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I. INTRODUCTION

There have been many previous and present day applications of pulsed superimposed alternating current on direct current to the field of electrochemistry. Electro-reduction, electroplating, and electrolysis are some of the phases of electrochemistry to which this special type of electrical energy has been applied.

Although inorganic and organic chemical syntheses have been the principal methods of preparation for paint pigments, some types of pigments have been prepared by means of electrolysis. Lead chromate is an important example. As yet, no extensive work has been done on the production of lead chromate utilizing alternating current superimposed on direct current or periodically reversed direct current as the sources of electrical energy.

In the electrolytic preparation of lead chromate, direct current has been used. This practice required that the lead anode be covered with some material, usually linen, to prevent it from becoming coated with lead chromate. The deposition of lead chromate on the anode soon rendered that electrode passive, thereby causing current flow to cease, which in turn lowered the yield of lead chromate. Since the current flow is stopped by the deposition, the operation is a batch process. In addition to low yield and batch production, non-uniform color variations have been incurred in the final product when simple direct current production was employed.

It was the purpose of this investigation to study the effect of varying the direct to reverse time ratio of periodically reversed direct current from 1.0 to 20.0 on the production of lead chromate at an average anode current density of 0.0058 amperes per square centimeter, and to study the effect of 60 and 510 cycles per second from 0.00079 to 0.01 amperes per square centimeter of superimposed alternating current on the yield of lead chromate prepared by the electrolysis of a bath containing potassium chromate and sodium nitrate between lead electrodes.

II. LITERATURE REVIEW

This portion of the investigation is concerned with a review of the existing literature pertaining directly to the research problem. The section includes the following headings: properties of lead chromate, methods of preparing lead chromate, electrolysis with periodically reversed direct current, and electrolysis with alternating current superimposed on direct current.

Properties and Uses of Lead Chromate

Both chemical and physical properties are given in this section.

Lead chromate⁽⁵⁰⁾ (chrome yellow, crocoite), PbCrO_4 , having a molecular weight of 323.22 is a bright yellow crystalline powder whose melting point is 844 °C and specific gravity is 6.12. Medium^(25, 29) chemically pure lead chromate has a specific gravity of 5.96. Medium or normal lead chromate is probably the most widely used color in the chemical pigment industry. Chrome yellows^(22, 25) are available in a wide range of shades from a very light greenish yellow known as primrose yellow, to the reddish shade medium yellow, followed by the chrome oranges. The lightness of the shades varies from shade 00, of the hundred part color scale, to almost 19⁽⁷¹⁾. The most widely commercially acceptable medium yellows will contain approximately 95 per cent normal lead chromate. Chrome yellows are not alkali or acid fast

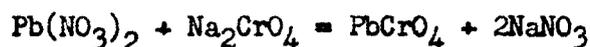
and they will not withstand extremely high baking temperatures without discoloration. Although chrome yellows discolor at elevated temperatures, they are known for possessing excellent light fastness at normal temperatures^(22, 60). Lead chromate in the form of chrome yellows is used in paints and enamels, also kalsomine, but not in casein paints or finishes that are to be applied to surfaces that are alkaline, such as cement or stucco. Being lead pigments, chrome yellows will blacken in the presence of sulfides⁽²²⁾. Medium chrome yellow is actually the best money value primarily because it carries a maximum amount of normal lead chromate. The excellent covering power⁽⁵⁰⁾ of lead chromate makes it useful in manufacturing printing inks as well as in the protective coating industry. Upon heating above the melting point, lead chromate decomposes giving off oxygen. On this account, the compound is useful in analytical work for organic combustions.

Methods of Preparing Lead Chromate

This section deals with both chemical and electrochemical methods of preparing lead chromate. Advantages and disadvantages of existing processes are emphasized. The information given here on chemical or inorganic processes is presented for comparison with electrochemical methods.

Chemical Methods of Preparing Lead Chromate. These paragraphs deal with the production of lead chromate by inorganic precipitation methods. An attempt will be made to point out the advantages and disadvantages of such processes.

Precipitation of Lead Chromate from a Solution of a Soluble Lead Salt and a Solution of Sodium or Potassium Chromate or Dichromate. The large scale preparation^(50, 66) of lead chromate is usually carried out continuously by reacting lead acetate or nitrate with a solution of sodium chromate. The equation for the reaction is:



The process must be carried out under carefully controlled conditions of concentration, temperature, and hydrogen-ion concentration. Sodium sulfate is usually added to the reaction mixture to co-precipitate lead sulfate, the amount depending on the particular shade of yellow desired and varying from about 2 to 50 per cent lead sulfate in the

finished product. The lead sulfate acts not only as a diluent to produce lighter shades such as primrose yellow, but influences the crystal characteristics of the lead chromate such that it makes it more resistant to darkening from sulfides in the air. Being of high specific gravity, the lead chromate produced in this manner settles rapidly, and may be washed by decantation without trouble.

Industrially, the lead chromate - sodium nitrate slurry passes through a series of counter-current thickeners and into a continuous centrifuge and is dried at a low temperature.

Vauquelin⁽⁶⁷⁾ and Berzelius⁽¹⁴⁾ obtained normal lead chromate by precipitation from a solution of lead nitrate or acetate by the addition of potassium chromate or dichromate. The usual precipitate is yellow and, according to Anthon⁽¹⁰⁾, the color is paler when the lead chromate is precipitated from a cold solution. Precipitation from a solution of a higher temperature would produce a darker product. According to Vauquelin⁽⁶⁷⁾, a trace of potassium chromate in the precipitate also darkens the color. It has been found⁽⁶⁶⁾ that alkali in the form of sodium carbonate added to the reaction mixture will produce deeper orange shades of lead chromate, and acid as an additive will produce lighter shades.

Dede and Bonin⁽²⁴⁾ pointed out that the precipitation of lead chromate from a solution of a soluble lead salt and potassium chromate is incomplete in acetic acid solution if much chloride is present. This point was clarified somewhat by Karaoglanoff and Sagortscheff⁽⁴⁷⁾ who found that with lead chloride as the soluble lead salt, some $Pb_2Cl_2(CrO_4)$ is formed.

In precipitating the mixed sulfate-chromate pigment it is important to have an excess of sodium chromate because lead sulfate would then react to form lead chromate⁽⁶⁶⁾.

Precipitation of Lead Chromate by the Reaction of Chromic Acid and a Sparingly Soluble Lead Compound in the Presence Water and a Control Agent. Harshaw⁽³⁶⁾ patented a process for preparing lead chromate by the addition of a chromic acid solution to a mixture of a sparingly soluble lead compound and water. An addition or control agent was also used in the reaction mixture to render the sparingly soluble lead compound more soluble. To cite an example: 69 parts by weight of litharge were stirred into a slurry with 400 parts of water by weight, and one part of acetic acid was added. An 8 per cent solution of chromic acid was gradually added to the slurry and lead chromate was precipitated. Lead carbonate or basic lead carbonate may be used in place of lead oxide as the sparingly soluble lead compound, and nitric acid, hydrofluoric acid, fluo-boric acid, fluo-silicic acid, hydrochloric acid, perchloric acid, and formic acid may be used in place of acetic acid as the control or addition agent.

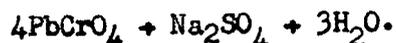
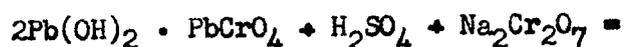
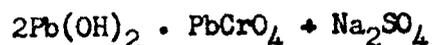
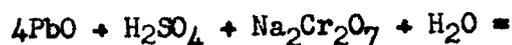
The function of this addition agent is to increase the solubility or reactivity of the lead compound. The chromic acid is added to the slurry at a rate equivalent to the rate of solution of the lead compound. Since the amount of addition agent present determines the amount of the lead compound that dissolves, it is a deciding factor upon which to base the rate of addition of the chromic acid solution. It can be seen that the larger the amount of addition agent used, the faster may be the rate of addition of chromic acid solution, and accordingly the reverse condition applies too.

The shade of the product may be varied by the amount of control agent employed and the temperature. Generally, it is desirable to keep the amount of addition agent low varying from 0.5 to 3.0 per cent as referred to the theoretical amount which could react molecularly with the lead compound. Darker shades of product may be obtained by adding less than the equivalent amount of chromic acid. The lighter shades may be prepared by using sulfuric acid in place of acetic acid yielding lead sulfate in the final product as a color diluent.

Since large quantities of addition agent increase the cost of the process and require more washings of the final product, it is understood that the use of small amounts is more feasible than the use of larger quantities. This being true, it follows that the rate of addition of chromic acid solution must be

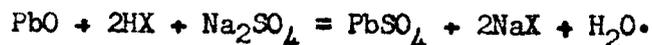
relatively small requiring a longer period of time to produce a given amount of product. This is a distinct disadvantage of the process.

Tarr and Hartford⁽⁶⁴⁾ proposed a process similar to that of Harshaw⁽³⁶⁾, but gave different theories for the formation of the product. Their process was based on the fact that so-called "insoluble" lead compounds are soluble to some extent in water. A mixture of an acid and a soluble chromate or bichromate was added to a rapidly agitated slurry of an insoluble lead compound and water. The rate of addition of the mixture was such that the solution remained alkaline throughout the process. The following equations illustrate the process:



The process is distinguished from a previous process by the fact that the lead sulfate produced at first is not subsequently converted to chromate, but the chromate is formed by further reaction of the unreacted litharge. Also, the process of Tarr and Hartford is differentiated from that of Harshaw by the fact that the acid employed is not used to dissolve the insoluble

lead compound, but is used to control the amount of lead sulfate in the final product. The following equation illustrates this point:



The process has the advantage of employing rather inexpensive raw materials, namely, litharge, sodium bichromate and sulfuric acid. It should be pointed out that the strict control conditions of the process constitute a disadvantage for the Tarr and Hartford⁽⁶⁴⁾ process as well as for the Harshaw⁽³⁶⁾ process.

Other Work. Horning⁽³⁸⁾ prepared lead chromate possessing unusual light fastness and minute particle size. These results were obtained by the addition of a water-soluble inorganic reducing agent to the reaction mixture such as a soluble metal sulfide or polysulfide, or soluble bivalent tin salts. It was found that the amount of reducing agent necessary need not exceed 4 per cent by weight of lead chromate prepared, the pH of the suspension containing the lead chromate being maintained between 4.5 and 6.5 during addition. Soluble metal sulfides or polysulfides employable included those of sodium, potassium, calcium, ammonium, or barium and examples of stannous salts usable included the stannous halides or the stannous sulfates. A quoted method of preparing lead chromate was given as follows: a solution of 165.5 kilograms of lead nitrate in 3500 liters of

water was treated with a solution of 11.2 kilograms of soda ash and subsequently with a solution containing 50 kilograms of sodium bichromate and 17 kilograms of sodium sulfate. A solution of 2 kilograms of stannous chloride was then added followed by 10 kilograms of soda ash and 5 kilograms of sodium sulfate each dissolved in water. The pigment after washing and drying was a light yellow of excellent light fastness.

Horning(38) also pointed out that mixtures of the previously mentioned water-soluble inorganic reducing agents could be used to advantage. The action of the reducing agent was not explained, but it appears that a surface reaction takes place with the lead chromate particles sufficient to alter the shade slightly, but renders the lead chromate highly resistant to light.

Horning(38) also claimed his reducing agents restrained the crystal growth of the lead chromate, thereby producing a product of very fine particle size.

Wagner(70) prepared a higher basic lead chromate of the form $PbCrO_4 \cdot PbO + yPbO$ (where y is equal to at least one). It was found that this new type of mixed salt had a strong passivating effect on iron, and was therefore considered suitable for rust prevention purposes. The preparation of such mixed salts succeeded because the basic lead salts and alkali chromate were reacted with a large excess of free alkali.

Wagner(70) gave in his patent the following example: 52 grams

of potassium chromate were dissolved in a tenfold amount of water and diluted with 3600 cubic centimeters of water. This solution was precipitated in a hot condition with 186 grams of basic lead acetate dissolved in 900 cubic centimeters of water. To this was added 180 grams of caustic potash dissolved in 1800 cubic centimeters of water. The mixture was heated further for 15 to 20 minutes until a uniform orange-brown to red-brown precipitate was formed the composition of which corresponding to the formula, $\text{PbCrO}_4 \cdot \text{PbO} + \text{PbO}$.

Electrochemical Methods of Preparing Lead Chromate. These paragraphs deal with the electrochemical methods of preparing lead chromate. The methods given here are compared with those given previously.

The Luckow Process. Much work has been done on the electrolytic preparation of lead chromate by Luckow. His first experiments are described in a patent⁽⁵³⁾ issued in 1894 which gives the electrolytic methods for preparing white lead, lead chromate, and lead dioxide. For the preparation of lead chromate, lead electrodes were electrolyzed in a solution of sodium chromate. Lead chromate formed on the anode and built up an adhering layer causing the voltage to rise resulting in the evolution of oxygen and the formation of lead dioxide. The adherence of lead chromate to the anode and the production of lead dioxide were both undesirable results, since further

production of lead chromate was curtailed and the black lead dioxide spoiled the color of the final product. These difficulties were overcome by subsequent experiments described in the same patent. The Luckow process employs a 1.5 per cent solution of a mixture of two salts, the anion of one forming a soluble salt with the metal of the anode, and the anion of the other forming the insoluble salt desired. A common example of these two salts is sodium nitrate and potassium chromate, respectively. The salt mixture consisted of 80 parts of the first type, and 20 parts of the second. The anions producing the insoluble lead chromate, being present in a much smaller number than those of the second salt, are soon used up in the layer of solution next to the anode. These anions are replaced slowly because the anions of the salt which forms the soluble salt with the anode carry most of the current on account of their greater number. The lead ions of the anode, on dissolving, do not come in contact with the anions which form the insoluble salt with the anode, but the precipitate is formed at a slight distance from the anode and therefore does not stick, but falls to the bottom of the cell⁽⁵²⁾. Without the addition of the salt whose anion forms a soluble salt with the lead anode, the desired salt, lead chromate can not be produced with a satisfactory yield. For example, in electrolyzing a lead anode in a 0.12 per cent solution of potassium chromate, a mixture of lead peroxide and lead chromate was formed on the anode, but practically no yield

of lead chromate could be obtained⁽⁴⁰⁾. Even when the two previously described salts are in the right proportion, if the solution is too concentrated, the same difficulties are encountered. To further emphasize the effects resulting from the use of a mixed salt electrolyte, a salt mixture used by Luckow is illustrated and the action in the cell explained. Luckow found that if a mixture of sodium chromate and sodium nitrate is electrolyzed between lead electrodes, the anode dissolves steadily and lead chromate is formed abundantly, no longer adhering firmly to the anode. The formation of the first small amount of lead chromate, upon electrolysis, is not sufficient to render the anode passive, but it results in the removal of chromate ions from a thin film of solution adhering to the anode (impoverishment of the chromate ions). After this, lead is free to dissolve as lead nitrate which is soluble. But chromate ions steadily diffuse into the anode film from the bulk solution. They meet lead ions near the outer surface of this film, and lead chromate is formed at a distance from the surface of the anode. Due to this fact, the lead chromate does not form an adherent layer on the anode. Wagner⁽⁶⁹⁾ studied the mechanism of the anodic formation of lead chromate. He stated that, during the electrolysis of a solution of sodium chromate and sodium chlorate between lead electrodes, the boundary layer around the anode contains excess lead ions and flows downward by virtue of its higher density. Lead chromate is formed, in part, at a

distance of 0.01 to 0.1 centimeter from the anode by counter-diffusion of lead ions and chromate ions, and at the lower edge of the anode by mixing of boundary layer and bulk solution.

