum chloride, 20 per cent sodium chloride, and 5 per cent lithium chloride.

The remaining series of tests employed a bath containing only 80 per cent aluminum chloride and 20 per cent sodium chloride. The addition agents, lead chloride, aluminum thiocyanate, sodium cyanide, chromic oxide, and vanadium oxide, were added to the halide salts, always in concentrations of less than one per cent by weight.

The cathode and anode were copper and aluminum plates, respectively. The electrodes were prepared for electroplating by pickling. The electrolysis was performed with

the bath held at a constant temperature, the current density was varied while holding the time of electrolysis constant, and in other cases the time was varied while holding the current density constant.

The results were interpreted by evaluating the coating with regard to cathode, efficiency, thickness, uniformity, and corrosion stability.

Materials

The following materials were used in this investigation:

Aluminum. Technical grade, 3S aluminum. Obtained from the Reynolds Aluminum Co., Richmond, Virginia. Used as anodes in this investigation.

Aluminum Chloride. Anhydrous, reagent, lot No 50172. Obtained from Merck and Co., Inc., Rahway, New Jersey. Used as a constituent of the fused halide bath.

Aluminum Thiocyanate. Prepared by P. H. Watkins[89] by reacting aluminum chloride and ammonium cyanate in methanol, and vacuum evaporation of the solvent. Virginia Polytechnic Institute, Blacksburg, Virginia. Used as addition agent in fused halide bath.

Carbon Tetrachloride. C.P. Lot No GO 54 J. Obtained from General Chemicals Division of Allied Chemical and Dye Corporation, New York, N. Y. Used in attempts to dissolve aluminum chloride from the surface of aluminum plate.

Chromium(ic) Oxide. Technical, lot No 513460. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used as addition agent in halide bath.

Copper. Copper plate, technical grade. Analysis as Cu 99.9 per cent minimum. Traces of iron, silicon, calcium, and silver. Obtained from Economy Lumber Company, Christiansburg, Virginia. Used as the cathode in plating cell.

Copper Sulfate. C.P. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used as addition agent in fused halide bath.

Lead Chloride. C.P. Lot No 501537. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used as addition agent in fused halide bath.

Lithium Chloride. C.P. Lot No 521892. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used as component in fused halide bath.

Metal Lacquer. Clear, lot No CN2336. Obtained from Albert W. Rhine, Inc., Baltimore, Md. Used as protective coating for aluminum plate.

Phosphorus Pentoxide. C.P. Lot No 482312. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used as drying agent in desiccator.

Sodium Carbonate. C.P. Lot No 474804. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used in oxide coating of aluminum plate.

Sodium Chloride. C.P. Lot No 514018. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used as component in fused halide bath.

Sodium Chromate. C.P. Anhydrous, lot No 472981. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used in oxide coating of aluminum plate.

Sodium Cyanide. C.P. Lot No 514098. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used as addition agent in fused halide bath.

Sodium Dichromate. Laboratory grade. Obtained from Phipps and Bird, Inc., Richmond, Va. Used in oxide coating of aluminum plate.

Vanadium Pentoxide. C.P. Anhydrous, lot No 7406. Obtained from City Chemical Co., New York, N. Y. Used as addition agent in fused halide bath.

Apparatus

The following apparatus was used in this investigation:

Ammeter. Model 528, ac, range 0 to 5 and 0 to 15 amperes. Manufactured by Weston Electric Instrument Corp., Newark, N. J. Used to measure current to the heating element in the furnace.

Ammeter. Model 489, direct current, range 0 to 3 and 0 to 15 amperes. Manufactured by Weston Electric Instrument Corp., Newark, N. J. Used to measure current output by generator.

Ammeter. Model 30, direct current, range 0 to 1.5, 0 to 3, and 0 to 30 amperes. Manufactured by Weston Electric Instrument Corp., Newark, N. J. Used to measure current to plating cell.

Balance. Analytical, Chain-o-matic, capacity 100 grams, graduation 0.0001 gm. Manufactured by Seederer-Kohlbusch, Inc., Newark, N. J. Used to weigh electrodes and addition agents.

Balance. Capacity 1610 grams. Divisions 0.1 gm. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used to weigh oxide coating bath constituents.

Beaker. Pyrex glass, 500 ml. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to hold standard coulometer solution.

Beaker. Pyrex glass, 1000-ml. Obtained from Fisher Scientific Co., Silver Spring, Md. Used as conductivity cell.

Beaker. Pyrex glass, 800-ml. Obtained from Fisher Scientific Co., Silver Spring, Md. Used as conductivity cell.

Beaker. Pyrex glass, 250-ml. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to hold pickling and oxide baths.

Desiccator. Diameter 12 inches. Obtained from E. H. Sargent and Co., Chicago, Ill. Used to protect metal from atmosphere.

Generator. Direct current, 1720 revolutions per minute, 30 volts maximum output. Manufactured by the Mechanical Appliance Co., Milwaukee, Wis. Used to supply the current for plating.

Hot Plate. Serial No 02H7865, 660 watts, 120 volts. Manufactured by Edwin Wiegand Co., Pittsburgh, Pa. Used to heat oxide coating solution.

Motor. No 42072, type KH, 3 horse power, 1720 revolutions per minute, 220 volts, 8 amperes. Obtained from the Mechanical Appliance Co., Milwaukee, Wis. Used to drive generator.

Oven. Electric, model OV-8, serial No 9-270, 115 volts, 5 amperes. Obtained from Modern Electric Laboratory, Chicago, Ill. Used for drying equipment.

Rheostat. Rex, No 652938, 16 ohms, 5 amperes, 16 inches long. Manufactured by Rex Rheostat Co., Baldwin, Long Island, N. Y. Used to control current to electrolytic bath.

Rheostat. Rex, 65 ohms, 3 amperes, 16 inches long. Manufactured by Rex Rheostat Co., Baldwin, Long Island, N. Y. Used to control current to plating bath.

Rheostat. Rex, 0.5 ohm, 10 amperes, 16 inches long. Manufactured by Rex Rheostat Co., Baldwin, Long Island, N. Y. Used to control current to plating bath.

Miscellaneous Chemical Hardware. Ring stands, tongs, clamps, copper wire, electrical switches, and connections.

Thermometer. Range 0 to 100 °C, divisions 1 °C. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to measure temperature of oxide coating bath.

Thermometer. Range -10 to 360 °C, divisions 1 °C. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to measure temperature of fused halide bath.

Timer. Kodak, 60-minute, divisions 1/2-minute. Manufactured by Eastman Kodak Co., Rochester, N. Y. Used to time duration of electrolysis.

Variac. Input 115 volts, output 0 to 150 volts, 206 turns. Obtained from Weston Electrical Instrument Corp., Newark, N. J. Used to control current to furnace.

Voltmeter. Model 489, direct current, range 0 to 3, 0 to 7.5, and 0 to 150 volts. Manufactured by Weston Electrical Instrument Corp., Newark, N. J. Used to measure voltage to plating cell.

Description of Furnace. The furnace, Figure 2, page 78, used was heated by a 1000-watt heating element, controlled by a 206 turn variac. The heating element was wrapped around a five-inch diameter refractory furnace lining, six inches long, placed in the center of a transite box, twelve inches long, twelve inches wide, and six inches deep. Asbestos shorts were then placed in the void between the lining and sides of the box. Six hours were required for the furnace to reach a constant temperature at 3.9 amperes. The plating cell was a beaker inside the furnace. The lid for the plating cell was made out of one-half inch plywood covered with one-sixteenth inch thick asbestos cloth. The electrodes, one cathode in the center of the plating cell and two anodes spaced one inch on either side of the cathode were introduced through holes, one-sixteenth inch diameter, through the lid. The furnace was placed in a