Work of Le Blanc and Bindshedler. In 1902, Le Blanc and Bindshedler⁽⁵²⁾ performed similar, but more detailed studies of the electrochemical formation of lead chromate, in regard to Luckow's work. Their experimental apparatus consisted of a 2.5 liter battery jar, which was the electrolytic cell, in which were hung three electrodes. The surface area of all three electrodes was 170 square centimeters. In most tests the direct current density was maintained at a value of 0.0059 ampere per square centimeter. A drip apparatus was set up so that 20 cubic centimeters of 20 per cent chromic acid solution could be added to the electrolyte in an hour. This was done to keep the electrolyte neutral throughout the electrolysis. To provide agitation, a blast of air was blown through the solution. Products obtained were usually the bright yellow color of lead chromate, but after standing for a long time they took on a dirty orange-yellow tint.

Electrolyses were performed with 1.5 per cent solutions of various ratios of sodium chlorate to potassium chromate. The percentages of these chemicals used in four individual tests were 70-30, 65-35, 60-40, and 50-50, respectively. For these tests, the current yield decreased, giving values of 96 per cent,

46 per cent, 20 per cent, and approximately zero percent, in that order. It appears that the more dilute the chromate ion in the electrolyte, the greater is the current yield. In all of these tests the current rose due to the formation of the product on the anode. It was possible to reduce the voltage to normal by scratching the surface of the anode to remove the product.

A series of experiments was performed using various percentages of a mixture of 80 per cent sodium chlorate and the remainder potassium chromate as the electrolyte. For percentages of 3, 6, and 18, the current yields were 100, 96, and 46 per cent, respectively. Rising of the voltage drop across the cell was experienced in all of these tests too.

Six and 12 per cent solutions of a mixture of 90 per cent sodium chlorate and 10 per cent potassium chromate were used in another series of experiments. These tests gave 98 and 100 per cent current yields, respectively.

Other research was carried out employing salts other than sodium chlorate. These salts were sodium nitrate, sodium acetate, and sodium butyrate. For the nitrate tests, 1.5 per cent solutions of 20, 30, 35, and 40 per cent potassium chromate were employed as the electrolyte. The remainder of the chemical mixture was sodium nitrate in an amount equivalent to sodium chlorate. For these four experiments, current yields of 99, 96, 94, and 55 per cent, respectively, were obtained. Studies

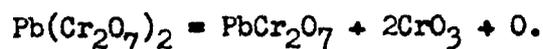
with sodium acetate gave yields of 96, 100, and 79 per cent. These three tests were carried out using 1.5 per cent solutions of 20, 30, and 35 per cent potassium chromate, the remainder being sodium acetate in amounts equivalent to sodium chlorate, respectively.

Two tests were performed with sodium butyrate. The first electrolyte consisted of a 1.5 per cent solution of 20 per cent potassium chromate and enough sodium butyrate to be equivalent to 80 per cent sodium chlorate. This test resulted in a current yield of 96 per cent. The second experiment performed with a 1.5 per cent solution of 30 per cent solution of potassium chromate and enough sodium butyrate to be equivalent to 70 per cent sodium chlorate gave a current yield of 58 per cent.

A series of electrolyses was performed using various percentages of pure potassium chromate solutions. Comparatively low current yields were obtained in all cases due to the formation of a superoxide on the anode.

Other Electrochemical Studies. Elbs and Nubling⁽²⁷⁾ found that in the electrolysis of very dilute solutions of chromic acid solutions between lead electrodes, lead chromate alone is obtained; with more concentrated solutions -- up to 40 or 50 per cent -- there is evidence of the formation at the anode of plumbic chromate, $Pb(CrO_4)_2$, or of a mixture of lead chromate and lead dioxide. Very concentrated solutions -- 130 grams of chromium trioxide per 100 cubic centimeters of

water -- a solution is obtained which evolves oxygen when allowed to stand and deposits lead dichromate when electrolyzed. The quantity of oxygen evolved is in accordance with the following equation:



According to Just⁽⁴⁵⁾, the potential difference between a lead anode and a solution containing bivalent lead ions depends very much on the anodic current density (probably owing to the local increase of the concentration of the lead ions) so that at high current densities it may rise to the normal value for lead dioxide. When this is the case, lead dioxide is, of course, formed on the anode.

Huick⁽³⁹⁾ electrolyzed a 1.5 per cent solution of a mixture of sodium chlorate (95 parts) and sodium dichromate (5 parts) to obtain lead chromate.

Comparison Between Chemical and Electrochemical Methods of Preparation. Continuous, commercial production of lead chromate was summarized in a publication by Downie⁽²⁶⁾. He stated that, although chemical methods of preparing the compound have appeared in great detail in existing literature, no two pigment manufacturers use exactly the same conditions. The use of alternative starting materials, namely, sugar of lead and basic lead acetate, with varying concentrations of soda and sulfuric acid, besides temperature changes, are all

taken advantage of to produce the desired shade. It has been claimed that the same range of variety can be simulated by the electrolytic system, but this relates more to academic investigation. This is because the balance required to insure continuous electrolysis is easily upset, and even as it is, the making of one entirely uniform brand requires careful and regular testing. The process thus differs from the large majority of electrolytic methods which can be left to function more or less automatically without attention. When it is known that only one particular shade of chrome yellow is to be in demand, the work can proceed unrestricted, but once a fresh brand is desired, many reactions can be disturbed and require no small amount of chemical and electrical testing before conditions are fully stabilized.

Such being the case, it may be concluded that there would be little point in pursuing a process with limitations of this kind. It should be observed, however, that whereas ordinary chemical production necessitates the use of costly sugar of lead or basic lead acetate, the electrolytic process starts with metallic lead at a fraction of the outlay. Apart from this, lead containing bismuth, silver, and other valuable constituents can be conveniently utilized, as these are left intact in the insoluble anode slimes, and do not interfere with the process.

On a continuous process, lead chromate has been obtained at a rate of 4.5 pounds per kilowatt. This is an average figure, although it can vary to some extent, depending on

whether sulfur yellow or dark chromes are required. Current is applied at from 2 to 3 amperes per square foot of anode surface, which means the corrosion of the anodes is slow compared with that in electrolytic refining of lead, where the amperage ranges from 18 to 70 amperes per square foot. Thus, in estimating the respective costs of the process as compared with the ordinary chemical system, there is greater depreciation and maintenance charges, and the additional current required for corroding the lead. On the other hand, the chemical process is more expensive in requiring lead carbonate or basic lead acetate as the raw material, unless some subsidiary means of reconvertng the potassium and sodium acetates to lead acetate is employed.

Electrolysis With Periodically Reversed Direct Current

This section deals with the theory, production, and application of periodically reversed direct current.

Jernstedt⁽⁴²⁾ aroused a great amount of interest by electroplating with periodically-reversed, direct current in 1947. Previously in England⁽⁹⁾ one concern was making use of periodic reverse plating as long ago as 1925. In the process, the article being plated is made cathodic, the current is reversed making the article anodic for a short period of time, and then the current is reversed again making the article cathodic. This cycle is repeated continually during the electrolytic treatment of the article.

Definitions. Before further pursuing the subject at hand it may be well to define certain terms⁽⁴¹⁾ peculiar to periodic-reverse plating.

Cathode Current Efficiency. Cathode current efficiency is the percentage of coulombs which is effective in depositing a metal on the article being plated while it is cathodic. The cathode current efficiency is the same for either cycle of the periodic-reverse current.

Periodic-Reverse-Cycle Efficiency. Periodic-reverse-cycle efficiency is equal to the net time of the plating divided by the total cycle time, provided the switching efficiency be 100 per cent.

Switching Efficiency. Switching efficiency is equal to the sum of the time of plating and the time of deplating divided by the total time of a cycle multiplied by 100. This is a measure of the time lost due to failure to accomplish full reversal instantaneously and depends on a combination of mechanical and electrical factors.

Effective Current Density. The effective current density is that which by direct current methods would cause the deposition of the same amount of metal in the same time as obtained with a given periodic-reverse process. The following equation may be helpful:

$$ECD = (CCD)(PRSE)$$

where:

ECD = effective current density, amp/sq cm

CCD = cathode current density, amp/sq cm

PRSE = periodic-reverse switching efficiency, per cent.

Principles of Periodic-Reverse Plating. The following paragraphs deal with the object of periodic-reverse plating, description of the process, use of complex wave forms, characteristics of deposit, advantages, limitations, applications, and equipment for current reversal.

Object of the Process. The object of periodic-reverse plating is to produce a deposit of superior qualities of strength, elasticity, density, conductivity, and freedom from flaws such as surface roughness and porosity.

Description of the Process. The underlying principle⁽⁹⁾ of periodic-reverse plating is that deposition is carried out for a predetermined short period of time by conventional direct current after which the current is reversed and the article is made anode, usually for a shorter period of time and at the same⁽⁴¹⁾ or at higher⁽⁹⁾ current density than in the cathodic plating stage. During the direct current portion of each cycle, a thin deposit is applied in the usual manner. When the current is reversed, the high spots and rough projections are partially depleted⁽⁹⁾ in preference to any low or unplated spots. Periodic reverse plating may be likened to electrodeposition accompanied by continuous electrolytic polishing.

Any metal depleted from the base member by the reverse current is driven⁽⁹⁾ into the solution immediately adjacent to it so that an abnormally high local concentration of metal ions is present when plating is resumed during the next interval of direct cathode current. The plating during the next direct current interval is greatly improved since it is applied to a smoother and brighter surface. Also, the efficiency of the plating stage⁽⁹⁾ is improved owing to the high concentration of metal ions near the surface of the article being plated. Even scratches, recesses and internal surfaces are alleged to be covered almost as efficiently as any other portion of the base and a much higher speed^(32, 33, 34) is possible owing to the high concentration of metal ions in the vicinity of the metal surface.

It has been stated⁽⁹⁾ that metal plated by continuous direct current is of higher quality during the initial portion of the plating period. The metal plated later tends to become crystalline and to build up at projections and other spots where there is current concentration or the presence of more metallic ions in the adjacent electrolyte. Bregman⁽¹⁶⁾ states that the more sacrificial the plating cycle, that is, the more closely does the plating period approach the deplating period, the better the quality of the plate. However, a sacrificial cycle requires a relatively long total plating time for a given thickness of deposit. In general⁽⁴²⁾, about 10 to 50 per cent or more of each increment previously plated is deplated, depending on the quality of the plate desired.

Use of Complex Wave Forms. In periodic-reverse plating the time-current curve may be of any desired form provided the energy of the deplating current is at least 10 per cent of that of the plating current. This was stated in a patent assigned to Westinghouse⁽⁸⁾. Apparently very little or no work has been done to compare simple periodic reverse plating with plating techniques employing more complicated current forms. Figure 1, page 25, gives the time-current curves for some of the basic types of electroplating wave forms.

Characteristics of Deposit. Periodic reversal of the plating current preferentially removes what may be considered unsound and inferior metal⁽¹⁾ deposited in the plating stage of

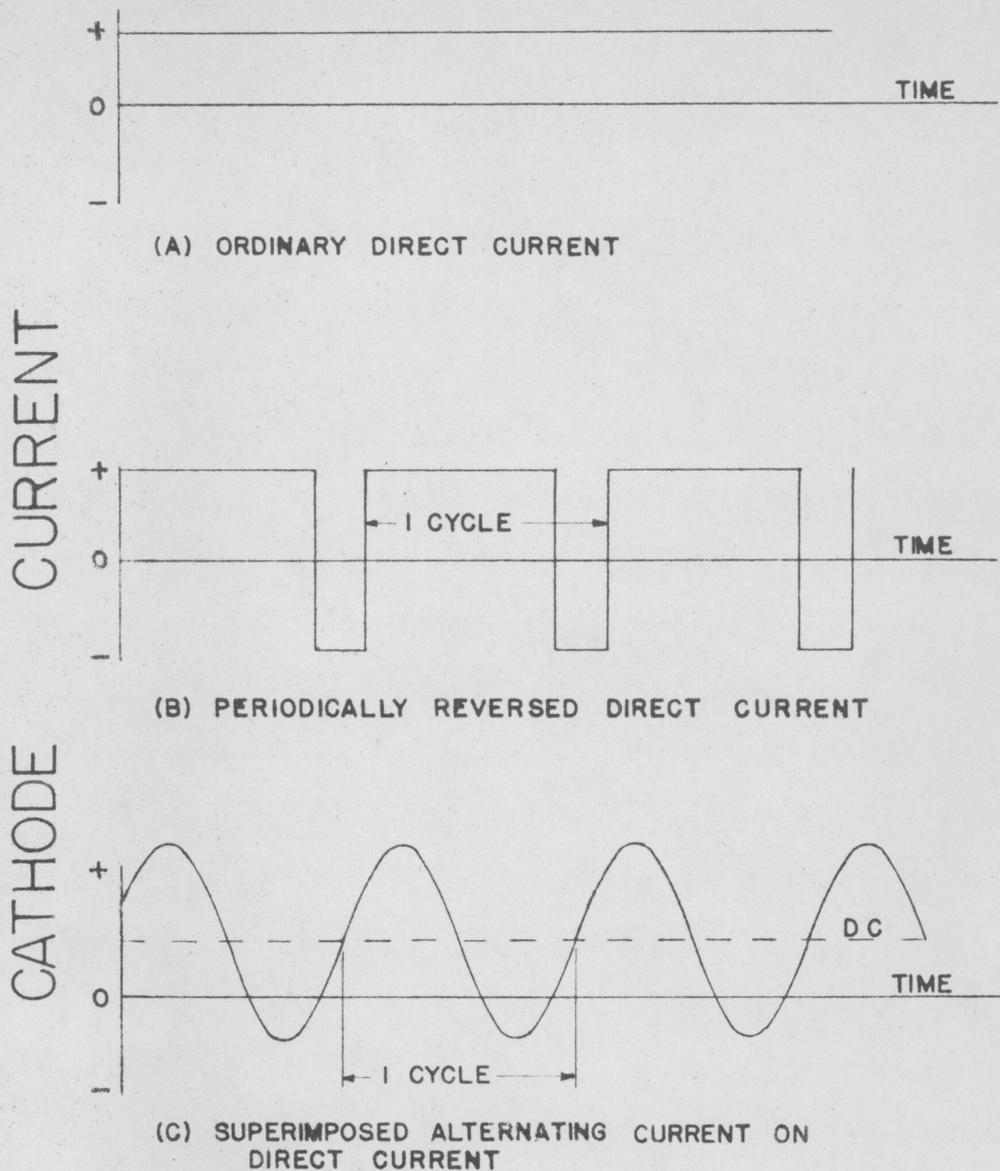


FIGURE 1. TIME-CURRENT CURVES FOR VARIOUS WAVE FORMS

JERNSTEDT, G. W.: PERIODIC REVERSE-CURRENT ELECTRO-PLATING. MET. FINISH., 45, NO. 2, 69 (1947).

the cycle and results in the build-up of many thin layers of sound metal to form a deposit superior to that formed by continuous, direct-current methods. In many cases⁽¹⁶⁾ buffing or polishing of the article may be eliminated since the deposit is brightened by the current reversal. Jernstedt⁽⁴¹⁾ stated that the throwing power with periodic-reverse current is increased greatly as is evidenced by the uniform distribution of metal on the edges and in the center of a panel. Also, scratches, pores, and nodes in the base metal that are generally emphasized by conventional plating methods tend to be smoothed over by employing periodic-reverse plating techniques. Copper has been plated over engraved initials without the loss of any detail. Thus, periodic-reverse plating is beneficial in filling deep, thin scratches, whereas wide scratches are faithfully reproduced without exaggeration.

Advantages of Periodic Reverse Plating. Periodic-reverse plating works much better with some electrolytes than others. In several cases⁽⁴²⁾ no improvement was detected in deposits formed by periodic-reverse plating as compared to direct-current plating. However, a definite and substantial improvement was evident in most acid and alkaline electrolytes. In general, where periodic-reverse plating is successful, one or more of the following advantages is evident as compared to normal, direct-current methods:

1. better appearance of plate^(56, 42),
2. heavier deposits obtainable⁽¹⁶⁾,
3. better mechanical properties obtainable^(9, 13, 16),
4. faster plating speeds^(16, 41, 42),
5. higher conductivities⁽⁹⁾,
6. higher resistance to corrosion⁽⁹⁾,
7. improved anode corrosion⁽⁴¹⁾,
8. reduction of costs⁽⁴¹⁾,
9. reduction in quantity of addition agents required⁽¹⁶⁾.

Limitations of Periodic-Reverse Plating. One of the feature limitations of periodic-reverse plating is that of poor switching efficiencies possessed by current-reversing equipment. This results in higher plating or power costs. The theory of periodic-reverse plating is not easily applied since many factors influence the results desired. Such factors are the shape of the time-current curve, duration and magnitude of direct and reverse currents, and type of plating solution employed. Another limitation of the process is that the overall electrical efficiencies in periodic-reverse plating are rather low⁽¹⁶⁾ because of the deplating portion of the cycles.

Applications of the Periodic-Reverse Plating Process.

Details of the following applications of the periodic-reverse plating process to electroplating are omitted since they do not

deal primarily with the problem at hand. References are given should the reader desire more detailed information.

1. rochelle copper cyanide bath^(8, 16, 48)
2. copper bath with inorganic brightener⁽¹⁶⁾
3. inorganic copper bath^(56, 16)
4. acid copper bath^(16, 44)
5. du Pont copper cyanide bath⁽⁸⁾
6. bright brass bath^(8, 44)
7. bright tin bath⁽⁴⁴⁾
8. bright zinc bath^(8, 16, 44)
9. bright silver bath^(8, 16, 44)
10. gold baths^(8, 16, 44)
11. nickel, cobalt, and nickel-cobalt alloy baths⁽⁴⁾
12. bright cadmium bath^(16, 44)
13. hard chromium bath^(9, 13)

Current-Reversal Equipment. The success of the periodic-reverse process depends on rapid current reversal. If the current does not build up to the maximum amount immediately after reversals in the cycle, the process becomes less efficient. A few commercially available periodic reversers are listed here:

1. Hill Cross pulse selector⁽¹⁾
2. Plater's Research Corporation electronic relay⁽²⁾
3. combined reverse-current and rectifier units⁽⁶⁾
4. cam-operated switches⁽⁸⁾

These reversers, although not operating on the principle, accomplish the same result of periodically-reversing, direct current.

Electrolysis With Alternating Current

Superimposed on Direct Current

Several years ago in Germany⁽⁷⁴⁾, the discovery was made that by superimposing an alternating current on a direct current, better plating results were obtained. The subject of pulsating-current wave forms offers many possibilities not only to the plating industry, but also to the whole electrochemical field in general. This section of the literature review deals with the general principles and applications of alternating current superimposed on direct current. Also included is a section relating to electrical circuits for achieving superimposed, alternating current on direct current.

Theory. The following paragraphs pertain to the underlying principles, theory, and advantages of superimposed, alternating current on direct current along with a comparison with periodic-reverse plating:

Underlying Principles. The underlying principle of superimposed, alternating current on direct current is that, by suitable electrical equipment, an alternating current component is introduced into the conventional direct current circuit. The two components, being additive, give a resulting

wave form of a different character than that of the individual components. In considering the ratio of alternating current to direct current, three general cases present themselves.

Case 1. For the first case, the maximum value of the alternating current component is less than the direct current component. In this way, the maximum current in the circuit is always positive, and equivalent to a pulsating direct current.

Case 2. The maximum value of the alternating-current component is equal to the direct-current component. The current falls to zero periodically and is equivalent to an interrupted direct current.

Case 3. The third case occurs when the maximum value of the alternating current component is greater than the direct current component. This causes the current to reverse its direction periodically.

It is the third case which is of the greatest importance at the present time. The deposition is carried on for a short period of time, depending on the frequency of the alternating current, after which the current reverses itself and the plated article is made anodic, for a shorter time and at a lower current density than in the cathodic plating process. The cycle is repeated making the article alternately cathodic and anodic until the desired plate thickness is obtained.

The theoretical, limiting, current density for a given cathode reaction is the maximum possible rate of deposition of a given ion species. Any attempt to further increase the current must result in a shift of the cathode potential from values covering the range over which the ion species under consideration can be deposited to a range at which some other ion species will be deposited. In an aqueous system containing only one species of metal cations in aqueous solution, this other ion species must necessarily be hydrogen. The limiting current density is directly proportional to the concentration of the cathode film, and the diffusion coefficient of the salt furnishing the dischargeable ion. Therefore, to achieve the maximum limiting current density for a given cathode reaction, a salt having a large diffusion coefficient should be employed, and the concentration of the cathode film should be as large as possible. Also, the thickness of the cathode film should be as small as possible. Agitation can satisfy the last condition, but superimposed alternating current serves the purpose of decreasing the cathode film thickness and also increases the metal ion concentration at the electrode-solution boundary.

It has been stated⁽⁹⁾ that metal plated by continuous, direct current is of much higher quality during the initial portion of the plating period. The metal plated later tends to become more crystalline and to build up at projections and other spots where there is current concentration or the presence

of more metallic ions in the adjacent electrolyte. By the use of superimposed, alternating current, with alternations at definite intervals, deposition is always limited to the initial portion of the normal, direct-current period. Any metal depleted from the base by the alternating current is driven into the solution immediately adjacent to it so that an unusually high, local concentration of metal ions is present when plating is resumed during the following interval of cathodic deposition. The efficiency of plating is improved due to the higher concentration of metal ions near the metal surface. In essence, the continual plating of a base metal with superimposed, alternating current is the same process as plating carried out with periodically-reversed, current.

Advantages of Alternating Current Superimposed on Direct Current. The following list summarizes the advantages resulting from electrodeposition carried out with alternating current superimposed on direct current:

1. increased rate of deposition,
2. improved brightness of deposit,
3. improved smoothness of deposit,
4. permits heavier, smoother deposits,
5. decreased porosity of deposit,
6. improved metal distribution (throwing power),
7. increased hardness of deposit,
8. increased density of deposit.

The electrolytic process is very flexible since wave forms having, literally, an infinite number of variations are possible. All of the advantages cannot be obtained at the same operating conditions, but by proper control any one desired feature may be emphasized.

Theoretical Lowering of Voltage by Alternating Current.

Glasstone⁽³¹⁾ was the first to recognize the fact that, when an alternating current is superimposed on a direct current and the voltage drop across an electrolytic cell through which the current is flowing is measured directly, the voltage read will be the average of a varying voltage. He took this into account when he used a direct method for measuring the voltage in an investigation of the action of small alternating currents on an electrode polarized by direct current under such conditions that no reverse current ever flowed through the electrolytic cell during the course of a whole cycle. Under these conditions the average potential of a polarized electrode could be measured by the direct method with simultaneous direct and alternating current in the circuit. The arithmetic mean of the alternating and direct current should give an approximate measure of the average potential that would be expected with an alternating current superimposed on a direct current if the former exerted no great effect on the electrode. A comparison of this value

with that experimentally determined would give a rough idea of the actual influence of alternating current on the polarized electrode.

Wier⁽⁷²⁾ has expanded the idea of Glasstone considerably. He stated that if there is no specific effect of the alternating current, then the mean voltage will depend on the shape of the polarization (current-potential) curve for the direct current only. Any specific effect would be in addition to the change in voltage derived on the basis of the polarization curve.

Goodwin and Knobel⁽³⁴⁾ superimposed, alternating current on direct current and studied the effect of three factors on the hydrogen overvoltage on platinum, lead, and copper cathodes. They found that the effect of the frequency was small and that the effect of the superimposed alternating current was independent of the kind of electrodes and the current density. The ratio of the alternating current to the direct current was found to be the most important factor. It was claimed⁽³⁴⁾ that the lowering of the overvoltage was the result of the formation of oxygen by the reverse current. This was based on the observation that no appreciable lowering was observed until the alternating to direct current ratio was large enough to produce an actual reversal of the current.

Glasstone⁽³¹⁾ investigated the effect of small alternating currents (with no reversal of current) on cathodic and anodic overvoltages for a number of different metals in normal

sulfuric acid and sodium hydroxide solutions. His results indicated that lowering of the voltage takes place only in a limited number of cases. He claimed that previous literature values of lowering of overvoltage by alternating currents are of doubtful value because the electrical circuits were so arranged that the voltmeter indicated only the average value.

Atanasiu and Elum⁽¹²⁾ gave a critical evaluation of the literature on electrolysis with alternating current. The depolarizing action of alternating current, which is weaker as a pulsating current, alters the course of reactions at the cathode and anode because of the following: decrease of polarization voltage and overvoltage, increase of anode activity by decreased passivity, decrease of cathode deposition yield, and change of electrode capacity. The voltage drop upon electrolysis (particularly for alternating current), aside from the economy of electrical energy, permits the isolation of intermediate products in oxidation and reduction reactors. Increase of anodic activity (decrease of passivity), especially for pulsating direct current, is advantageous for the extraction and refining of metals and for the dissolution of alloys, but disadvantageous in oxidation-reduction reactions because of the attack on the anode. In cathodic deposition, the action of alternating current or pulsating direct current decreases

the yield and, in some reactions, results in poorer quality deposition. To improve the metallic deposition, high frequency alternating current has been used.

Other Theoretical Investigations. Steiner⁽⁶³⁾ studied the influence of an alternating current component superimposed on direct current in a number of metal salt solutions. Single phase alternating current of 50 cycles per second was used. The cathode-ray oscillogram of the alternating current component of the cathodic polarization was discussed. In particular, the influence of the alternating current component on the form of the metallic deposits was investigated. No conclusions were drawn from the character of the deposits in relation to the influence of the alternating current component on the current distribution. Ghosh⁽³⁰⁾ studied the action of a high-frequency, alternating current on single voltaic cells and on electrolytic cells for both reversible and irreversible processes. His work is summarized as follows:

1. When an alternating current of high frequency, about 500 cycles per second, passes through a cell consisting of two platinum electrodes in any electrolyte, the electrode potentials change, thus indicating that some chemical action at the electrode surface takes place in that short amount of time.

2. When an alternating current passes through a reversible voltaic cell, there is no change in the electrode potential. If, however, one of the electrodes consists of a metal covered with its insoluble salts, the alternating current has a pronounced effect on the electrode.
3. A greater amount of current could be supplied by a cell with one reversible and another irreversible electrode, when an alternating current is in the circuit.
4. In cells like (Cd-ZnCl₂-Hg), (Cd-ZnCl₂-Pt), and so on, the electromotive force of the mercury or platinum electrode approaches the value of the zinc electrode on the passage of the alternating current.
5. In perfectly reversible electrolytic cells the alternating current has no action when impressed on the cell along with direct current.
6. Should the electrolytic cell be irreversible, the alternating current greatly increases the current strength through the circuit.
7. The increase in current strength is due to the diminution in the back electromotive force of polarization.
8. This diminution of the discharge potential is also observed in electrolytic cells consisting of two cathodes and two anodes, the alternating current passing between the anodes or the cathodes, but not passing through the whole circuit.

The work performed by Ghosh took no account of the ratio of alternating to direct current.

Cooper⁽²³⁾ gave a detailed description of the effect that a superimposed, alternating current has on the direct current of an electrolytic cell. The three general cases were discussed, but no definite explanation of the effect was suggested.

Epelboin⁽²⁸⁾ studied the electrolytic phenomena at electrodes caused by superimposing alternating current of small amplitude onto the direct current. For aqueous solutions and fused salts with inert electrodes, the variation of impedance is equivalent to a resistor in series with a fixed capacity. For nickel electrodes in mixed perchloric acid and acetic anhydride the capacity is six times the theoretical based on complete absorption of ClO_4^- on the electrode.

Heinrich and Klemenc⁽³⁷⁾ derived general equations for the case where alternating current is flowing between two electrodes while they are both either cathodes or anodes in a direct current circuit. A third electrode is placed between the other two. It is shown that the effect of alternating current is not directly proportional to its intensity, but is expressible by a complex function. For the special case that the direct current connection is made at such a place on the transformer winding that the induced potentials and resistances are equal on both sides, the two outer electrodes will not change polarity as long as the alternating current is greater than $\sqrt{3/8}$ of the direct current.

For the special case that only two electrodes are used, to which both alternating current and direct current are applied, the electrodes will not change polarity unless the alternating current is greater than $\sqrt{3/2}$ of the direct current.

Glasstone and Reynolds⁽³²⁾ studied the effect of high frequency currents on polarized electrodes. They accounted for a decrease in polarization of an electrode resulting from the application of high frequency on the assumption that the high frequency caused an increase in the rate of diffusion of the depolarizer to the electrode. They pointed out that when a circuit containing a large self-inductance is suddenly broken, the potential falls more rapidly than it does when the circuit is broken under normal conditions. It thus appears that electrical discharges aid those processes which tend to remove electrochemically active material from the electrode, and alternating current may act the same way. The magnitude and mechanism of the high frequency effect appeared to be the same at both anode and cathode. Glasstone and Reynolds⁽⁴³⁾, in a subsequent publication, related a study of the effect of high frequency oscillations on the limiting current density for 100 per cent electrode efficiencies which indicated that the high frequency effect cannot be due to its influence on the chemical reaction at the electrode, but is related to an increase in the rate of diffusion of the depolarizer. They pointed out that the high frequency effect is probably brought

about by a mechanical disturbance in the electrolyte. This effect cannot be due to local heating at the electrode, but may be caused by the oscillatory rotation of the molecular dipoles constituting the water used as the solvent. The effect is also increased by an increase in viscosity and decreased by agitation of the solution or raising its temperature.

Comparison of Superimposed Alternating Current Plating With Periodic Reverse Current Plating. In regard to the effects obtained on plating, periodic reverse current plating is similar to the use of superimposed alternating current on direct current. The major differences in the processes are found in the wave forms obtained and the manner in which the current reversal is obtained. The current may be reversed for periodic reverse plating⁽⁴³⁾ either by reversing the field excitation of the direct current generator or by means of a current reversing contactor on the low voltage output of the generator. Either method requires a timer to secure the periodic reverse cycles to be used. When rectifiers are employed, heavy-duty, low-voltage contactors may be used. The use of contactors in the plating circuit results essentially in a square type of wave form, since the current builds up almost instantaneously to its full value in either direction. For a generator, when the field is reversed, two or three seconds are required after each reversal before the full current becomes available.