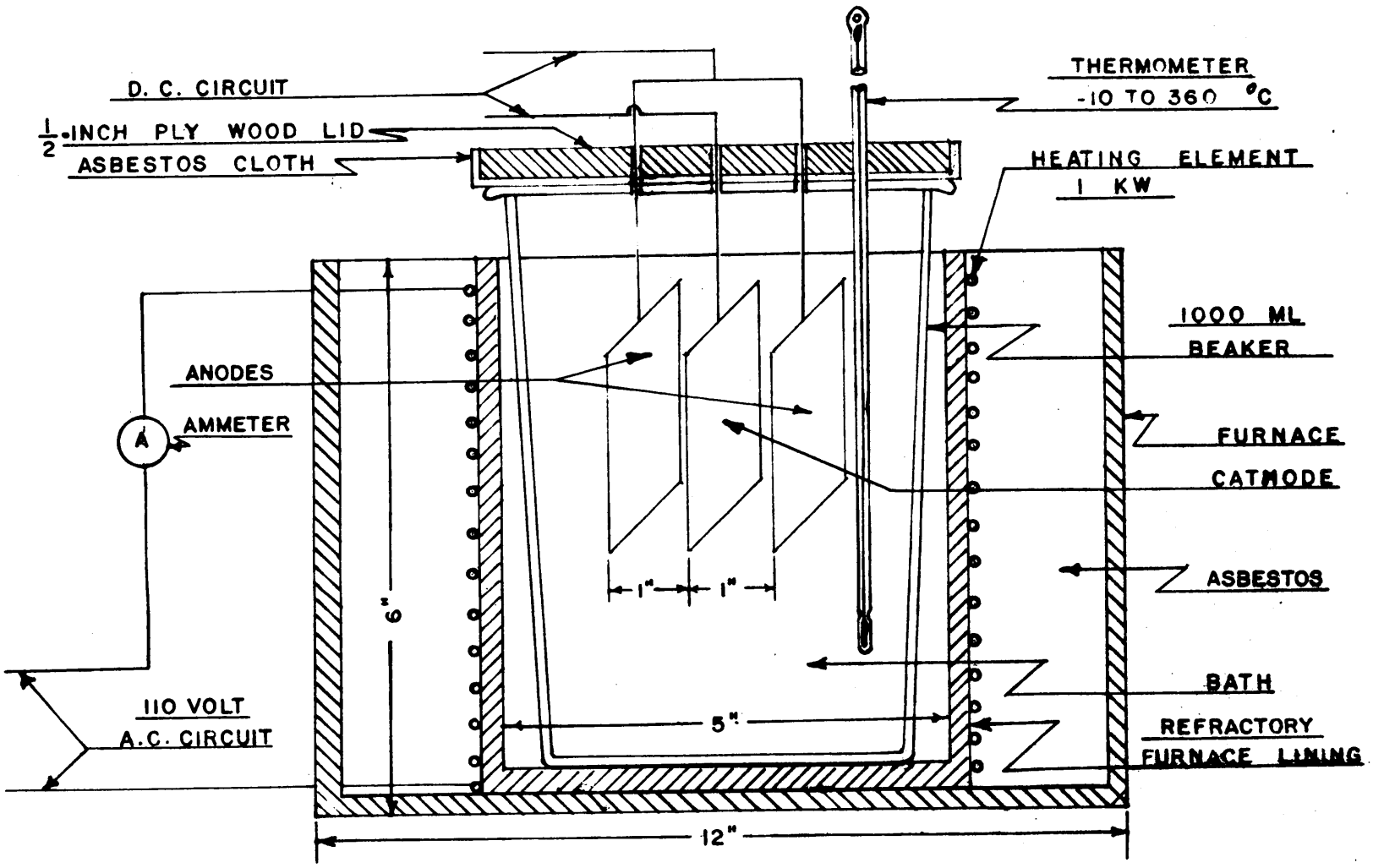

FIG. 2 DIAGRAM OF FURNACE AND ALUMINUM PLATING CELL

hood so that any vapors escaping from the bath were isolated from the room.

Method of Procedure

Bath Composition. First, a series of tests were made using a bath containing 75 per cent aluminum chloride, 20 per cent sodium chloride, and 5 per cent lithium chloride. This bath, recommended[13] for electrodeposition of aluminum on steel, did not give good deposits. Since a bath of 80 per cent aluminum chloride and 20 per cent sodium chloride gave good results on copper cathodes after a short electrolysis, it was decided to continue study with this combination.

Addition Agents. After a satisfactory plate had been obtained from the bath, and these plates had been evaluated, the effect of adding certain materials was observed. Some of these materials were chosen because they had shown promise in tests by Couch and Brenner[3]. Aluminum thiocyanate and vanadium pentoxide were added because it was believed that vanadium pentoxide should improve the coating, and because aluminum thiocyanate, having been newly prepared, had never been tried before. Lead chloride was added at 0.5 and 1.0 per cent of the bath; sodium cyanide at 0.1 and 0.5 per cent; chromic oxide at 0.5 per cent;

vanadium pentoxide at 0.1 per cent; and aluminum thiocyanate at 0.5 and 1.0 per cent. For each addition, separate copper coupons were plated at various current densities, for constant plating time. In certain series, the plating time was varied while the current density was kept constant.

Surface Treatment. It was soon noted that the plated coupons reacted readily with the atmosphere and a plate of aluminum that had been fairly good, could be easily brushed off as oxide. To preserve the specimen for later comparison, tests were made to find a method of surface treatment.

The surface treatments used consisted of lacquering with egyptian lacquer, treatment by the modified Bauer-Vogel and Alrok processes[67].

The plates sampled were removed from the bath, washed in water, dried in an oven for about a minute at 260 °F, and weighed on an analytical balance. The plate was observed under a low power microscope and these observations were recorded. When the lacquer was applied, it was put on with a soft brush, and dried in the air.

When pieces were treated by the modified Bauer-Vogel process, a portion of the coupon was immersed in an aqueous

solution of five per cent sodium carbonate at 195 °F, for three to five minutes, rinsed in cold water, dried with a cloth, and exposed to laboratory atmosphere for 24 hours.

When the Alrok process was used, a portion of the coupon was immersed in a solution of two per cent sodium carbonate and 0.1 per cent potassium dichromate for 20 minutes at 150 °F. The sample was immersed in a warm solution of five per cent potassium dichromate, rinsed, and dried.

Electroplating Procedure. The plating operation was started by bringing the furnace to the operating temperature (about 356 °F). This was done by controlling the alternating current through the furnace to 3.9 amperes. Approximately six hours was required to reach a constant temperature of 356 °F.

While the furnace was approaching a constant temperature, the constituents used in the bath were weighed on a beam balance. In order to eliminate the possibility of moisture in the bath the sodium chloride and lithium chloride were preheated in an electric oven for seventy-two hours at a temperature of 350 °F. The aluminum chloride was weighed first and the sodium and lithium chloride were weighed and placed over the aluminum chloride in the beaker as another precaution against the aluminum chloride absorbing moisture from the atmosphere. The beaker containing the halides was placed in the furnace

and the contents fused. After melting, which occurred at approximately 320 °F, the mixture was heated to 356 °F.

The aluminum anodes and copper cathode were placed in their respective pickling baths, removed, washed, and weighed on an analytical balance. They were heated to 260 °F before introduction into the plating bath to bring their temperature closer to the temperature of the bath. This eliminates freezing of the bath on the cold plates. They were suspended in the plating bath from clamps on adjustable electrical leads.

After the electrodes were introduced into the bath, the direct current was regulated by a rheostat, and the amount of current used was measured by means of a copper coulometer. The copper electrode used in the copper coulometer was weighed before and after the test to determine the exact amount of current used.

Method of Correlation. The cathode efficiency was determined by obtaining the gain in weight of the cathode divided by the theoretical gain in weight assuming one-third a gram atom of aluminum deposited per faraday. The anode efficiency was determined by the loss in weight of the anode divided by the theoretical loss in weight, using the same electrochemical equivalence.

The porosity as well as the character of the plate was determined visually under the microscope, while the ductility was determined by bending the cathode as sharply as possible into a 180° bend.

The current density was varied with each addition agent in order to determine the optimum current density for each addition agent. Too high a current density may form a dark, burned appearing deposit. Too low a current density appeared as a dull, granular deposit. Optimum current density gave, in some cases, a bright, smooth deposit.

Data and Results

The experimental data and observations are assembled in Tables I through VI, pages 86 through 92.

The test numbers are the same as the coupon and the amperes used in the electrodeposition were measured by a copper coulometer. The temperature was measured by a thermometer immersed in the bath. The current density was calculated from the amount of current used, and the area of each coupon separately measured. The plating results are based on the current efficiencies, color, density, uniformity, and ductility. Corrosion results were based on observations of the samples protected and unprotected after 24 hours in the laboratory atmosphere or in the desiccator.

It should be pointed out that the tables as recorded do not enable one to compare readily the results obtained with different addition agents, so a few notes are included here. The addition of vanadium pentoxide seemed to give plates of the best adherence and ductility as well as an interesting, smooth deposit at high current densities. Furthermore, the results indicate the presence of this agent improves the corrosion resistance of the plate. The results obtained

with this agent are of sufficient promise to warrant further study to determine the optimum concentration and conditions.

Lead has a smoothening effect but does not improve corrosion resistance of the plate. Chromic oxide improves corrosion but does not effect improvement in smoothness or ductility of the plate.

In summary, the comparison may be stated as follows:

Tables I-A and I-B, pages 86 and 87, contain the data obtained while plating from a bath of aluminum chloride and sodium chloride without addition agents. Results from the same bath as that used in Tables I-A and I-B except that anhydrous lead chloride in concentrations of 0.5 and 1.0 weight per cent was added, are in Table II, page 88.

Table III, page 89, contains the results when aluminum thiocyanate was added to the bath. In this table, the column head "Corrosion of Plates" applies to both protected and unprotected coupons in the atmosphere and desiccator since all results were the same.

Tables IV, V, and VI, pages 90, 91, and 92, report data for results with chromic oxide, sodium cyanide, and vanadium pentoxide, respectively.

TABLE I-A

Effect of Current Density and Surface Treatment on Aluminum Electroplated from a Bath of Aluminum Chloride and Sodium Chloride

Bath Composition: 80 per cent Aluminum, 20 per cent Sodium Chloride Copper Cathode Aluminum Anode One Inch Apart

Test No.	Current	Temperature	Current Density	Efficiency[a] Cathode	Efficiency[a] Anode	Time	Protective Coating[b]		Plating Results	Corrosion Results of Protected[b] and Unprotected Plate after 24 Hours in Atmosphere	Corrosion of Plate in Air[b] at 15 to 20 °C after 24 Hours in Desiccator
	amp	°C	amp/sq ft	%	%	min		amp x min	Color, Density, Uniformity, Ductility		
24	0.40	185	10.6	123	316	60	Alrok[c]	24	Dark deposit, porous, discontinuous, plate cracked on bending 180°, good test using 5 per cent caustic soda.	Plate turned darker than plates not protected 24 hours after applying Alrok. Otherwise, corrosion rate about the same.	Corroded at approximately the same rate as other plates.
25	0.40	185	10.6	47.4	243	60	Alrok	24	Heavy, gray, porous and rough, discontinuous and streaked, good caustic test, ductile.	Plate remained same color, heavy gray, although both plates turned slightly darker.	Plate turned slightly darker, than other plates.
26	0.40	185	10.6	44.4	156	60	Alrok	24	Gray, porous, discontinuous, and streaked; good caustic test, ductile.	All plates remained same gray color.	Plate turned slightly darker.
27	0.40	185	11.1	65	147	60	None	24	Gray, porous, discontinuous, good caustic test, ductile.	Protected and unprotected plates became spotted.	Plate remained a more uniform color.
28	0.30	185	8.2	33.1	210	60	None	18	Gray, less porous than above plates, slightly streaked, ductile.	Again both plates became spotted.	Plate turned slightly darker, but a more uniform color.
43	0.30	180	8.02	28.6	44.5	60	M.B.V.[d]	18	Dark, very thin plate, nodular, discontinuous, ductile.	Plates corroded at same rate. Both corroded in 24 hours.	Corroded in 24 hours.
44	0.30	180	8.55	50.3	398	60	M.B.V.	18	Dark, very thin plate, nodular, discontinuous, ductile, anode disintegrated.	Both plates corroded in 24 hours, down to base metal.	Corroded in 24 hours to base metal.
45	0.30	180	10.5	53	328	60	M.B.V.	18	Dark, thin plate, nodular, discontinuous, ductile, anode disintegrated.	Both plates corroded in 24 hours, down to base metal.	Corroded in 24 hours.
46	0.30	180	9.6	48.3	253	60	M.B.V.	18	Gray, smooth, uniform plate, ductile, anode disintegrated.	M.B.V. treated plate turned darker.	Corroded in spots to base metal.
47	0.30	180	10.5	40.3	219	60	M.B.V.	18	Gray, smooth, uniform plate, ductile, anode disintegrated.	Both plates corroded same, turned darker.	Plate turned darker.
48	1.00	180	27.4	71.0	131	60	M.B.V.	60	Light gray, smooth and non-porous, continuous, ductile, anode disintegrated.	Both plates turned slightly darker and uniformly so.	Plate did not corrode as much as other plates.
49	0.75	182	21.3	45.6	274	60	M.B.V.	45	Light gray, smooth and non-porous, continuous, ductile, anode disintegrated.	Both turned slightly darker and in spots corroded to base metal.	Plates turned darker but did not corrode to base metal.
61	0.75	180	18.6	41.6	137	60	M.B.V.	45	Dark gray, discontinuous, ductile, thin.	Spots corroded to base metal.	
62	1.0	180	24	40.6	160	60	M.B.V.	60	Light gray and shiny in spots, slightly porous, ductile, plate adherent.	Shiny spots became dim, plates corroded in spots.	
63	0.9	180	30.6	25.8	135	60	M.B.V.	54	Light gray, continuous, ductile, adherent.	Some corrosion in spots.	
64	1.10	180	40.4	22.9	154	60	M.B.V.	66	Light gray, uniform, ductile, adherent.	Corrosion in spots.	
65	0.50	180	18.2	46.2	112	60	M.B.V.	30	Lighter gray, uniform, ductile, adherent, non-porous, shiny streaks.	Corrosion uniform on both plates.	
66	0.20	180	8.6	44.1	121	60	M.B.V.	12	Light gray, uniform, ductile, adherent, non-porous. Best of above 61 to 66 series.	Slight corrosion but no change in color.	

Continued on Table I-B.

TABLE I-B

Effect of Current Density and Surface Treatment on Aluminum Electroplated from a Bath of Aluminum Chloride and Sodium Chloride

Bath Composition: 80 per cent Aluminum, 20 per cent Sodium Chloride. Copper Cathode, Aluminum Anode, One Inch Apart

Test No.	Current	Temperature	Current Density	Efficiency[a]		Time	Protective Coating[b]		Plating Results	Corrosion Results of Protected[b] and Unprotected Plate after 24 Hours in Atmosphere	Corrosion of Plate in Air[b] at 15 to 20 °C after 24 Hours in Desiccator
				Cathode	Anode						
	amp	°C	amp/sq ft	%	%	min		amp x min	Color, Density, Uniformity, Ductility		
73	0.20	185	6.91	92.4	324	90	Lacquer[e]	18	Light gray, powdered in spots, shiny around edge, chipped on bending 180°, uniform, adherent.	Remained light gray and uniform. Lacquer did not help	
74	0.20	185	6.94	61.9	184	60	Lacquer	12	Gray, uniform, slightly porous, ductile, adherent.	Both plates remained the same, lacquer did not help.	
75	0.20	185	7.01	43.2	192	30	Lacquer	6	Light gray, smooth, uniform, ductile, adherent.	Plates remained same color.	
76	0.20	185	7.09	71.4	43.3	15	Lacquer	3	Light gray, smooth, uniform, ductile, adherent.	Plate not protected turned spotted, protected plate did not.	
77	0.20	210	6.90	9.05	54	30	Lacquer	6	Dark gray, smooth, uniform.	Both plates corroded to base metal.	
78	0.20	200	6.90			30	Lacquer	6	Dark gray, smooth, uniform, ductile.	Corroded to base metal.	
79	0.20	190	6.90			30	Lacquer	6	Dark gray, smooth, uniform, ductile.	Corroded to base metal.	
80	0.20	180	6.93	59.7	348	30	None	6	Gray, smooth, non-porous, uniform, ductile.	Slight corrosion.	
93	0.20	180	14.9	15.2	367	90	Lacquer	18	Light gray, ductile, uniform, and non-porous.	Flakes corroded off.	
94	0.20	180	14.9	74.7	140	60	Lacquer	12	Same	Corrosion not noticeable on any plates.	
95	0.20	180	14.9	64.6	100.5	30	Lacquer	6	Same	Same	
96	0.20	180	14.9	96.6	129	15	Lacquer	3	Same	Same	
97	0.20	180	14.9	17.3	316	45	Lacquer	9	Gray, ductile, and discontinuous.	Corroded to base metal.	
98	0.20	180	14.9	66.5	281	15	Lacquer	3	Light gray, ductile, uniform.	Corrosion not noticeable on all plates.	
99	0.20	180	14.9	72.1	341	45	Lacquer	9	Same	Same	
100	0.10	180	8.7	104.8	251	90	Lacquer	9	Light gray, uniform, non-porous, ductile.	Same	
101	0.10	180	8.7	71.3	348	60	Lacquer	6	Same	Same	
102	0.10	180	8.7	94.5	286	30	Lacquer	3	Same	Same	
103	0.10	180	8.7	29.8	570	90	Lacquer	9	Same	Same	
104	0.10	180	8.7			15	Lacquer	1.5	Same	Same	

(a) Efficiency calculated on basis of deposition and solution of one-third gram atom of aluminum per faraday.