To achieve current reversal with superimposed alternating current it is necessary only that the maximum value of the alternating current must be greater than that of the direct current component. The wave form obtained is usually sinusoidal, although special wave types are possible.

As a rule, periodic reverse plating utilizes equal values of current and voltage during the plate and deplate portions of the cycle used. Only in certain specialized cases would the two current values be different. On the other hand, the root mean square values for the current are different when alternating current is superimposed on direct current. The plating current is always higher than the deplating current and the ratio of the two is a function of the direct current component and the amplitude of the alternating current. The term $\left[\frac{AC_{\max}}{DC} - 1 \right]$ is a measure of the extent to which the reversal of the current takes place. The plating and deplating times are different when superimposed, alternating current is used (the same is true for periodic-reverse plating). While the plating and deplating times are controlled by the adjustment of a timer in periodic reverse plating, the plating and deplating times for superimposed alternating current are a function of (1) the value of the direct current component, (2) the amplitude of the alternating current component, and (3) the frequency of the alternating current.

Applications. The applications of superimposed alternating current on direct current given here are treated briefly in regard to details.

Application to Electrodeposition of Metals. The following is a list of applications of superimposing alternating current on direct current to the electrodeposition of metals:

1. electrodeposition of aluminum^(7, 3, 46)
2. electrodeposition of gold⁽⁷⁴⁾
3. electrodeposition of cadmium^(8, 15, 17)
4. electrodeposition of antimony⁽¹⁸⁾
5. electrodeposition of bright zinc^(8, 17)
6. electrodeposition of bright tin^(8, 17)
7. electrodeposition of copper-lead alloys⁽⁶⁵⁾
8. electrodeposition of copper⁽¹⁹⁾
9. electrodeposition of uncommon metals^(18, 20)

Other Applications. Safranek and coworkers⁽⁵⁹⁾ studied electroforming methods for the manufacture of aluminum wave guides employing superimposed alternating current on direct current as the source of electrical energy. It was found that wave guide segments produced without alternating current were so highly stressed that cracking usually resulted.

Smith⁽⁶¹⁾ has obtained a patent for a method of anodic polishing a metal of the group consisting of copper, brass, and electrically deposited silver in a cyanide bath. The method

consists of immersing the article in a cyanide bath and subjecting the metal to electrolytic polishing action resulting from the intermittent application of a positive potential of varying value to the piece, as an anode, and to a cathode. The varying potential is composed of a direct current potential in series with an alternating current. The alternating-current potential is applied for a time of 0.5 to 0.9 second with an interval of at least 0.6 second between each application. The peak alternating-current potential is always less than the direct-current potential.

The du Pont Company⁽⁸⁾ has presented a method for smoothing rough deposits with alternating current. Alternating current is employed not as part of the plating operation, but as a subsequent or interim operation which may be performed in the same solution to smooth a copper layer already electrodeposited. With alternating-current smoothing, no mechanical polishing is required and nickel and chromium subsequently deposited are of adequate brightness even though the smoothed copper is not itself mirror-bright. Smoothness is the important consideration.

Oza⁽⁵⁸⁾ studied the anodic behavior of A-A type nickel in a normal sulfuric acid solution using platinum cathodes. Oza believed that superimposed alternating current on direct current would reduce passivity and speed up the plating of nickel and other metals that become passive at low current densities.

He found that anodes made passive by the application of conventional direct current were made active by the subsequent application of alternating current. The effect of superimposed-alternating current on direct current was presumed to depend upon the amount of direct current, the ratio of alternating to direct current, and the frequency of the alternating current. Kirby⁽⁴⁹⁾, using equipment of his own design, made a study of the passivity of A-A type nickel. He found that the superimposition of an alternating current of 10 milliamperes per square centimeter on nickel electrodes in an agitated normal sulfuric acid bath at 74 to 79 °F increased the limiting direct current density from 18 milliamperes per square centimeter to 250 milliamperes per square centimeter. Other results indicated that superimposed alternating current on the anode increases the anode direct current efficiency.

Lawrence⁽⁵¹⁾ studied the effect of superimposed-alternating current on nickel deposition from a Watts-type bath. He found that an increase of the alternating current caused the high current density side of the test plate to become blistered and cracked, while the test plate had a bright appearance on the lower portion of the current density range.

Electrical Circuits for Obtaining Superimposed-Alternating Current on Direct Current. Wier⁽⁷³⁾ stated that two main features were desirable in designing the electrical circuit to measure the

effect of the superimposed alternating current on direct current in the electrodeposition of aluminum on dissimilar metals. He found that it was necessary to vary the alternating current and direct current independently and to read them separately and directly. The original circuit used by Wier⁽⁷²⁾ is similar to the one shown in Figure 2. Two variable rheostats were connected in parallel with the cell. One of the rheostats was connected through a variable transformer to the alternating current supply, which was 110 volts, 60 cycles per second. In order to prevent the direct current from entering the alternating part of the circuit, a 28 microfarad condenser was placed in the line between the cell and the alternating current rheostat. An iron core inductance was placed in the direct current line between the cell and the direct current rheostat and meters. It was found that the inductance was not sufficient to prevent the alternating current from entering the direct current circuit. An inductance of the proper magnitude was not available, so the percentage of the total alternating current passing through the cell was determined by a calibration procedure. A subsequent publication by Wier⁽⁷²⁾ employed the circuit diagram of Figure 2, which eliminated the need for the calibration.

Teres⁽⁶⁵⁾ used the circuit diagram of Figure 3, in his attempts to electrodeposit copper-lead alloys with the use of superimposed-alternating current. The alternating power used for superimposition on the direct current was derived from a 60 cycle

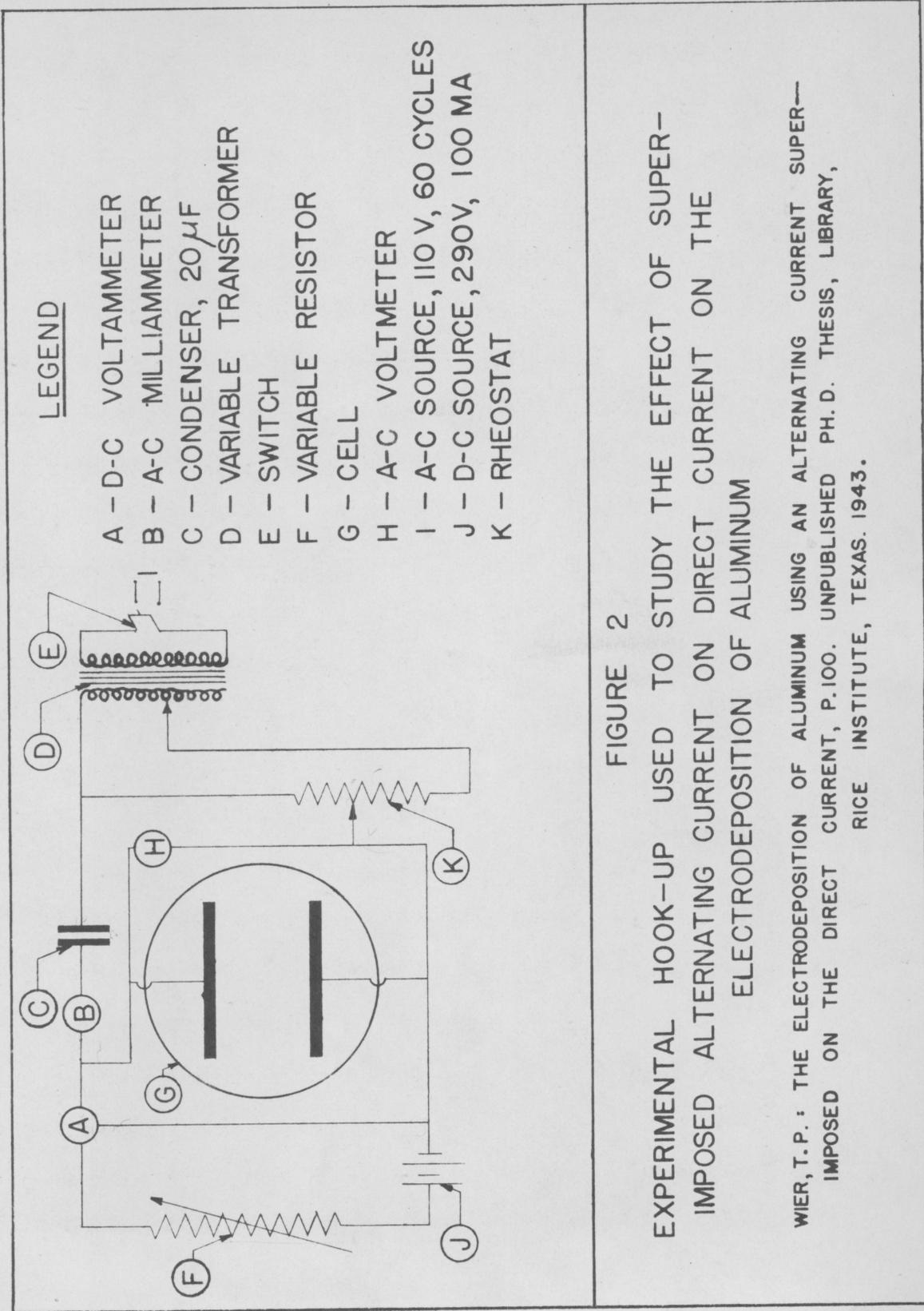


FIGURE 2
 EXPERIMENTAL HOOK-UP USED TO STUDY THE EFFECT OF SUPER-
 IMPOSED ALTERNATING CURRENT ON DIRECT CURRENT ON THE
 ELECTRODEPOSITION OF ALUMINUM

WIER, T.P.: THE ELECTRODEPOSITION OF ALUMINUM USING AN ALTERNATING CURRENT SUPER-
 IMPOSED ON THE DIRECT CURRENT, P.100. UNPUBLISHED PH.D. THESIS, LIBRARY,
 RICE INSTITUTE, TEXAS. 1943.

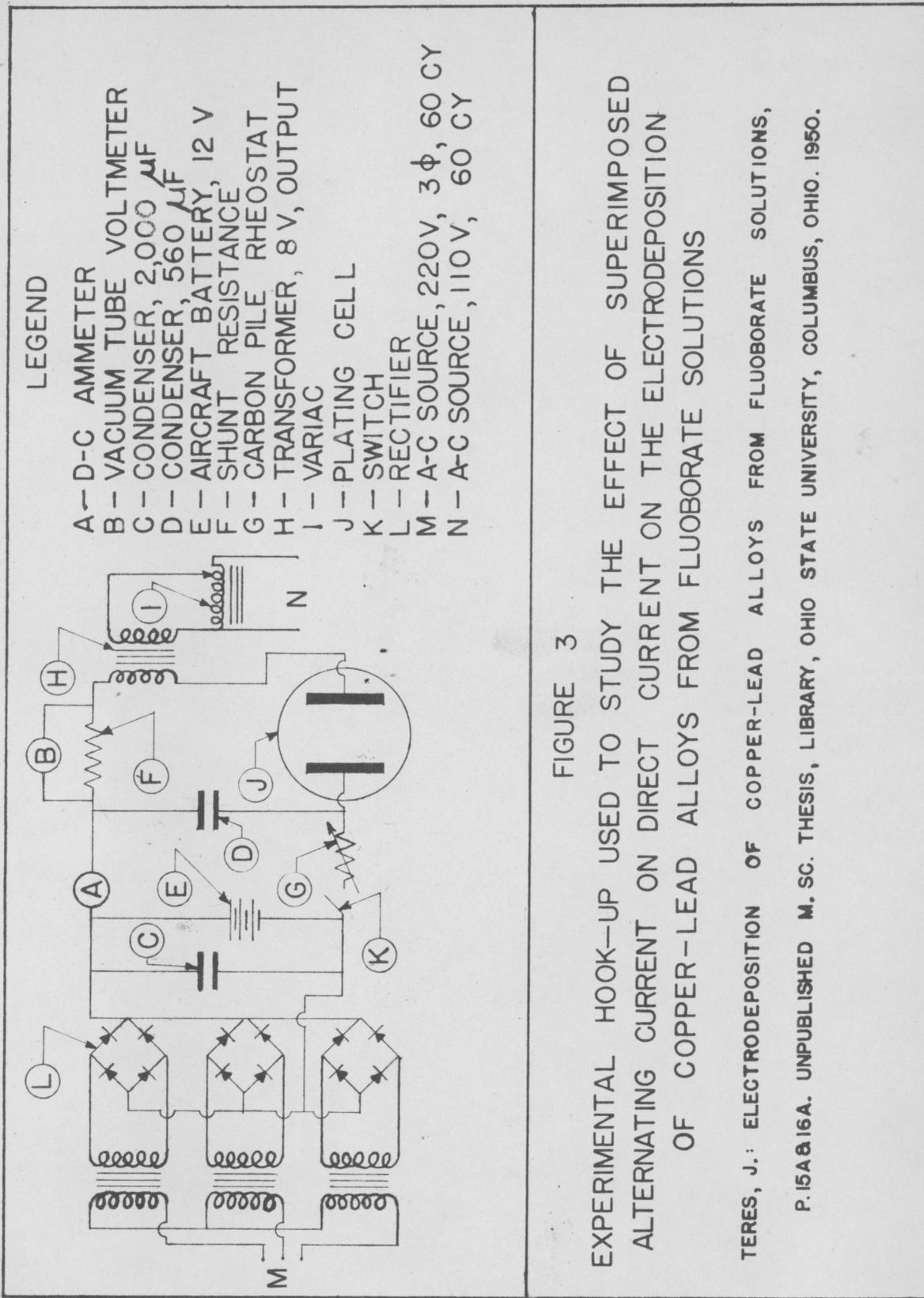


FIGURE 3
 EXPERIMENTAL HOOK-UP USED TO STUDY THE EFFECT OF SUPERIMPOSED
 ALTERNATING CURRENT ON DIRECT CURRENT ON THE ELECTRODEPOSITION
 OF COPPER-LEAD ALLOYS FROM FLUOBORATE SOLUTIONS

TERES, J.: ELECTRODEPOSITION OF COPPER-LEAD ALLOYS FROM FLUOBORATE SOLUTIONS,
 P.15A&16A. UNPUBLISHED M. SC. THESIS, LIBRARY, OHIO STATE UNIVERSITY, COLUMBUS, OHIO. 1950.

per second, 110 volt line through a step-down transformer capable of delivering a maximum of 10 amperes at 8.0 volts. Between the power line and the transformer was connected a constant voltage transformer and autotransformer; the former reduced line voltage fluctuations and the latter acted as an adjustment for the alternating current. A bank of four 140 microfarad condensers were used as a by-pass for the alternating current, serving the dual purpose of keeping it out of the direct current ammeter and reducing the interaction that adjustment of the carbon pile rheostat would otherwise have had on the alternating current. The alternating current was measured by means of a 0.1 ohm, constantan shunt across which was placed a multirange, alternating-current, vacuum-tube voltmeter. This alternating-current ammeter equivalent was not affected by direct current.