(b) Coupons were cut into three parts: one part treated with protective coating and exposed to laboratory atmosphere, one part untreated, stored in desiccator, and one part untreated, exposed to laboratory atmosphere.

(c) "Alrok" treatment consists of immersion of coupon in a solution of 2 per cent sodium carbonate and 0.1 per cent potassium dichromate for 20 minutes at 150 °F. The coupon is then immersed in 5 per cent potassium dichromate and then rinsed.

(d) M.B.V. treatment consists of immersion of coupon in an aqueous solution of 5 per cent sodium carbonate and 1.5 per cent sodium chromate at 195 °F for 3-5 minutes, then rinsed in water.

(e) Lacquer treatment consists of applying a coat of egyptian metal lacquer CN 2336.

TABLE II

Effect of Current Density and Surface Treatment on Aluminum Electroplated from a Bath of Aluminum Chloride, Sodium Chloride, and Lead Chloride

Bath Composition: Four Parts Aluminum Chloride and One Part Sodium Chloride. Copper Cathode, Aluminum Anode, One Inch Apart

Test No.	Lead Chloride Concentration	Current	Temperature	Current Density	Efficiency[a]		Time	Protective Coating[b]	Plating Results		Corrosion Results of Protected and Unprotected Plates[b]	Corrosion of Plate in Air[b] at 20 to 24 °C after 24 Hours in Desiccator
					Cathode	Anode						
	wt %	amp	°C	amp/sq ft	%	%	min		min x amp	Color, Density, Uniformity, Ductility		
36	1.0	0.50	180	13.1	44.9	336	60	M.B.V.[d]	30	Gray, slightly rough, discontinuous, ductile, good caustic test.	Both plates turned spotted.	Plate turned uniformly darker.
37	1.0	0.40	180	10.6	56.8	400	60	M.B.V.	24	Gray, slightly rough, uniform, ductile, good caustic test.	Plates remained uniform in color.	Plate turned uniformly darker.
38	1.0	0.40	180	10.2	90.4	167	60	M.B.V.	24	Light gray, slightly rough, uniform plate color, good caustic test, ductile.	Unprotected plate turned dark and corroded to base metal. Protected plate remained light gray.	Plate turned darker.
39	1.0	0.40	180	10.6	46.0	253	60	M.B.V.	24	Light gray, smooth, and uniform plate color, good caustic test, ductile.	Both plates remained uniform color.	Plate turned darker.
40	1.0	0.30	180	9.2	44.7	192	60	M.B.V.	18	Light gray, smooth, and uniform, good caustic test, ductile.	Both plates remained uniform color.	Plate turned only slightly darker.
41	1.0	0.25	180	9.17	43.9	461	60	M.B.V.	15	Gray, smooth, and uniform, good caustic test, ductile.	M.B.V. treated plate became darker.	Plate turned slightly darker.
42	1.0	0.35	180	12.5	42.3	202	60	M.B.V.	21	Light gray, slightly rough, uniform color, and plate, good caustic test.	M.B.V. treated plate became darker.	Plate turned slightly darker.
29	0.5	0.40	180	14.6	30.8	29.3	60	Alrok[c]	24	Dark gray, slightly rough, streaked, ductile, good caustic test.	Protected and unprotected plates turned slightly darker.	Plate corroded extensively.
30	0.5	0.40	180	9.6	61.5	20.7	60	Alrok	24	Light gray, smooth, discontinuous shiny patches, ductile, good caustic test.	Protected and unprotected plates remained same color.	Plate turned darker and spotted.
31	0.5	0.30	180	10.1	52.5	95.1	60	Alrok	18	Light gray, slightly rough, uniform color, ductile, good caustic test.	Unprotedted plate remained uniformly gray. Protected plate turned spotted.	Plate turned darker uniformly.
32	0.5	0.45	180	13.3	76.2	167	60	Alrok	27	Light gray, slightly rough, uniform color, ductile, good caustic test.	Both plates remained same uniform color.	Plate remained same light gray.
33	0.5	0.35	180	10.7	56.4	249	60	Alrok	21	Light gray, slightly rough, discontinuous, ductile, good caustic test.	Both plates turned spotted.	Plate turned streaked.
34	0.5	0.35	180	7.48	65.3	298	60	Alrok	21	Light gray, slightly rough, discontinuous, ductile, good caustic test.	Unprotected plate turned darker.	Plate turned darker.
35	0.5	0.35	180	13.5	55.3	207	60	Alrok	21	Light gray, slightly rough, discontinuous, ductile, good caustic test.	Both plates remained same uniform color.	Plate turned uniformly darker.

(a) Efficiency calculated on basis of deposition and solution of one-third gram atom of aluminum per faraday.

(b) Coupons were cut into three parts: one part treated with protective coating and exposed to laboratory atmosphere, one part untreated, stored in desiccator, and one part untreated, exposed to laboratory atmosphere.

(c) "Alrok" treatment consists of immersion of coupon in a solution of 2 per cent sodium carbonate and 0.1 per cent potassium dichromate for 20 minutes at 150 °F. The coupon is then immersed in 5 per cent potassium dichromate and then rinsed.

(d) M.B.V. treatment consists of immersion of coupon in an aqueous solution of 5 per cent sodium carbonate and 1.5 per cent sodium chromate at 195 °F for 3 to 5 minutes, then rinsed in water.

TABLE III

Effect of Current Density and Surface Treatment on Aluminum Electroplated from a Bath of Aluminum Chloride, Sodium Chloride, and Aluminum Thiocyanate.

Bath Composition: 80 per cent Aluminum Chloride, 20 per cent Sodium Chloride Copper Cathode Aluminum Anode, One Inch Apart

Test No.	Conc. of Aluminum Thiocyanate	Current	Temperature	Current Density	Efficiency		Time	Protective Coating(a)	Plating Results		Corrosion of Plates
					Cathode	Anode					
	wt %	amp	°C	amp/sq ft	%	%	min		min x amp	Color, Density, Uniformity, Ductility	
50	0.5	0.50	180	11.30	6.91	230	60	M.B.V.	30	Smooth and powdery, uniform	Powder flaked away., Protected plate the same.
51	0.5	0.30	180	7.47	20.9	190	60	M.B.V.	18	Gray powder, uniform, non-porous; powder scaled away when bent 180°.	Powder easily removed.
52	0.5	0.25	180	6.18	36.1	123	60	M.B.V.	15	Gray powder, uniform, non-porous; plate scaled when bent 180°.	Powder flaked away.
53	0.5	0.65	180	16.00	19.4	128	60	None	39	Same	Same
54	0.5	0.75	180	17.95	16.1	117	60	None	45	Same	Same
55	0.5	0.90	180	23.1	15.4	240	60	None	54	Same	Same
56	0.5	1.00	180	25.4	15.1	279	60	None	60	Same	Same
57	1.0	0.30	180	7.70	12.8	322	60	None	18	Gray powder, discontinuous.	Same
58	1.0	0.50	180	12.8	10.5	229	60	None	30	Gray powder, continuous, smooth, non-porous.	Same
59	1.0	0.40	180	10.9	14.5	237	60	None	24	Same	Same
60	1.0	0.70	180	23.5	13.5	151	60	None	42	Same	Same

(a) M.B.V. treatment consists of the coupon being immersed in an aqueous solution of 5 per cent sodium carbonate and 1.5 per cent sodium chromate at 195 °F for 3 to 5 minutes. The coupons were cut into three parts: one part given treatment and exposed to laboratory atmosphere, one part untreated and stored in desiccator, one part untreated and exposed to laboratory atmosphere.

TABLE IV

Effect of Current Density and Surface Treatment on Aluminum Electroplated from a Bath of Aluminum Chloride, Sodium Chloride, and Chromic Oxide

Bath Composition: 80 per cent Aluminum Chloride, 19.5 per cent Sodium Chloride, and 0.5 per cent Chromic Oxide
Copper Cathode, Aluminum Anode, One Inch Apart

Test No.	Current	Temperature	Current Density	Efficiency		Time	Protective Coating		Plating Results	Corrosion Results of Protected and Unprotected Plate after 24 Hours in Atmosphere
				Cathode	Anode					
	amp	°C	amp/sq ft	%	%	min		amp x time	Color, Density, Uniformity, Ductility	
67	0.50	180	21.8	32.1	168	60	M.B.V.(a)	30	Gray, uniform, ductile, adherent, non-porous.	Both plates became slightly darker.
68	0.25	180	10.9	61.4	214	60	M.B.V.	15	Light gray, but few darker streaks. Ductile, uniform, adherent, non-porous.	Unprotected plate became slightly darker.
69	0.75	180	30.6	17.4	173	60	M.B.V.	45	Gray, uniform, ductile, adherent, non-porous.	Both plates slightly flaked away.
70	0.30	180	14.4	21.3	169	60	None	18	Light gray, uniform, ductile, adherent, non-porous.	Corroded by flaking away.
71	1.0	180	40.2	20.7	197	60	Lacquer(b)	60	Dark gray, uniform, ductile, adherent. Plate burned.	Corroded to base metal.
72	0.10	180	4.02	22.5	167	60	Lacquer	6	Light gray, uniform, ductile, adherent, non-porous.	Lacquer protected plate somewhat from corrosion.

(a) M.B.V. treatment consists of the coupons being immersed in an aqueous solution of 5 per cent sodium carbonate and 1.5 per cent sodium chromate at 195 °F for 3 to 5 minutes. The coupons were cut into two parts; one part was treated and one part untreated. Both parts were then exposed to the atmosphere for 24 hours.

(b) Lacquer treatment consists of coating one-half of the plated coupon with egyptian lacquer, CN 2336, and exposing both the protected and unprotected specimen to the atmosphere.

TABLE V

Effect of Current Density and Surface Treatment on Aluminum Electroplated from a Bath of Aluminum Chloride-Sodium Chloride-Sodium Cyanide

Bath Composition: Four parts Aluminum Chloride and One Part Sodium Chloride. Copper Cathode, Aluminum Anode, One Inch Apart

Test No.	Conc. of Sodium Cyanide	Current	Temperature	Current Density	Efficiency[a]		Time	Protective Coating[b]		Plating Results	Corrosion Results of Protected Plate after 24 Hours in Atmosphere
					Cathode	Anode					
	wt %	amp	°C	amp/sq ft	%	%	min		min x amp	Color, Density, Uniformity, Ductility	
81	0.1	0.10	180	7.46			60	Lacquer	6	Gray, continuous, ductile, adherent.	Lacquer did not help.
82	0.1	0.20	180	15.35	17.5	166	60	Lacquer	12	Gray, continuous, smooth, adherent. Plate with lacquer cracked on bending.	Both plates same. Flaked off in spots.
83	0.1	0.30	180	22.50	18.2	131	60	Lacquer	18	Light gray, smooth, adherent, uniform, ductile.	Spots corroded to base metal.
84	0.1	0.40	180	34.00	6.74	154	60	Lacquer	24	Gray, powder, non-porous, smooth, adherent, uniform. Plate peeled on bending.	Plates remained uniform color.
85	0.1	0.50	180	41.00	11.20	130	60	Lacquer	30	Light gray, uniform, non-porous, adherent, ductile.	Slight corrosion.
86	0.1	0.50	180	18.65	15.6	132	60	Lacquer	30	Light gray, uniform, smooth, adherent, ductile.	Same
87	0.1	0.60	180	56.70	16.4	117	60	Lacquer	36	Gray, discontinuous, rough, plate possibly burned.	Corroded to base metal.
88	0.5	0.15	180	14.9	35.1	277	60	Lacquer	9	Dark gray, powder, discontinuous.	Same
89	0.5	0.25	180	24.8	19.8	208	60	Lacquer	15	Same	Same
90	0.5	0.35	180	32.0	3.82	223	60	Lacquer	21	Same	Same
91	0.5	0.45	180	34.5	1.20	186	60	Lacquer	27	Same	Same
92	0.5	0.55	180	42.2	0.81	260	60	Lacquer	33	Same	Same

(a) Efficiency calculated on basis of deposition and solution of one-third gram atom of aluminum per faraday.

(b) Lacquer treatment consists of applying a coat of egyptian metal lacquer CN 2336.

TABLE VI

Effect of Current Density and Surface Treatment of Aluminum Electroplated from a Bath of Aluminum Chloride, Sodium Chloride, and Vanadium Pentoxide

Bath Composition: Four Parts Aluminum Chloride and One Part Sodium Chloride. Copper Cathode, Aluminum Anode, One Inch Apart

Test No.	Vanadium Pentoxide Concentration	Current	Temperature	Current Density	Efficiency		Time		Protective Coating[a]	Plating Results	Corrosion Results of Protected Coupon after 24 Hours in Atmosphere
					Cathode	Anode					
	wt %	amp	°C	amp/sq ft	%	%	min	min x amp		Color, Density, Uniformity, Ductility	
106	0.1	0.10	180	8.52	99	790	60	6	Lacquer	Light gray, shiny, ductile, continuous.	Formed powder on surface but surface remained covered.
107	0.1	1.00	180	76.52	74.3	596	60	60	Lacquer	Same	Same
108	0.1	0.55	180	47.30	8.9	198	60	33	Lacquer	Same	Same
109	0.1	1.00	180	84.80	0.21	258	60	60	Lacquer	Same	Same
110	0.1	0.55	180	41.80	10.6	256	60	33	Lacquer	Same	Same
111	0.1	0.10	180	7.81	51.5	273	60	6	Lacquer	Same	Same
112	0.1	0.75	180	58.60	27.3	476	60	45	Lacquer	Same	Same
113	0.1	0.33	180	27.30	20.7	137	60	20	Lacquer	Same	Same
114	0.1	0.20	180	17.00	18.3	88	15	3	Lacquer	Light gray, ductile, very thin plate.	Corroded in spots to base metal while covered with lacquer.
115	0.1	0.40	180	34.00	4.60	180	15	6	Lacquer	Same	Same
116	0.1	1.20	180	103.00	-	430	15	18	Lacquer	Shiny, bright, ductile, very thin plate.	Same
117	0.1	2.30	180	197.00	6.90	105	15	35	Lacquer	Same	Same
118	0.1	2.80	180	240.00	3.78	270	15	42	Lacquer	Seems to be best plate, very thin plate. Bright, very good.	Plate remained on this specimen the longest time.
119	0.1	3.00	180	275.00	2.03	302	15	45	Lacquer	All plates below here seemed to be slightly burned. Very thin plate, bright.	Corroded to base metal while covered with lacquer.
120	0.1	4.00	180	366.00	-	360	15	60	Lacquer	Same	Same
121	0.1	5.00	180	458.00	0.01	280	15	75	Lacquer	Same	Same
122	0.1	6.00	180	509.00	-	402	15	90	Lacquer	Same	Same

(a) The whole coupon was coated with egyptian lacquer, CN 2336, and exposed to the atmosphere.

Sample Calculations

Samples of the type calculations made in this investigation are presented in this section.

Calculation of Cathode Efficiency. The current used in this investigation was measured using a copper coulometer which was considered to be one hundred per cent efficient. In these calculations it was assumed that one-third gram atom of aluminum was dissolved or plated per faraday. The calculations used are for test 25, Table I-A, page 86.

$$\text{Theoretical equivalents used} = \frac{\text{gain in wt. of coulometer, gm}}{\text{equivalent wt. of copper, gm}}$$

$$\text{Theoretical equivalents used} = \frac{0.4119}{31.8} = 0.0129 \text{ gm}$$

$$\text{Actual equivalents used} = \frac{\text{gain in wt. of cathode, gm}}{\text{equivalent wt. of aluminum, gm}}$$

$$\text{Actual equivalents used} = \frac{0.0554}{9} = 0.00615 \text{ gm}$$

$$\text{Cathode efficiency} = \frac{\text{actual equivalents used}}{\text{theoretical equivalents used}} \times 100$$

$$\text{Cathode efficiency} = \frac{0.00615}{0.0129} \times 100 = 47.4 \text{ per cent}$$

IV. DISCUSSION

The discussion of the investigation of the effects of addition agents upon the physical properties of aluminum plated from a bath of aluminum chloride and sodium chloride includes the results obtained, recommendations, and the limitations imposed upon this experimental work.