Oza⁽⁵⁸⁾ and Kirby⁽⁴⁹⁾ give simpler, although similar circuit diagrams for studies concerning the effect of superimposed, alternating current on the anodic behavior of nickel. The circuit diagrams used by Oza and Kirby are given in Figures 4 and 5, respectively.

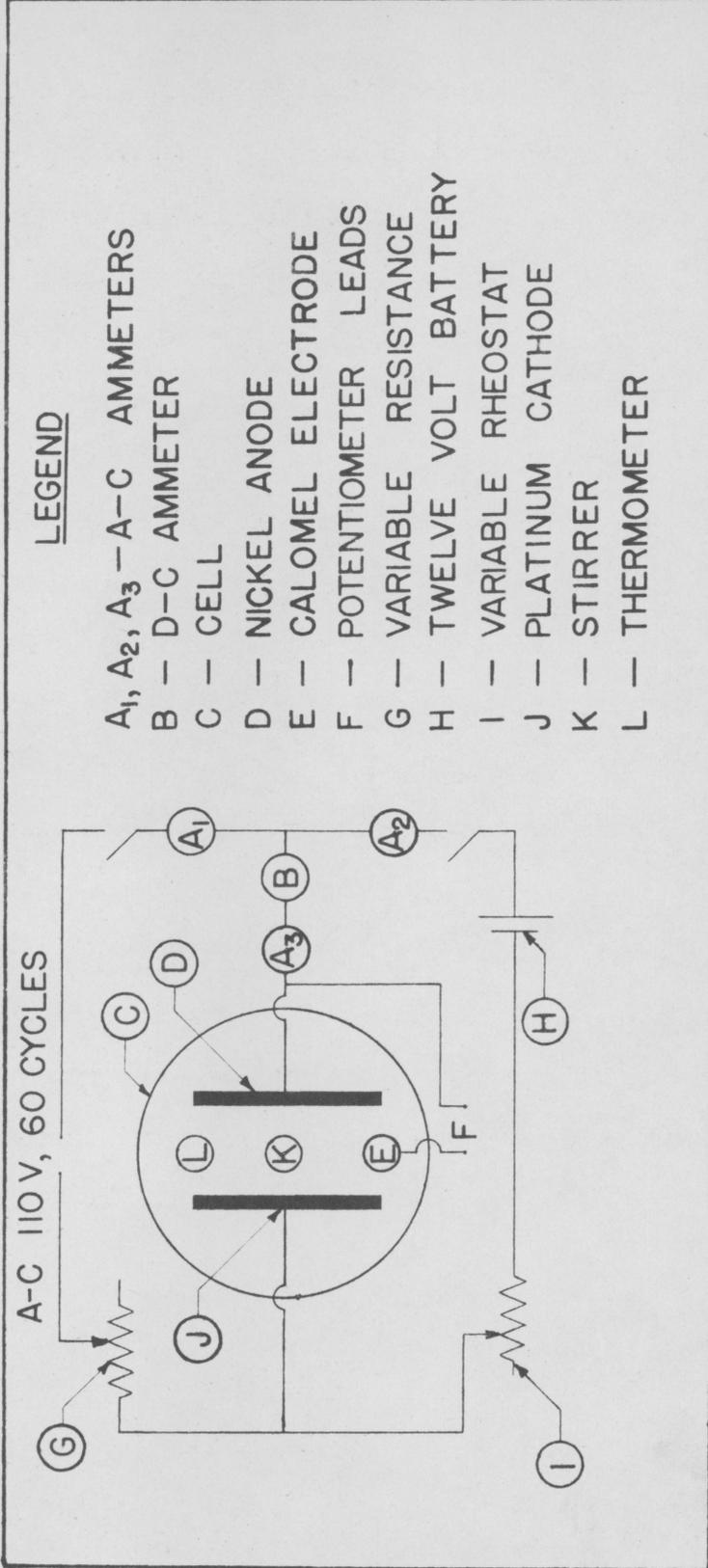


FIGURE 4

EXPERIMENTAL HOOK-UP USED TO STUDY THE EFFECT OF SUPER-IMPOSED ALTERNATING CURRENT ON DIRECT CURRENT ON THE ANODIC BEHAVIOR OF NICKEL

OZA, B. C.: ANODIC BEHAVIOR OF NICKEL, P. 43. UNPUBLISHED M. SC. THESIS, LIBRARY, VIRGINIA POLYTECHNIC INSTITUTE, BLACKSBURG, VIRGINIA. 1948.

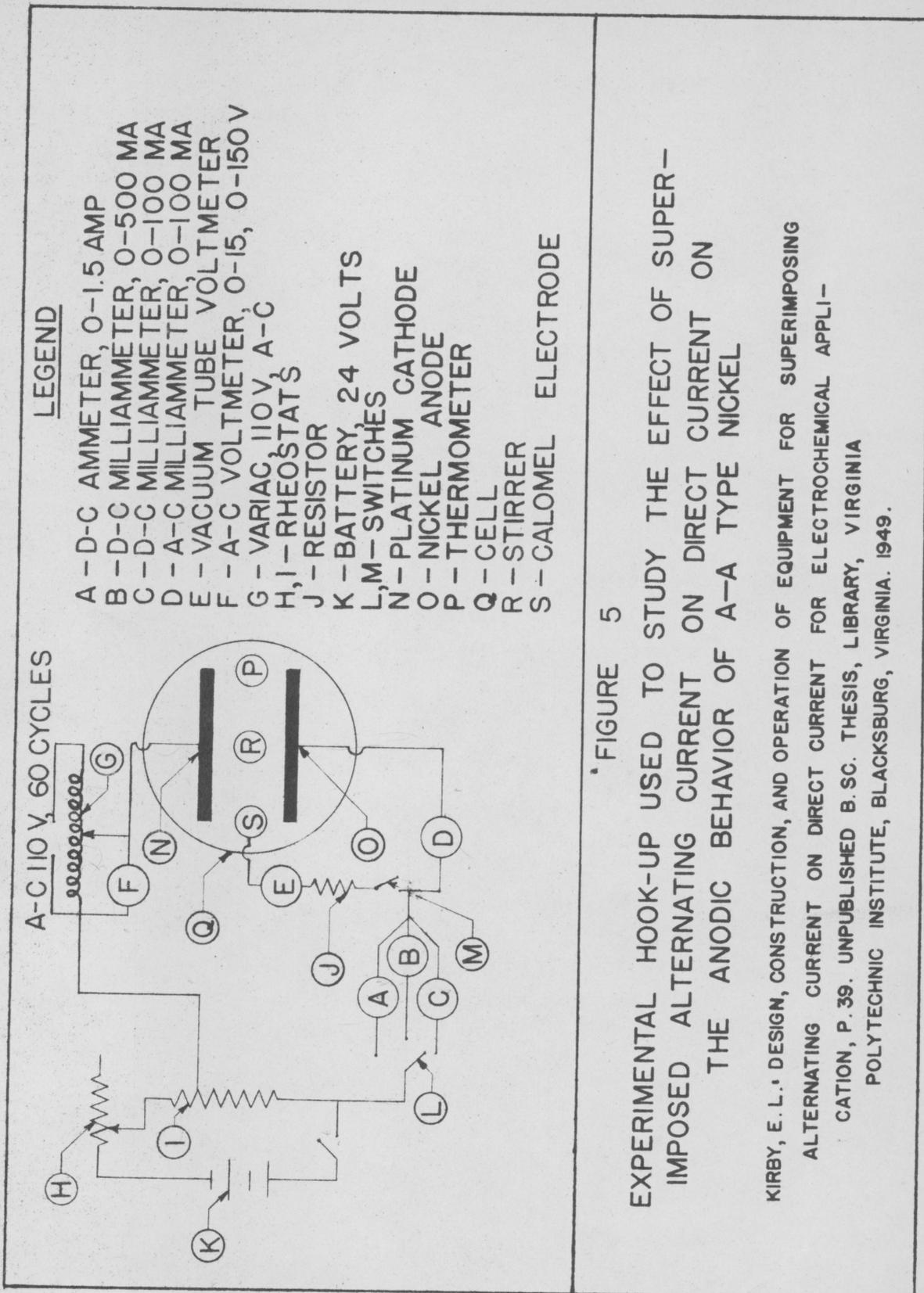


FIGURE 5
 EXPERIMENTAL HOOK-UP USED TO STUDY THE EFFECT OF SUPER-
 IMPOSED ALTERNATING CURRENT ON DIRECT CURRENT ON
 THE ANODIC BEHAVIOR OF A-A TYPE NICKEL

KIRBY, E. L.' DESIGN, CONSTRUCTION, AND OPERATION OF EQUIPMENT FOR SUPERIMPOSING
 ALTERNATING CURRENT ON DIRECT CURRENT FOR ELECTROCHEMICAL APPLI-
 CATION, P. 39. UNPUBLISHED B.S.C. THESIS, LIBRARY, VIRGINIA
 POLYTECHNIC INSTITUTE, BLACKSBURG, VIRGINIA. 1949.

III. EXPERIMENTAL

This section of the study includes all information relating to actual laboratory materials, apparatus, data obtained, and results calculated.

Purpose of Investigation

It was the purpose of this investigation to study the effect of varying the direct to reverse time ratio of periodically reversed direct current from 1.0 to 20.0 on the electrolytic production of lead chromate at an average anode current density of 0.0059 amperes per square centimeter, and to study the effect of 60 and 502.3 ± 7.7 cycles per second from 0.00113 to 0.01546 amperes per square centimeter of superimposed alternating current on the yield of lead chromate prepared by the electrolysis of a bath containing potassium chromate and sodium nitrate between lead electrodes.

Plan of Experimentation

The following portion of this investigation deals with the sources of literature consulted in preparing for the actual experimental portion of this study. Also included in this section are a general procedure that was used during the study, and a method of evaluation of the results obtained from the calculations performed with the data taken during the experimental portion of the study.

Literature Search. The main source of information for this study was Chemical Abstracts. From this publication, various patents and other published articles pertaining to the chemical and electrochemical preparations of lead chromate were obtained and reviewed. Various other books were consulted for theoretical background, and other periodicals for more recent work. The specific chemical and physical properties of the chemicals involved were found in handbooks and other existing sources of information.

General Procedure. The actual procedure performed during the experimental portion of this study may be divided into three parts: that work which was done with direct current, that work which was done employing periodically reversed direct current, and that work which was done utilizing superimposed alternating

current on direct current. In all cases, the electrodes were lead sheet. When lead chromate was prepared by use of direct current, an electrical circuit was set up such that the direct current component could be measured. Tests performed using periodically reversed direct current were done with a circuit set up in such a manner that the net current passing through the cell and the total current passing through the circuit could be measured. When superimposed alternating current on direct current was used as the source of electrical energy, a circuit was set up such that the alternating and direct current components could be measured. The frequencies of alternating current studied were 60 and 502.3 ± 7.7 cycles per second.

Evaluation of Results. In all of the tests performed, the various gains and losses in weight of the electrodes of cell and copper coulometers were determined and recorded for use in calculations. The weight per cent lead chromate in each of the products was determined using a standard volumetric analysis. For the periodically reversed direct current tests, various ratios of direct to reverse time were plotted against purity of lead chromate. This same method of evaluation was used in conjunction with the tests performed with superimposed alternating current on direct current.

Materials

The following paragraphs deal with the names and specifications of the materials used during the experimental portion of this investigation.

Acid, Hydrochloric. Concentrated chemically pure solution, Code No 1095, Lot No E-412001, assay 35 to 37 per cent HCl. Obtained from General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used to dissolve samples for lead chromate analyses.

Acid, Sulfuric. CP, 95.5 minimum per cent, Catalog No A-300. Obtained from Fisher Scientific Co., Silver Spring, Md. Used in lead analyses.

Chromium Trioxide. Catalog No 489. Obtained from Phipps and Bird, Inc., Richmond, Va. Used in solution to maintain pH of various electrolytes at 6.0.

Copper Sheet. Purity, 99.99 per cent. Obtained from Christiansburg Lumber Co., Christiansburg, Va. Used as electrode material in coulometer.

Lead Material. Sheet, 1/16 inch thick. Obtained from A. D. Mackay, Inc., 198 Broadway, New York, N. Y. Used to make lead electrodes for use in cell.

Methyl Alcohol. Reagent grade, acetone-free, Catalog No 467. Obtained from Distillation Products Division, Eastman Kodak Co., Rochester, N. Y. Used to dry electrodes.

Potassium Chromate. Reagent grade, Code No 2105, Lot No J085. Manufactured by General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used as a component of electrolyses baths.

Potassium Iodide. A. C. S., Lot No J352, Code No 2120. Obtained from General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used in the quantitative analysis of lead chromate.

Sodium Nitrate. CP, Lot No 475196. Manufactured by Fisher Scientific Co., Silver Spring, Md. Used as a component of the electrolyses baths.

Sodium Thiosulfate. Reagent grade, Lot No E252, Code No 2307. Obtained from General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used in the quantitative analysis of lead chromate.

Starch. Soluble. CP, Lot No 510216. Obtained from Fisher Scientific Co., Silver Spring, Md. Used as indicator solution in conjunction with the quantitative analysis of lead chromate.

Water. Distilled. From Virginia Polytechnic Institute well water. Prepared in an electrically heated copper still. Used in preparing various solutions and electrolytes.

Apparatus

The following apparatus was used in carrying out the experimental portion of this investigation.

Ammeter. Model 301 direct current, multi-stage, range 0-1.5, 0-3.0, 0-30.0 amperes, graduations 0.02, 0.1, and 1.0, respectively. Manufactured by Weston Electrical Instrument Co., Newark, N. J. Used to measure direct current in various electrolysis circuits.

Ammeter. Model 523 alternating current, multi-scale, 60 cycle, range 0-5.0, 0-15.0 amperes, graduation 0.1 ampere. Manufactured by Weston Electrical Instrument Co., Newark, N. J. Used to measure alternating current in various electrolysis circuits.

Ammeter. Alternating current, radio frequency, Type B, thermocouple element, reference No 10A/8481, 0.7 ohm resistance, range: 0.0 to 0.5 amperes. Obtained from Allied Radio Corp., 100 North Western Ave., Chicago, Ill. Used to measure high frequency alternating current.

Aspirator. Brass, Catalog No 9-965, Richards type. Obtained from Fisher Scientific Co., Silver Spring, Md. Used as a source of vacuum for section filtering various samples and chemicals.

Balance. Analytical, chainomatic, Serial No 142238, sensitivity = 0.0001 g, capacity = 200 g. Manufactured by Seederer-Kohlbusch, Inc., Jersey City, N. J. Used to weigh various chemicals and products.

Balance. Triple beam, range = 0 to 21.1 kg, 1.0 g graduations. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to weigh bulk chemicals for solutions.

✓ Battery. Model No 1724 AH, Part No AH 3151, 24 v, 17 amp-hr at 5 hour rate, sp. gr. at full charge: 1.285. Manufactured by Delco-Remy Division, General Motors Corp., Anderson, Ind. Used as a source of direct current.

Beaker. Pyrex glass, 500 ml. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to hold standard coulometer solutions and for electrolytic cells.

Buret. Schallbach, straight stopcock, 100 ml, 0.1 graduations, Catalog No 3-740. Obtained from Fisher Scientific Co., Silver Spring, Md. Used for titrations in quantitative analysis of lead chromate.