Discussion of Results

The effects of addition agents upon the electrodeposition of aluminum from a fused halide bath has been noted in the tables of experimental results, but lack of a quantitative method of expressing these effects necessitates certain discussion of the observations.

Deposition of Aluminum from a Bath Containing Aluminum Chloride-Sodium Chloride-Lithium Chloride. First attempts to electrodeposit aluminum were made with a bath of 75 per cent aluminum chloride, 20 per cent sodium chloride and 5 per cent lithium chloride. The bath was operated at 356 °F and several plates of aluminum were obtained on copper. However, most of the plates were not uniform, but were brittle, porous, and corroded completely away within a day or two. Several of the

plates could be washed or scraped off with a dull blade. The current densities used ranged from approximately 3 to 30 amperes per square foot.

The cathode efficiencies were low, ranging from 0 to 4 per cent, but at a current density of 12.8 amperes per square foot the cathode efficiency was about 60 per cent. However, this high efficiency occurred only twice while plating 24 plates. Most of the plates obtained corroded away within a few days. Several of the plates were treated by the Alrock process[67] to form an oxide coating, but this failed to prevent severe corrosion.

Electrodeposition from a) Aluminum and Sodium Chloride Bath. For electrodeposition from a bath of 80 per cent aluminum chloride and 20 per cent sodium chloride, a current density of 10.6 amperes per square foot was used in electroplating the copper coupons in the series numbered 24 to 28, Table I-A, page 86, and the plating results were nodular and porous, but ductile and continuous. The operating temperature was 356 °F and under these conditions there was little difference in any of the plates except plate 25 which was of a slightly darker color. This was probably caused by impurities in the bath.

The best current density was found by varying the current density from 6.0 to 30.0 amperes per square foot. Plates 43

and 44 obtained at 8.0 and 8.5 amperes per square foot, respectively, were very poor. Since these were the first two coupons obtained from the new bath, impurities in the bath may account for the poor plates. Also, the cathodes used were not pickled properly. The plates obtained were easily scaled away. The current density range of 10.2 to 24.2 amperes per square foot gave the most adherent and uniform plates of the series 43 to 48. However, the plates were nodular.

Plate 61 was a poor plate as it was again the first to be plated from a new bath. The plates of series 62 to 66 were continuous, ductile, and nodular. Plate 62 obtained at a current density of 24.0 amperes per square foot, was the best plate. However, it had a slightly bright appearance around the edges, the middle being dull. This was a duplicate of series 43 to 49.

To study the effect of temperature, plates 77 to 80, Table I-B, page 87, were plated at a current density of approximately 6.95 amperes per square foot, time of operation being 30 minutes, while a variation in temperature of 356 to 410 °F was used. The optimum temperature seemed to be 356 °F because a cathode efficiency of 59.7 per cent was obtained, which is the highest for the plates 77 to 80.

Optimum Time of Plating. To determine the optimum time of plating, a series of runs, 93 to 99, Table I-B, page 87, was made. The temperature was kept constant at 356 °F and the current density was 14.9 amperes per square foot. The current density used in obtaining plates 100 to 104 was 8.7 amperes per square foot and a temperature of 356 °F, while again the operating time was varied from 90 to 15 minutes. Attempts were made to correlate the time of operation versus cathode efficiency but this could not be done. However, a specific trend could be found. In both cases, the cathode efficiency decreased as the time of operation increased, and the efficiency always was higher for any specific time for a current density of 14.9 amperes per square foot. On the basis of uniformity, luster and ductility, the plates obtained at a current density of 14.9 amperes per square foot, were better than those obtained at 8.7 amperes per square foot. The plates obtained up to 60 minutes at 14.9 amperes per square foot were good, but on longer deposition, the deposit flaked off.

Effects of Addition of Lead Chloride. The aluminum plate obtained from a bath containing 0.5 weight per cent lead chloride in a bath of four parts aluminum chloride and one part sodium chloride (plates 29 to 35, Table II, page 88, showed

some improvement over the plates obtained from the bath of aluminum and sodium chloride alone. The plates were obtained using a current density ranging from 7.5 to 14.6 amperes per square foot, and they varied in color (gray) with the darkest color being obtained at a current densith of 14.6 amperes per square foot. All plates were adherent, ductile, and uniform. All plates indicated that a smoothing effect was obtained when lead chloride was used as an addition agent at a concentration of 0.5 weight per cent.

The aluminum plate obtained from a bath containing 1.0 weight per cent lead chloride (plates 36 to 42) were all light gray in color but none possessed a shining appearance although the adherence of the plate to the base metal was good and the plates could have been polished to a luster. The plates could not be scraped from the base metal with a dull blade. A current density ranging from 9.17 to 13.1 amperes per square foot was used so that the current density used in obtaining the best plate in the series 29 to 35 could be compared to this series of 36 to 42. The light gray color of plates 36 to 42 compared favorably with the 29 to 35 series, while the best plate was obtained in the former series using a current density of 13.3 amperes per square foot (plate 32), the best plate in the latter series was obtained using a current density of 9.2 amperes per square foot (plate 42). Plate 32 was apparently better than

plate 40. Thus, a better plate is obtained at a sacrifice in speed of plating.

The corrosion of the 29 to 35 series was less than series 36 to 42 over an extended period of two months. The later series showed variations in corrosion while plates 32 and 40 showed less corrosion than the remaining plates in either series.

The cathode efficiencies of the bath containing 0.5 weight per cent lead chloride ranged from 52.5 to 76.2 per cent while the efficiencies of the bath containing 1.0 weight per cent lead chloride ranged from 42.3 to 56.8 per cent. These efficiencies are comparable to those obtained by others[13] when no lead was added.

It was found that at either concentration of lead chloride the plates were smoother than plates obtained with no lead present.

Aluminum Thiocyanate Addition Agent. The aluminum thiocyanate used had been stored under nitrogen in order to prevent contamination. A bath containing 0.5 and 1.0 weight per cent aluminum thiocyanate was used to obtain plates 50 to 56 and 57 to 60, respectively. In this discussion each remark refers to the plates obtained using either concentration of the addition agent as all of the plates obtained were poor. The

aluminum was deposited as a dark powder which could be easily washed or scraped off. In cleaning the plate after removal from the plating bath, the powder could have been washed away. However, care was taken to avoid loss. Removal of some of the powder could be the reason for the low cathode efficiencies of 6.9 to 20.6 amperes per square foot.

Since the deposit was a powder, to make sure that it contained aluminum, it was tested using a five per cent caustic soda solution, in which it dissolved readily.

Apparently, the presence of thiocyanate in the bath results in poorer plates than when no addition agent is present.

Chromic Oxide Addition Agent. The addition of chromic oxide to the bath in the concentration of 0.5 weight per cent gave plates (series 67 to 72), Table IV, page 90, of a light gray color. The deposits were smooth, uniform, ductile, and adherent. The adherence was tested by scraping with a dull blade while the ductility was tested by bending the plates 180 degrees around a rod of one-eighth inch diameter. All plates were uniform but the plate obtained using a current density of 40.2 amperes per square foot turned dark and was burned. Although all plates were good, those made with the lower current densities were smoother than the ones made at the higher current

densities. The nodules increased as the current density increased, but the roughness never became excessive.

The current density varied from 4.14 to 40.2 as the efficiency varied from 20.7 to 32.1, but the two did not vary proportionally.

The best plate of the series 67 to 72 is plate 70 which was obtained using a current density of 14.4 amperes per square foot for 60 minutes, while the temperature of the bath was held constant at 356 °F.

The plates were not bright but the corrosion over a period of two months did not eat to the base metal. It appears that the presence of chromic oxide in the aluminum plating bath imparts considerable corrosion resistance to the resulting plate, but the speed of plating cannot be increased.

Sodium Cyanide Addition Agent. Sodium cyanide was used at 0.1 weight per cent and the plates 81 to 87, Table V, page 91, were obtained while a current density varying from 7.46 to 56.7 amperes per square foot was used. Plate 87, which was obtained using a current density of 56.7 amperes per square foot, was dark and appeared to be burned while plate 85 was light in color, adherent, ductile, and uniform, and was plated at 41.0 amperes per square foot. Plate 85 appeared to be the best plate of the group. Plates 82, 83, and 84, obtained using

15.35, 25.5, and 34.0 amperes per square foot current density, respectively, cracked and scaled when tested for ductility.

The cathode efficiencies for plates 85 and 86 were 11.2 and 15.6 per cent, respectively. This is much lower than is desirable for efficient electroplating. All plates except 85 and 86 could be scraped off using a dull blade while the above pair could only be scratched.

Plates 88 to 92 were obtained using the same range of current densities, 14.9 to 42.2 amperes per square foot, and a concentration of 0.5 weight per cent sodium cyanide. Plates 88 to 89 are lighter in color than the remaining plates which seem to be burned. As the current density increases from 14.9 to 42.2 amperes per square foot, the cathode efficiencies decrease from 35.1 to 0.81 per cent. The most desirable plate in this series is 89 which was obtained using a current density of 24.8 amperes per square foot.

The addition of sodium cyanide to the aluminum bath results in low cathode efficiency and does not improve the quality of the plate.

Vanadium Pentoxide Addition Agent. Vanadium pentoxide is reddish and of rhombic crystalline form. A concentration of 0.1 weight per cent was used in a bath of 80 per cent aluminum

and 20 per cent sodium chloride. Plates 106 to 113, Table VI, page 92, were electroplated for one hour while the current density was changed for each plate, the lowest and highest current density being 8.52 and 84.8 amperes per square foot. Over this wide range of current densities the physical properties of the aluminum plate remained practically constant. There was no variation in color, ductility, uniformity, or porosity. All plates were very ductile, being tested by bending several times 180 degrees and back to its original position. None of the plates approached a bright appearance although all were light gray.

Plates 114 to 122 were also plated from a bath containing 0.1 weight per cent vanadium pentoxide. The duration of electrolysis was 15 minutes, but the current densities imposed upon each plate were much greater than in the preceding series. The current density varied from 17.0 to 509.0 amperes per square foot. Plates 114 and 115 were light gray in color and were obtained at 17.0 and 34.0 amperes per square foot.

The current density was stepped up to 509 amperes per square foot and plate 122 obtained at this current density was mirror bright. The intermediate plates were also mirror bright; however, plate 118 obtained at a current density of 240 amperes

per square foot was the most bright. Plate 118 also resisted corrosion longer than any other of the series.

Vanadium pentoxide as an addition agent gave the best results in this investigation; however, there are several serious drawbacks. The plates obtained at current densities over 100 amperes per square foot were very bright, but they were also very thin and in one month corroded in spots to the base metal. Also, the cathode efficiencies were at times negative which may be a result of the cathode being corroded by the bath before being plated by aluminum. Further work should be done investigating the use of vanadium pentoxide as addition agent before the degree of improvement can be evaluated.

Anode Corrosion. The corrosion of the aluminum anodes was severe. The anode efficiency was always in excess of 100 per cent and ran as high as 500 per cent at times. The efficiency usually was in the neighborhood of 200 to 400 per cent. This high efficiency is an indication that there is a chemical reaction between the constituents of the bath and the anode. This high efficiency was encountered during all of the tests.

Protective Measures. The aluminum plates were protected from corrosion by applying a solution which gave the aluminum an oxide finish. An "Alrok"[67] process specifies immersion of the work in a solution of 2 per cent sodium carbonate and 0.1 per

cent potassium dichromate at a temperature of 151 °F for a period of 20 minutes. The pores of the oxide film are sealed by subsequent immersion in a solution of 5 per cent potassium dichromate, and the parts are rinsed. This treatment was applied to plates 25 to 35 with little success in preventing corrosion.

The modified Bauer-Vogel[67] process was also tried on plates 36 to 69. This treatment involves immersion of the work in an aqueous solution of 5 per cent sodium carbonate and 1.5 per cent sodium chromate at 194 °F for a duration of 3 to 5 minutes, then rinsing in water. This forms a slate gray surface. The plate treated by this bath did not show any reduction in corrosion as compared to plates not treated.

As plates 24 to 90 were divided into three sections, one section of the plates was placed in a desiccator in order to keep the plate out of contact with the moisture in the atmosphere. The drying agent in the desiccator was phosphorous pentoxide. These precautions failed to inhibit the rate of corrosion.

Another measure taken was that of applying metal lacquer to a series of plates. This application should have prevented atmospheric contact, thereby giving the plate a better chance to remain intact. Again, the results were negative; the plate was corroded, in some cases even to the base metal. Apparently,

corrosion of the aluminum plate does not require presence of moisture, and is probably due, as has been pointed out previously, to aluminum chloride absorbed in the plates.

Limitations

This investigation was carried out under the following conditions:

Plating Cell. The plating cell consisted of a pyrex 1000-milliliter beaker fitted with a plywood lid covered with asbestos. The anode and cathode were one-inch apart.

Direct Current. The electroplating was performed using direct current only, at a maximum of 30 volts.

Bath Composition. Plates 1 to 25 were produced using a bath of 75 per cent aluminum chloride, 20 per cent sodium chloride, and 5 per cent lithium chloride. A bath of 80 per cent aluminum chloride and 20 per cent sodium chloride was used to obtain plates 24 to 28, 43 to 49, 61 to 66, and 93 to 104.

The latter bath composition was also used in conjunction with 0.5 and 1.0 weight per cent lead chloride, 0.5 and 1.0 weight per cent aluminum thiocyanate, 0.5 weight per cent chromic oxide, 0.1 and 0.5 weight per cent sodium cyanide, and 0.1 weight per cent vanadium pentoxide.

Current Density. Most of the investigation was performed using a current density varying from 5 to 30 amperes per square foot. However, higher current densities, 8.52 to 509 amperes per square foot, were used in plating series 106 to 122.

Time of Operation. The majority of these electrodepositions were of one hour duration. However, plates 73 to 80 and 93 to 104 were obtained with time intervals from 15 to 90 minutes. Fifteen minutes operation time was used in obtaining plates 114 to 122.

Temperature. Operating temperature was 356 °F for all cases except series 77 to 80 which were performed at a temperature varying from 356 to 410 °F.

Recommendations

The recommendations which evolved from observations made during this investigation of electroplating aluminum from a fused halide bath are as follows:

Modification of Equipment. The equipment used in this investigation should be modified into an air-tight apparatus through which some inert gas could be introduced for the purpose of shielding the melt from the atmosphere. It is also recommended that a method be devised for the purpose of agitating the bath, so that a study might be made concerning agitation effects upon the electrodeposition. This might be done by bubbling an inert gas through the bath.

Further Vanadium Pentoxide Studies. The possibility of the use of vanadium pentoxide as an addition agent in the aluminum and sodium chloride bath should be investigated extensively. In this investigation, the smoothest and brightest plate was obtained at a current density of 240 amperes per square foot with a time of operation of 15 minutes. This leads to the recommendation that studies should be made in which the time of operation is varied while using various current densities, probably above 200 amperes per square foot. This addition agent promises to permit increase in speed of aluminum

plating which is a necessity if this coating is to compete with commercial tin plate.

Reverse Current Studies. Since aluminum can be plated from a fused halide bath containing aluminum chloride, it is recommended that a study be made of the effect of periodic-reverse current while electrodepositing aluminum. Addition agents should also be studied while using the periodic-reverse current system of plating.

Superimposed Alternating Current Studies. Previous investigators of other metal electro-plates have superimposed alternating current on direct current with commendable results. This should also be studied during electrodeposition of aluminum. Also, its effect on electrodeposited aluminum from baths containing addition agents should be studied.

Other Addition Agents. Since vandium pentoxide considerably improved the aluminum plate, it would be well to investigate the effect of compounds of other elements which are in the neighborhood of vanadium in the periodic chart.

Effect of Other Compounds. Now that the effect of addition of a few of the metallic compounds on the electrodeposition of aluminum have shown promise, the effect of some other metallic compounds, such as chromium trioxide, ferric oxide, and nickel chloride, at different concentrations, should be studied.

Further Study of Lead and Chromium Compounds. The effect of lead chloride and chromic oxide at different concentrations and temperatures as well as mixtures of the two should be investigated. Since one improves smoothness and the other improves corrosion resistance, the addition of both to the bath may combine the individual improvements.

Effect of Treating Plated Samples. Since a small concentration of aluminum chloride in or on the surface of the coupon increases the rate of corrosion, a study of the effect of treating plated samples, possibly by heat or chemical soaking, to remove the aluminum chloride and improve the corrosion resistance of the plate, should be made.

Investigation of Methods of Aluminum Plating on Other Metals. An investigation of bath composition and effect of addition agents on aluminum electroplated on steel, die castings, magnesium, and aluminum and other metals, should be made.