Cathode-Ray Oscillograph. Type 274-A, Catalog No 1420A, Serial No 2306, 115/230 v, ac, 50-60 cy, 50 w, single phase. Manufactured by Allen B. Dumont Laboratories, Inc., Passaic, N. J. Used in calibrating vacuum tube voltmeter for measuring

high frequency voltage, and for obtaining alternating current wave forms.

Flask. Filter, pyrex glass, side tube, Catalog No 10-180, 500 ml capacity. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to contain filtrates while suction filtering analytical products and spent electrolytes.

Furnace. Type FD-204C, Serial No 34928, regulated temperature range, 22 to 1100 °C, 110 v, ac, 30.9 amp, 60 cy. Manufactured by Fisher Scientific Co., Silver Spring, Md. Used to dry lead sulfate in analysis of crude products.

Generator. Model No 1198, 25 v, dc, 80 amp, 2400 rpm, 2 kw. Manufactured by Burke Electric Co., Erie, Pa. Used as a source of direct current.

Hot Plate. Autemp, 115 v, ac, 450 w. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to heat distilled water used in analytical work.

Motor. Serial No 822637, 220 v, ac, 3 amp, 1750 rpm, 3 phase, 60 cy, one hp, Catalog No 5644. Obtained from Sears, Roebuck and Co., New York, N. Y. Used to drive motor alternator.

Motor Alternator. No 607 MAWA, 25-29 v, dc, 80-90 amp, 0-11,000 rpm input; 115 v, ac, 13 amp, 1 phase, 0-2500 cy per

second output. Manufactured by Russel Electric Co., Chicago, Ill. Remodeled for use as source of variable frequency alternating current.

Motor, Induction. Serial No 4207, 220 v, ac, 8 amp, 1720 rpm, 3 phase, 3 cy. Obtained from Mechanical Appliance Co., Milwaukee, Wisc. Used to drive direct current generator.

Oven. Electric Utility, Model No OV-8, Serial No 8-270, 110 v, ac, 5 amp. Obtained from Model Electric Laboratories, Chicago, Ill. Used to dry various products and analytical samples.

Periodic Reverser. Model No 10, Serial No 130. Manufactured by Platers' Research Corp., New York, N. Y. Used to obtain periodic reverse current for electrolysis studies.

pH Meter, Glass Electrode. Model H2, 0-14 pH range, Serial No 36147. Manufactured by Beckman Instruments, Inc., South Pasadena, Cal. Used to measure pH of electrolysis baths.

Regulator, Voltage. Serial No 465196, 9 amp, 0-110 v. Manufactured by American Transformer Co., Newark, N. J. Used to adjust magnitude of 60 cycle alternating current.

Rheostat. Slide wire, 19.6 ohms, 4 amp. Obtained from Phipps and Bird, Inc., Richmond, Va. Used to control voltage

and current to electrolysis cells in direct and period reverse current studies.

Rheostat. Slide wire, 112 ohms, 2 amp. Obtained from Phipps and Bird, Inc., Richmond, Va. Used to control voltage and current to electrolysis cells in superimposed alternating current tests.

Rheostat. Slide wire, 125 ohms, 3 amp. Obtained from Phipps and Bird, Inc., Richmond, Va. Used to control voltage and current to electrolysis cells in superimposed alternating current tests.

Stirrer. Magnetic, variable speed type, 110 v, ac, 50 cy. Obtained from Laboratory Industries, Inc., Chicago, Ill. Used to agitate electrolytes while measuring pH.

Thermometer. General laboratory, engraved stem, mercury filled, 350 mm long, 75 mm immersion, range: -5 to 200 °C, subdivisions 1 °C. Supplied by Fisher Scientific Co., Silver Spring, Md. Used to measure the temperature of the electrolysis baths during tests.

Timer. Electrical "Time-It", graduation 0.1 sec, 110 v, ac, 60 cy, 5 w. Manufactured by Precision Scientific Co., Chicago, Ill. Used to measure the length of time of electrolysis.

Vacuum Tube Voltmeter. Model 209A, Serial No 6-13232, 115-120 v, ac, 50-60 cy, single phase. Manufactured by The Hickok Electrical Instrument Co., Cleveland, Ohio. Used to measure high frequency voltages in superimposed alternating current tests.

Voltmeter. Model 489, dc, 0-3, 0-7.5, 0-150 voltage ranges. Manufactured by Weston Electrical Instrument Co., Newark, N. J. Used to measure voltages in electrical circuits.

Weights. Serial No 4C2238, 1.0 to 100.0 g. Manufactured by Seederer-Kohlbusch, Inc., Jersey City, N. J. Used in conjunction with the analytical chainomatic balance.

Method of Procedure

The following paragraphs deal with the methods of procedure employed during the experimental portion of the investigation.

Operating Procedure for Direct Current Electrolyses. A mixture of 6.80 grams of potassium chromate per 1000 grams of distilled water and 8.14 grams of sodium nitrate per 1000 grams of distilled water was used as the electrolyte in the majority of the direct current tests. The resulting electrolyte is the same as was used by Le Blanc and Bindshedler⁽⁶⁹⁾.

The previously described electrolyte was electrolyzed for 4,840 seconds in a cell between three lead electrodes, the central one being the anode and the two outer ones being the cathodes. Figure 6, page 63, gives the schematic wiring diagram of the electrical circuit used in performing the direct current tests. Ammeter, A₂, was used as a rough setting of the current flowing through the circuit, and the coulometer, C, was employed to obtain a more accurate measure of this quantity. In all tests the electrodes were immersed to an area of 24.0 square centimeters, based on one side of an electrode, into the electrolyte. The immersed portion of a single electrode was 6.0 centimeters long and 4.0 centimeters wide. Temperature measurements of the bath before and after electrolysis were made for most of the

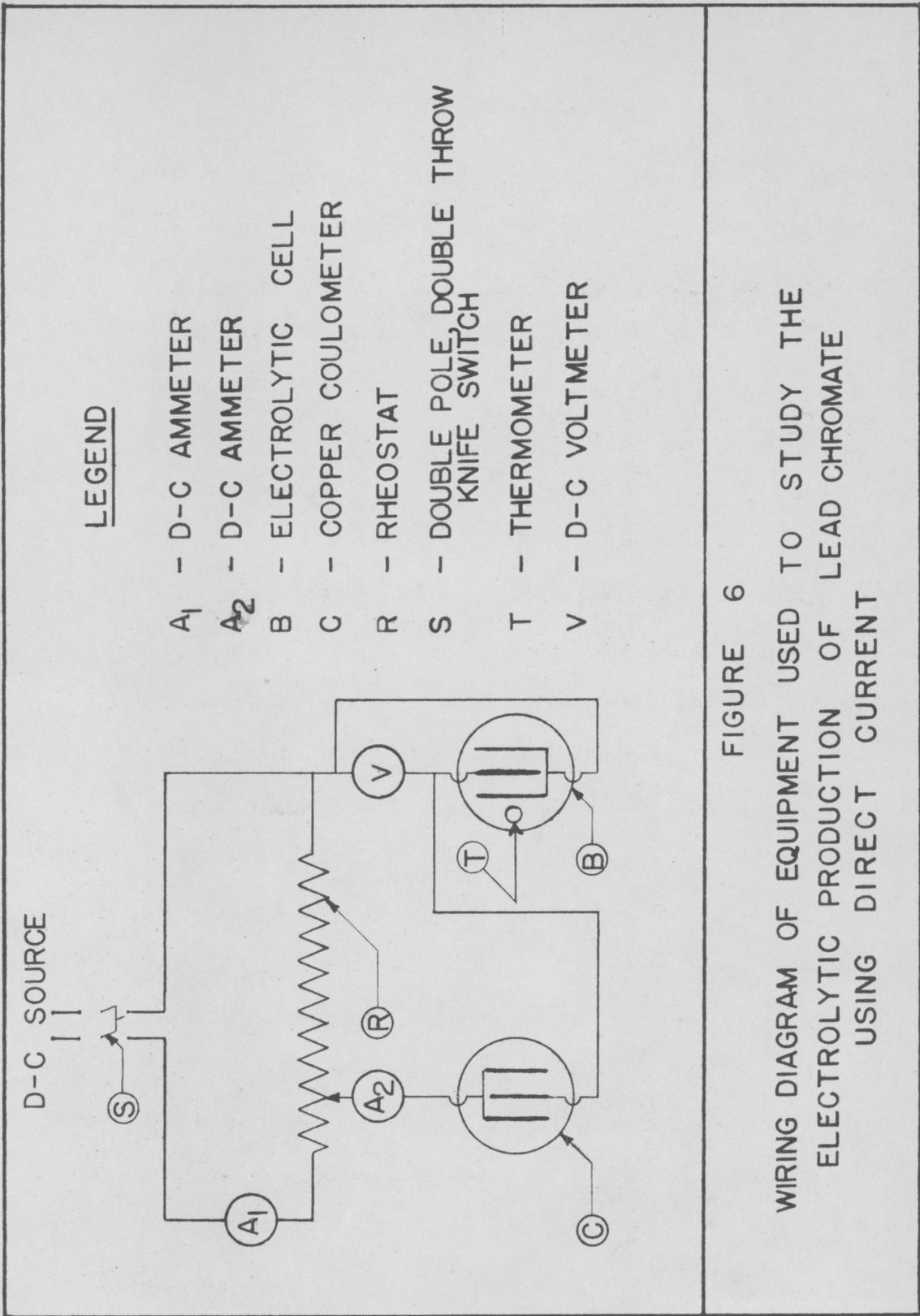


FIGURE 6

WIRING DIAGRAM OF EQUIPMENT USED TO STUDY THE
ELECTROLYTIC PRODUCTION OF LEAD CHROMATE
USING DIRECT CURRENT

tests. Upon completion of electrolysis, the current flow from the motor-generator set was terminated and the cell was removed from the rest of the equipment. Any crude lead chromate adhering to the anode was carefully removed with a toothbrush. The anode from the cell and the copper cathode from the coulometer were washed with cold and hot water and were subsequently allowed to dry after a final washing with methyl alcohol. The loss in weight of the lead anode and the gain in weight of the cathode from the copper coulometer were determined. The lead electrodes which were used in subsequent tests were cleaned with dilute nitric acid, rinsed with hot water, and were allowed to dry. Any coating was removed from the surfaces of the electrodes by scrubbing dry with paper towels.

Filtration of the spent electrolyte containing the crude lead chromate yielded a filtrate which was discarded and a residue which was the crude product. After suction filtering, the residue was washed with hot water. A weighed, medium porosity, sintered glass crucible was used to suction filter the spent electrolytes from all tests. After drying for approximately one hour at 200 to 220 °F, the crude product and sintered glass crucible were weighed and the weight of crude product was recorded. The products prepared were

stored in stoppered test tubes and weighing bottles prior to analysis.

A second electrolyte composed of 3.60 grams of potassium chromate per 1000 grams of distilled water and 11.62 grams of sodium nitrate per 1000 grams of distilled water was used as the electrolyte in some tests. This electrolyte is equivalent to one described by Le Blanc and Bindshedler⁽⁶⁹⁾. During the tests performed with the electrolyte just described, the pH was held constant at 6.0 by the periodic addition of a 2.0 weight per cent solution of chromic acid. The pH was measured by stopping the electrolysis periodically, placing the pH meter electrodes into the cell bath, and reading the value of the pH from the meter scale while the electrolyte was being stirred by means of a magnetic stirrer. Before each test, the unelectrolyzed bath was acidified to a pH value of 6.0. The average volume of a 2.0 weight per cent solution of chromic acid used for most of the tests was 44.4 milliliters. The electrolysis procedure for the two electrolytes was the same for all tests.

Operating Procedure for Periodically Reversed Direct Current Tests. Before tests were performed using periodically reversed direct current, the periodic reverser was

calibrated. Various settings of the reverse time and the direct time dials were made and their respective time cycles were measured by means of an electric timer. Using these data a family of curves was plotted showing the relationship between the direct to reverse time ratio, the direct time setting, and the reverse time setting.

The operating procedure for the periodically reversed direct current tests was much the same as that used for the direct current tests; the main differences being incurred by the use of the periodic reverser. The wiring diagram for the periodic reverse-current tests is given in Figure 7, page 67. A photograph of the set-up is presented in Figure 8, page 68, to better illustrate the arrangement of the circuit components. Two copper coulometers were used in these tests; one for measuring the total current flowing through the circuit, C_1 , and another to measure the net current flowing through the electrolytic cell, C_2 . The loss in weight of all three lead electrodes was determined upon the completion of the individual periodic reverse-current tests. In addition to this procedure, all traces of product were brushed from the surface of the three electrodes into the electrolyte. Various ratios of direct to reverse time were employed during the performance of these studies. The remainder of the operating procedure

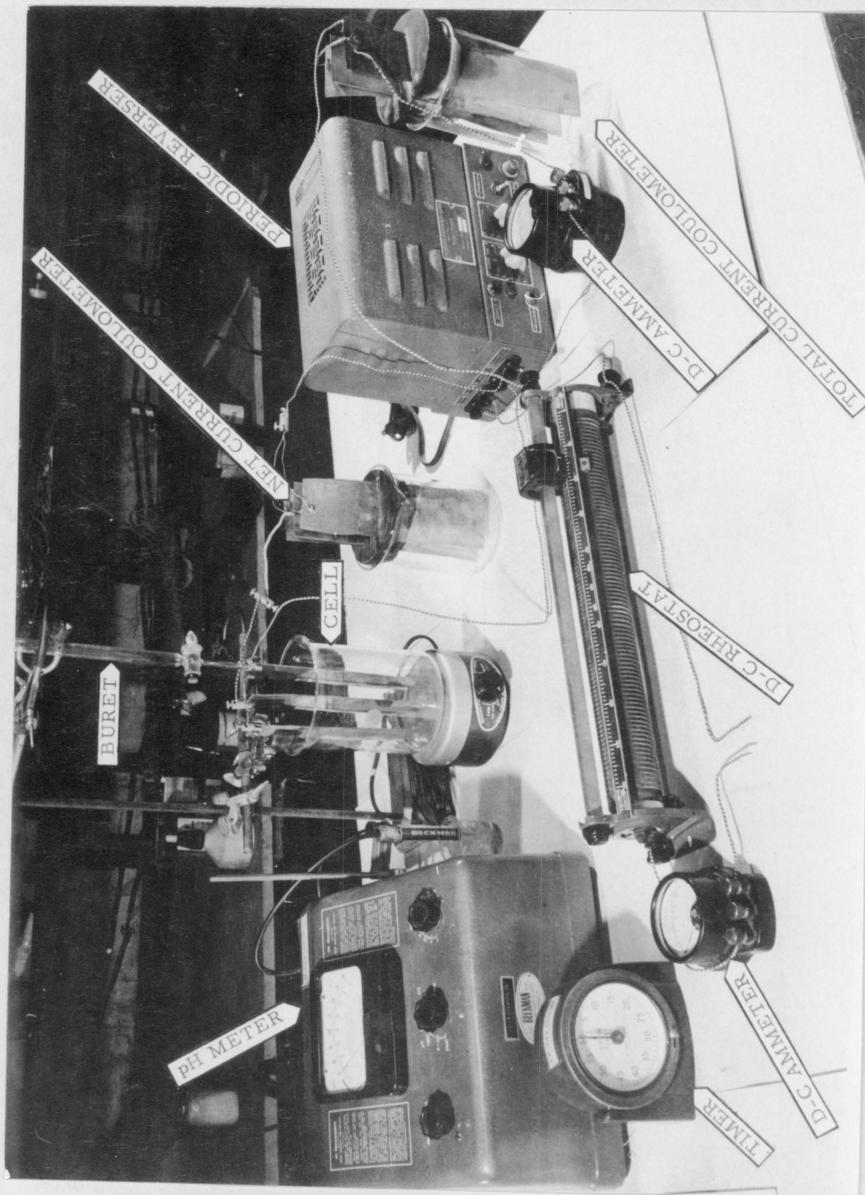


Figure 8. Photograph Showing Arrangement of Equipment Used for the Electrolytic Production of Lead Chromate Using Periodically Reversed Direct Current.

was the same as that used in conjunction with the direct current electrolyses.