Base Metal Surface Pretreatment. In electroplating the base metal is always pretreated, and it would be important to note the effect of pickling, blasting, abraiding, and amalgamating with zinc and mercury, on the adherence of the plate.

Temperature Studies. The effect of temperature on the properties of the plate, such as density, uniformity, adherence,

and ductility, should be studied while using a bath employing addition agents.

Reduction of Fuming. The noxious, copious fumes from the bath should be reduced, possibly by studying the effects of certain agents which may combine with the aluminum chloride, forming a complex with it. Such a substance is dibutyl amine.

V. CONCLUSIONS

A. From a study of plating aluminum from a bath of 75 per cent aluminum chloride, 20 per cent sodium chloride, and 5 per cent lithium chloride, using an anode of "3S" aluminum and a copper cathode, it was concluded that:

1. The cathode efficiency for plating aluminum on copper from a bath containing lithium chloride was less than the efficiency obtained from the melt containing only 80 per cent aluminum chloride and 20 per cent sodium chloride.

2. All plates of aluminum obtained corroded to the base metal within 24 hours after deposition.

B. From a study of plating aluminum from a melt of 80 per cent aluminum chloride and 20 per cent sodium chloride, using an anode of "3S" aluminum and a copper cathode, it was concluded that:

1. The optimum current density for plating was found to be 21.3 to 24.0 amperes per square foot.

2. The highest cathode efficiency, 59.7 per cent, was realized at a temperature of 356 °F. Also, the best corrosion resistance was obtained at an operating temperature of 356 °F.

3. The cathode efficiency decreased at the time of operation increased from 15 to 90 minutes.

4. The plates obtained up to 60 minutes at 14.9 amperes per square foot were adherent but on longer deposition, they flaked off.

C. The following conclusions were reached from a study of plating aluminum on copper from a bath of 4 parts aluminum chloride, and one part sodium chloride at a temperature of 356 °F, with lead chloride as an addition agent at 0.5 and 1.0 per cent concentration:

1. Lead chloride, used as an addition agent, produced a decided smoothening effect. However, at a concentration of 0.5 per cent lead chloride, smoother plates were obtained than when a concentration of 1.0 per cent was used.

2. It was found that the current density used in producing the smoothest of the plates obtained, when lead chloride at a concentration of 0.5 per cent was used, was 13.3 amperes per square foot.

3. A lower current density, 9.2 amperes per square foot, was required to obtain the smoothest plate when lead chloride was used at 1.0 per cent.

4. The concentration of 0.5 weight per cent lead chloride gave smoother plates than those obtained when a concentration of 1.0 weight per cent was used.

5. The corrosion rate was less when a concentration of 0.5 per cent lead chloride was used than when a concentration of 1.0 weight per cent lead chloride was used.

6. The cathode efficiencies of the bath containing 0.5 per cent lead chloride ranged from 52.5 to 76.2 per cent which were higher than the cathode efficiencies of 42.3 to 56.8 per cent that were obtained using 1.0 weight per cent lead chloride.

7. At either concentration of lead chloride, the plates were smoother than plates obtained when no lead chloride was present.

D. The conclusions drawn from a study of plating aluminum on copper from a bath of four parts aluminum chloride, one part sodium chloride, 356 °F temperature, and two concentrations of aluminum thiocyanate, 0.5 and 1.0 weight per cent, were as follows:

1. All deposits obtained under the above conditions were a dark powder which could be easily washed or scraped off.

2. The low cathode efficiency may be the result of poor adherence of the powder.

3. The presence of thiocyanate at 0.5 and 1.0 per cent concentration in the bath is detrimental to the quality of the plates obtained when no addition agent is present.

E. From a study using chromic oxide at a concentration of 0.5 per cent in a bath of four parts aluminum chloride and one part sodium chloride for plating on copper, at a temperature of 356 °F, the conclusions reached were:

1. Chromic oxide had a smoothening effect when used at 0.5 per cent concentration.

2. The optimum current density was found to be 14.4 amperes per square foot.

3. All plates were uniform, ductile, and adherent.

4. The presence of chromic oxide in the aluminum plating bath imparts corrosion resistance to the resulting plate.

F. Sodium cyanide, used at concentrations of 0.1 and 0.5 weight per cent, in a bath of four parts aluminum chloride and one part sodium chloride at a temperature of 356 °F for plating on copper, resulted in the following conclusions:

1. The concentration of 0.1 per cent sodium cyanide gave smoother deposits than when 0.5 per cent was used.

2. While using a concentration of 0.1 per cent sodium cyanide, the operating current density producing the smoothest and most adherent plate for the series was 41 amperes per square foot.

3. Cathode efficiencies were increased by 15 per cent at 0.1 per cent as compared to that at a concentration of 0.5 per cent sodium cyanide.

4. The addition of sodium cyanide to the aluminum plating bath does not improve the quality of the plate.

G. When vanadium pentoxide was used at a concentration of 0.1 per cent while plating aluminum on copper from a bath of four parts aluminum chloride and one part sodium chloride at 356 °F, the conclusions reached were as follows:

1. Current densities of 9 to 84 amperes per square foot gave dull gray plates of aluminum which were uniform and ductile.

2. High current densities, between 100 and 500 amperes per square foot, formed mirror bright surfaces, which were very thin.

3. At current densities of 9 to 84 amperes per square foot, the cathode current efficiencies decreased from 51 to below 5 per cent as the current density increased.

4. Cathode efficiencies were always below 5 per cent and sometimes negative for current densities of 100 to 500 amperes per square foot.

5. The aluminum deposited in this series at current densities from 9 to 84 amperes per square foot were more resistant to atmospheric corrosion than any other plates prepared.

6. Vanadium pentoxide gave deposits with the best ductility and corrosion resistance of any prepared in the presence of any addition agents used in this investigation.

H. The following conclusions were drawn concerning anode corrosion during the electrolysis and concerning the measures taken to protect the plates from atmospheric corrosion:

1. The anode corrosion efficiency was always in excess of 100 per cent, and usually was in the neighborhood of 200 to 400 per cent. These high efficiencies were probably the result of chemical corrosion between the bath and anodes superimposed onto the electrolytic corrosion.

2. None of the protective precautions, Alrok process[67], modified Bauer-Vogel process[67], or lacquering, helped retard the corrosion rate.

VI. SUMMARY

It was the purpose of this investigation to study the effect of addition agents on the electrodeposition of aluminum on copper from a fused bath of 80 per cent aluminum chloride and 20 per cent sodium chloride. The agents added and the concentrations studied were lead chloride, 0.5 and 1.0 per cent; aluminum thiocyanate, 0.5 and 1.0 per cent; chromic oxide, 0.5 per cent; sodium cyanide, 0.1 and 0.5 per cent; and vanadium pentoxide, 0.1 per cent.

The electrolysis was carried out in a 1000-millimeter beaker in a furnace heated by a 1000-watt element. The plating cell was fitted with a tight lid through which the electrodes could be adjusted.

The optimum current density range while plating from a bath of 80 per cent aluminum chloride and 20 per cent sodium chloride was 8.2 to 21.0 amperes per square foot. When aluminum was electroplated from a bath of 75 per cent aluminum chloride, 20 per cent sodium chloride, and 5 per cent lithium chloride, the plates did not adhere to the base metal. Also, the plates corroded to the base metal in a few days. The optimum temperature was found to be 356 °F.

Lead chloride, when added at a concentration of 0.5 and 1.0 per cent, produced a smoothening effect. The plates obtained at

the former concentration were smoothest. However, the plates were rather easily corroded by the atmosphere. In contrast, chromic oxide at 0.5 per cent did not improve the smoothness of the plate but did improve considerably the corrosion resistance of the plate. Addition of aluminum thiocyanate caused formation of a black powder which was non-adherent. Sodium cyanide at 0.1 and 0.5 per cent did not improve the ductility and corrosive resistance of the plate to any extent. Vanadium pentoxide gave corrosive resistance and ductility to the deposit at lower current densities of 10 to 100 amperes per square foot and thin mirror plates at current densities between 100 and 500 amperes per square foot. The vanadium pentoxide was used at a concentration of 0.1 weight per cent.

In attempts to protect the plates from corrosion, applications of chemical treatment to the aluminum plate failed, as also did an application of lacquer.

The results obtained with the addition of lead chloride, chromic oxide, and vanadium pentoxide warrant further study to determine optimum operating conditions and limits.

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