Operating Procedure for Electrolyses Performed With Alternating Current Superimposed on Direct Current. The operating procedure for the tests performed with alternating current superimposed on direct current was similar to that employed for the previous series of tests performed with direct current and periodically reversed direct current. The wiring diagram of the circuit used for the electrolyses performed with alternating current superimposed on direct current is given in Figure 9, page 70. Sixty cycle, 110 volt, alternating current was used for five of the experiments, and a motor-driven alternating current generator was employed in experiments requiring higher frequencies. Only one copper coulometer was used during these tests to measure the total direct current. Upon completion of the tests, the loss in weight of all three lead electrodes was determined. Various alternating current densities were employed during these tests while the direct current density was held constant at 0.00460 amperes per square centimeter.

For tests performed with high frequency alternating current superimposed on direct current, a rather lengthy start-up procedure was followed. The circuit was set up according to

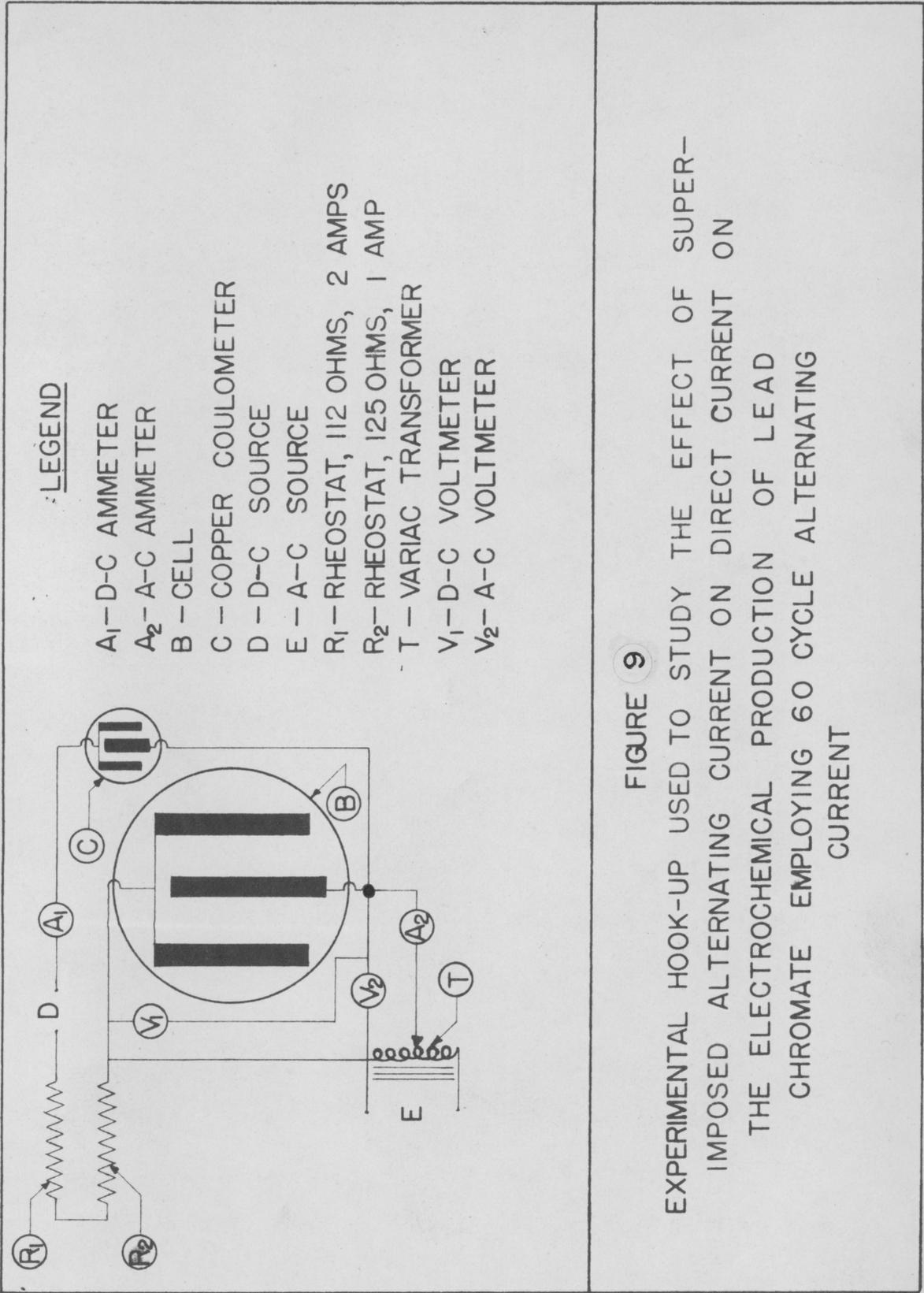


FIGURE 9
EXPERIMENTAL HOOK-UP USED TO STUDY THE EFFECT OF SUPER-
IMPOSED ALTERNATING CURRENT ON DIRECT CURRENT ON
THE ELECTROCHEMICAL PRODUCTION OF LEAD
CHROMATE EMPLOYING 60 CYCLE ALTERNATING
CURRENT

Figure 10, page 72. A photograph of the set-up is given in Figure 11, page 73, to better illustrate the arrangement of the circuit components. The alternating current generator supplying current to E was started, as was the direct current generator. Direct current was allowed to flow to the excitor coils of the alternating current generator. The current was increased by means of a large, rough adjustment, rheostat mounted on the generator until a reading was obtained from ammeter, A₂. After this, the predetermined reading was set on the ammeter by adjusting R₂. Readings were taken from A₂ and V₂ and the direct current flow to the alternating current generator was terminated. Direct current from a 24 volt aircraft battery was allowed to enter the circuit through the connections at D. The predetermined value for ammeter, A₁, was made as quickly as possible by adjusting rheostat, R₁. Readings from A₁ and V₁, were taken, and direct current was then reapplied to the excitor coils of the alternating current generator. At this point, the tests were begun. After the test had begun, readings of the alternating and direct current ammeters and voltmeters were taken. The remainder of the operating and shut-down procedure was identical with that used during the direct current and periodically reversed direct current electrolyses.

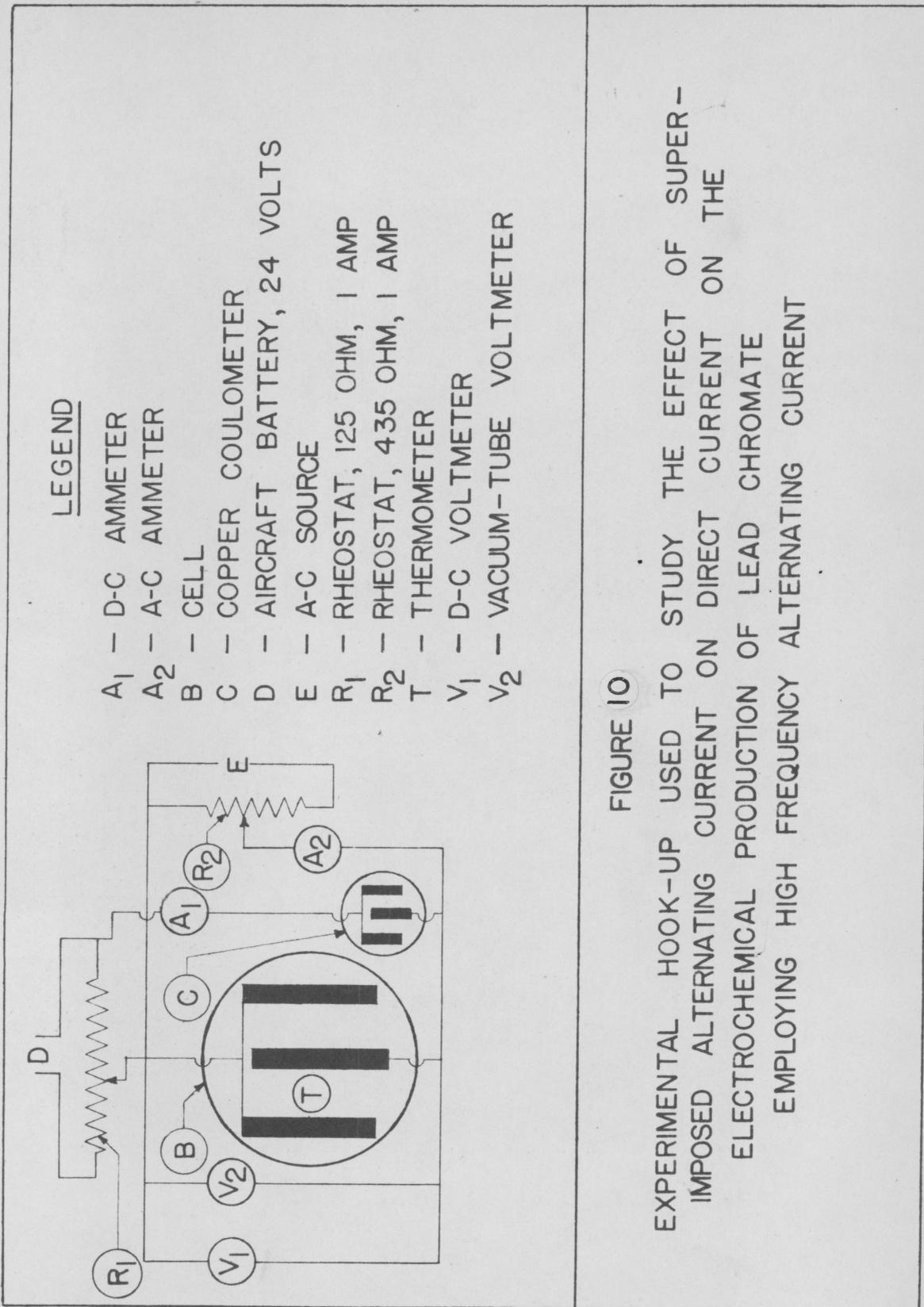


FIGURE 10

EXPERIMENTAL HOOK-UP USED TO STUDY THE EFFECT OF SUPER-
IMPOSED ALTERNATING CURRENT ON DIRECT CURRENT ON THE
ELECTROCHEMICAL PRODUCTION OF LEAD CHROMATE
EMPLOYING HIGH FREQUENCY ALTERNATING CURRENT

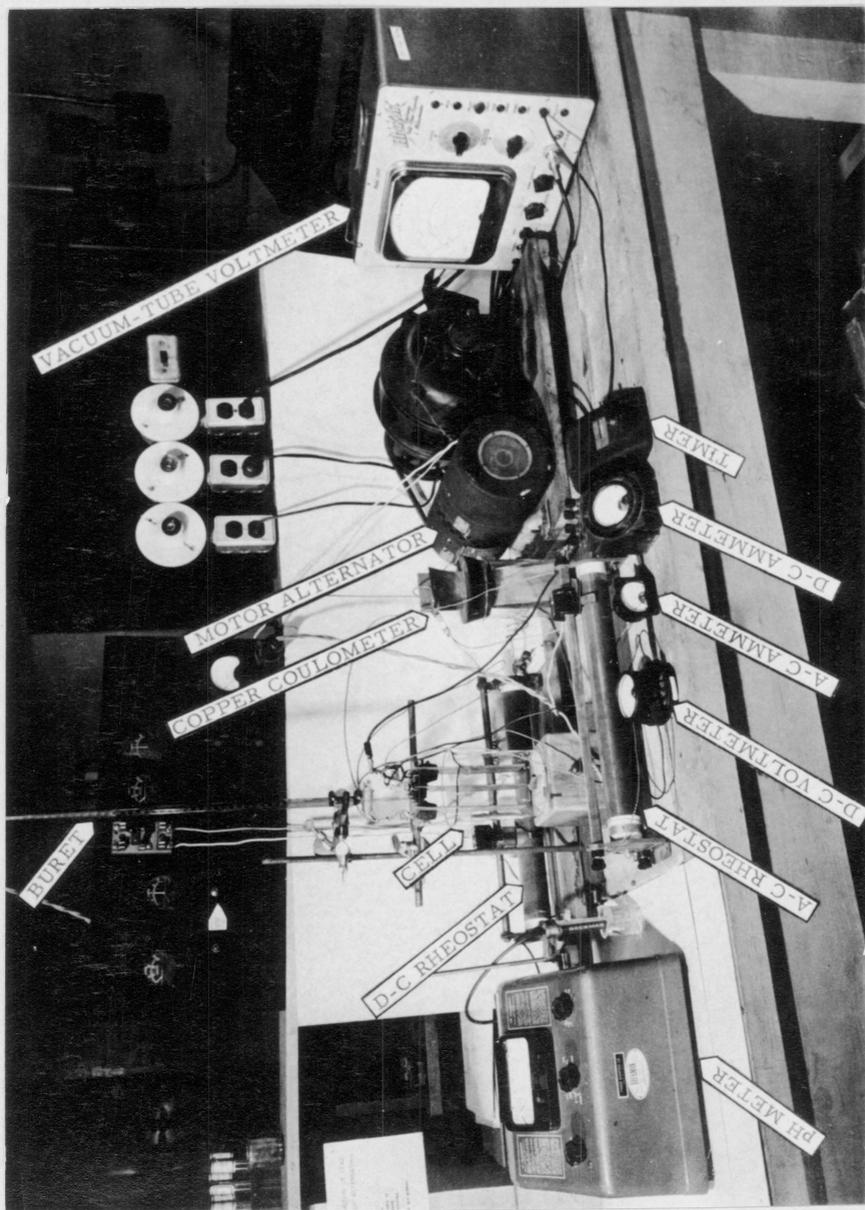


Figure 11. Photograph Showing Arrangement of Equipment Used for the Electrolytic Production of Lead Chromate Using High Frequency Alternating Current Superimposed on Direct Current.

Determination of Relationship Between Root-Mean-Square and Peak Values of High Frequency Alternating Current. For this procedure, a decade, non-inductive resistance box was placed in series with the cell shown in Figure 10, and a cathode-ray oscilloscope was connected in parallel with the resistance. Test conditions were simulated, and a wave pattern was obtained on the screen of the oscilloscope. After adjustment of the picture tube, x- and y- components were obtained from the grid screen over the face of the picture tube. A plot was made of x- and y^2 - in order to integrate, graphically, to obtain the area under the curve. The obtained area was divided by the x- component, yielding the value of y^2 . The square root of the value of y^2 was divided into the maximum y-component value. The quotient from this operation gave a conversion factor which, when multiplied by root-mean-square or meter readings for current, will yield the peak value for the current. The peak currents obtained were the values used in calculating peak alternating current densities.

The procedure just outlined was used specifically for 500 cycle per second alternating current. A similar procedure was carried out to determine the same conversion factor for 60 cycle alternating current. The value obtained,

by graphical integration methods, was comparable to that cited in the literature^(22a).

Calibration Procedure for Vacuum-Tube Voltmeter. A cathode-ray oscilloscope was employed as the calibration instrument for this procedure. Equipment was set up for the preparation of lead chromate using alternating current superimposed on direct current. A certain voltage drop across the electrolytic cell was obtained using 60 cycle alternating current as measured by a meter. The amplitude of this particular voltage on the oscilloscope was adjusted to some known value; ten divisions in this procedure, and the voltage recorded from the vacuum-tube voltmeter. A voltage of approximately 550 cycles per second of the same vertical amplitude was then set into the circuit with no 60 cycle current flowing. The vacuum-tube voltmeter value was then recorded and compared with the corresponding value obtained from the 60 cycle voltage. Various values of 60 cycle alternating current voltage were compared with the obtained high frequency voltages.

It was found that, within the voltage range to be employed, the difference between the two voltage measurements was not appreciable and did not warrant the construction of a calibration curve. Greater differences were observed between

the two values when values of greater than 100 volts were employed.

Analytical Procedure. The analytical procedure used in conjunction with this investigation consisted of lead chromate and lead analyses on most of the products obtained.

Lead Chromate Analysis. The lead chromate analysis performed on the products obtained was much the same as that given by Snell and Biffen⁽³⁾. The procedure is known as the iodometric method. A sample weighing from 0.4 to 1.0 gram was placed in a clean, dry 250 milliliter beaker. Six to 10.0 milliliters of 1:4 hydrochloric acid was added and the solution swirled to facilitate the solution of all lead chromate. The solution was then filtered through a clean, dry sintered glass crucible into a clean, dry suction flask. The residue was washed with hot, distilled water. After cooling, 20.0 milliliters of 20.0 weight percent potassium iodide were added to the filtrate. The filtrate was titrated with 0.10 normal sodium thio-sulfate solution. After the color faded to yellow, starch solution was added as the indicator and the titration was continued. The end point was reached

when the color of the solution changed from green to light yellow.

Lead Analysis. The procedure for the determination of lead in the samples was similar to that given by Toch⁽⁷⁾. The weighed sample was boiled for about five minutes in 20.0 milliliters of concentrated hydrochloric acid, adding one or two milliliters of ethyl alcohol drop by drop. The solution was diluted with approximately 100 milliliters of boiling distilled water. After boiling a few minutes longer, the solution was filtered and washed with more boiling distilled water. The filtrate was neutralized with ammonium hydroxide until a slight precipitate was present. It was then reacidified slightly, using an excess of not more than 1.5 milliliters of concentrated hydrochloric acid in 100 milliliters of solution. At this point the lead was precipitated as lead sulfide by bubbling hydrogen sulfide through the solution. The precipitate was filtered and washed with hydrogen sulfide water. After dissolution in hot, dilute nitric acid, the precipitate was boiled in 10.0 milliliters of 1:1 sulfuric acid. The resulting solution was boiled until heavy fumes of sulfur trioxide were evolved. After cooling,

35.0 milliliters of water were added and the solution was boiled for one minute. The precipitate was filtered through a clean, dry, weighed sintered glass crucible and was washed three times with 5.0 milliliter portions of 15.0 per cent sulfuric acid, and finally with a solution of 50 per cent ethyl alcohol to remove the sulfuric acid. The crucible and contents were dried in an oven for 10 minutes and were then heated at 600 °F for 20 minutes. The crucible was cooled and the precipitate weighed as lead sulfate.

Data and Results

The operating conditions, data and results obtained during the experimental portion of this investigation are presented in tabular form as is described in the following paragraphs.

Calibration Data for the Periodic Reverser. Table I, page 81, gives the calibration data for the Platers' Research Corporation periodic reverser.

Periodic Reverser Calibration Curves. Figure 12, page 82, gives the family of curves showing the relationship between the ratio of direct to reverse time and the dial settings for the Platers' Research Corporation periodic reverser used in this study.

Operating Conditions, Data and Results for the Electrolytic Production of Lead Chromate Using Direct Current. The operating conditions, data and results obtained from the performance of the direct current electrolyses are presented in Table II, page 83.

Operating Conditions, Data and Results for the Electrolytic Production of Lead Chromate Using Periodically Reversed Direct Current. The operating conditions, data and results obtained from the performance of

the periodically reversed direct current tests are reported in Table III, page 84.

Operating Conditions, Data and Results for the Electrolytic Production of Lead Chromate Using Alternating Current Superimposed on Direct Current. The operating conditions, data and results obtained from the performance of the tests using superimposed alternating current on direct current are given in Table IV, page 85.

Data from Oscilloscope Used for Plotting Wave Forms of Alternating Currents of 60 and 500 Cycles Per Second. Data used for plotting the wave forms of the alternating current used in this investigation are given in Table V, page 86.

Wave Forms of Alternating Current. The x-y plots showing the wave forms of the 60 and 500 cycle alternating currents are presented in Figure 13, page 87. These curves were obtained by plotting the data given in Table V, page 86.

TABLE I

Calibration Data for Platers' Research
Corporation Periodic Reverser

Reverse Time Setting divisions	Direct Time Setting divisions	Reverse Time sec	Direct Time sec
0	1	-----	2.3
0	3	-----	6.5
0	5	-----	10.7
0	7	-----	15.1
0	9	-----	19.2
1	0	0.28	-----
3	0	1.35	-----
5	0	2.68	-----
7	0	4.00	-----
9	0	5.30	-----

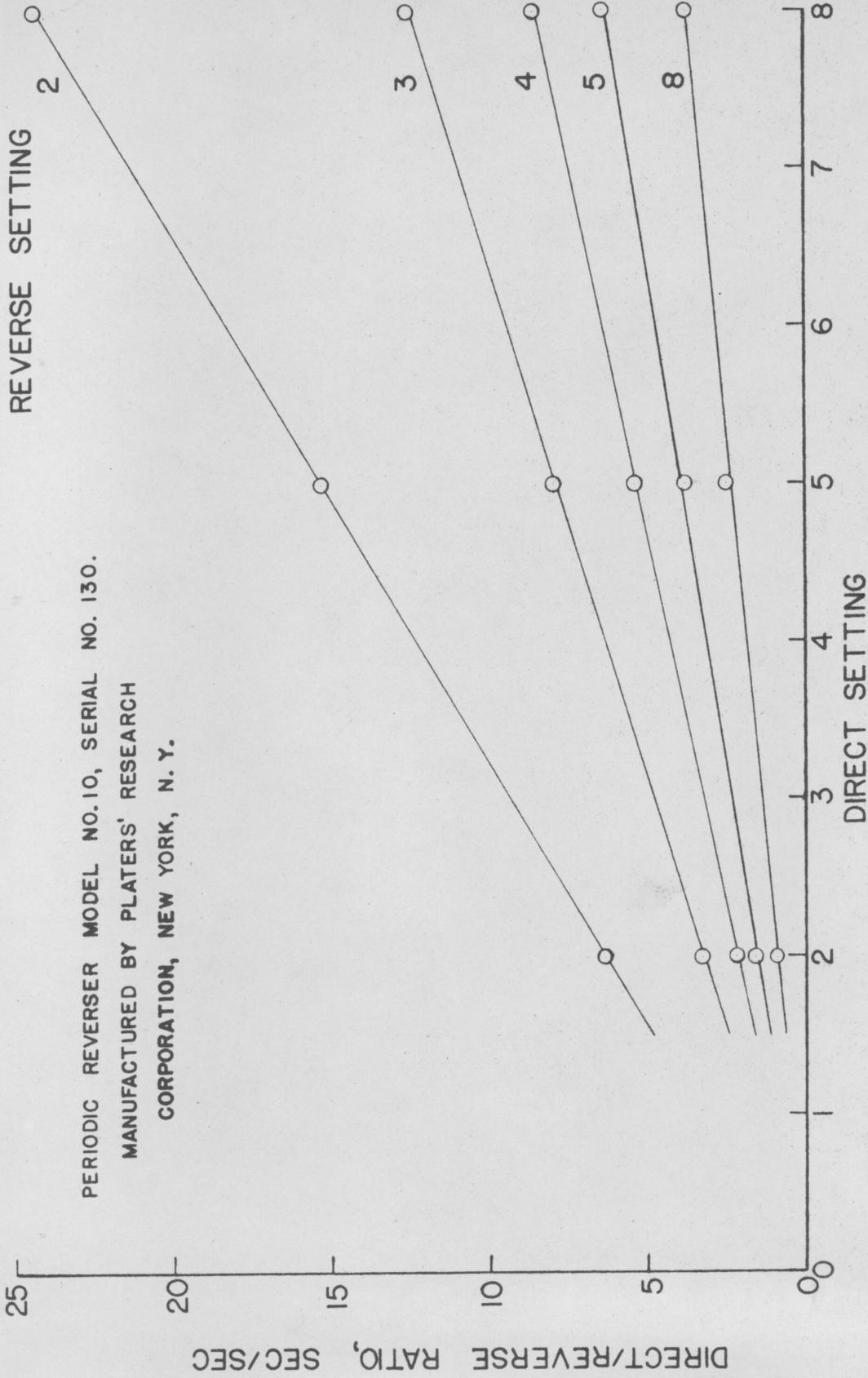


FIGURE 12. GRAPH SHOWING THE RELATIONSHIP BETWEEN THE RATIO OF DIRECT TO REVERSE TIME AND THE DIAL SETTINGS FOR THE PERIODIC REVERSER.

TABLE II
Operating Conditions, Data and Results Obtained From the
Electrolytic Production of Lead Chromate
Using Direct Current

TABLE II

Operating Conditions, Data and Results Obtained From the Electrolytic Production of Lead Chromate Using Direct Current

Test No	Total Current	Volume of Electrolyte Used	Time of Electrolysis	Current Densities		Loss in Weight of Anode	Weight of Coulometer Cathode		Bath Temperature		Current Efficiency ^e	Anode Corrosion Efficiency	Weight of Crude Product	Product Analysis		Observations
				Anode	Cathode		Before	After	Before	After				%	%	
	amp	ml	sec	amp/sq cm		grams	grams		°C	°C	%	%	grams	%	%	
1-812-46 ^a	0.285	525	4840	0.0059	0.0030	0.7891	68.8450	69.2991	31.0	----	----	53.5	0.9556	-----	-----	Black specks formed on anode and increased in size as electrolysis proceeded. Reddish-orange product.
2-812-60 ^a	0.279	550	4200	0.0058	0.0029	0.7708	69.2991	69.6848	28.0	----	6.82	61.5	0.9097	11.97	-----	Black specks formed on anode as before. Gases evolved at all electrodes. Reddish-orange product.
11-812-93 ^a	0.624	500	4840	0.0130	0.0065	1.8396	70.9737	71.9687	32.0	38.0	4.56	56.7	2.1134	10.91	94.52	Black specks formed on anode as before. Large amounts of gases evolved at electrodes. Reddish-orange product.
12-812-97 ^a	0.615	500	4840	0.0128	0.0064	1.9145	71.9687	72.9493	33.0	38.5	3.75	59.8	2.1819	8.55	-----	Same as above.
13-812-100 ^a	1.139	500	4840	0.0237	0.0119	3.1159	72.9493	74.7640	32.0	42.0	4.76	52.6	3.0901	14.22	70.00	Same as above.
14-812-104 ^a	1.145	500	4840	0.0239	0.0120	3.4728	74.7640	76.5913	32.0	----	----	58.4	3.5095	-----	-----	Same as above.
18-812-154 ^b	0.248	500	4840	0.0052	0.0026	1.3341	73.9480	74.3432	27.5	28.5	45.8	103.5	1.6916	54.3	-----	Hardly any black specks formed on anode. Gases evolved at all electrodes. Reddish-orange product.
19-812-157 ^b	0.259	500	4840	0.0054	0.0027	1.3833	74.3432	74.7571	27.0	28.5	40.6	102.5	1.7646	48.3	-----	Same as above.
27-812-218 ^c	0.215	500	4840	0.0049	0.0022	1.1808	76.4865	76.8290	25.5	25.5	98.1	105.9	1.8974	92.7	56.5	No black specks formed on anode. Gas evolved at cathodes only. Yellow product obtained.

^aElectrolyte composition — mixture of 6.80 grams K₂CrO₄/1000 grams distilled water and 8.14 grams NaNO₃/1000 grams distilled water.

^bElectrolyte composition — mixture of 3.60 grams K₂CrO₄/1000 grams distilled water and 11.62 grams NaNO₃/1000 grams distilled water.

^cElectrolyte composition as described under "b", and bath pH was held constant at 6.0 throughout test by addition of 2.0 weight per cent solution of CrO₃.

^dAnalysis of black scale removed from anode.

^eCurrent efficiency = $\frac{(\text{weight of product})(\% \text{ CrO}_3 \text{ as PbCrO}_4)(\text{M. W. of Cu})}{(\text{gain in weight of coulometer cathode})(\text{M. W. of PbCrO}_4)} \times 100.$

TABLE III

Operating Conditions, Data and Results Obtained
From the Electrolytic Production of Lead
Chromate Using Periodically Reversed
Direct Current

TABLE III

Operating Conditions, Data and Results Obtained From the Electrolytic Production of Lead Chromate Using Periodically Reversed Direct Current

Test No	Total Current ^f	Current Flow Through Cell		Current Density, Middle Electrode		Current Density, Two Outer Electrodes		Loss in Weight of Middle Electrode	Loss in Weight of Two Outer Electrodes	Weight of Coulometer Cathode				Bath Temp		Current Efficiency ^e	Corrosion Efficiency		Direct Time Per Cycle	Reverse Time Per Cycle	Direct/Reverse Ratio		Weight of Crude Product	Product Analysis		Observations					
		Direct Cycle	Reverse Cycle	amp	amp/sq cm	amp	amp/sq cm			grams	grams	Total		Before	After		°C	°C			%	%		sec	sec		sec/sec	amp/amp	grams	%	%
												Before	After																		
		Direct Cycle	Reverse Cycle	Direct Cycle	Reverse Cycle	Direct Cycle	Reverse Cycle			Direct Cycle	Reverse Cycle	Before	After	Before	After		Before	After			Before	After		Before	After		Before	After	Before	After	CrO ₃ as PbCrO ₄
5-812-68 ^a	0.329	0.329	0.328	0.0069	0.0068	0.0069	0.0068	0.0177	0.0109	62.3715	62.8895	70.1294	70.1307	----	----	-----	2.07	1.28	4.62	4.62	1:1	1.01:1	0.0301	----	----	Product formed on all electrodes - no gas.					
6-812-72 ^a	0.332	0.329	0.334	0.0069	0.0070	0.0034	0.0035	0.0085	0.0089	62.8955	63.4243	70.1307	70.1267	----	----	-----	0.99	1.02	4.62	4.62	1:1	0.99:1	0.0565	----	----	Same as above.					
15-812-107 ^a	0.727	0.843	0.613	0.0176	0.0128	0.0088	0.0064	0.0979	0.0914	66.3846	67.5443	76.5913	76.7750	29.5	31.0	-----	4.47	5.74	4.62	4.62	1:1	1.38:1	0.2244	----	----	Same as above.					
4-812-63 ^a	0.494	0.378	0.840	0.0079	0.0175	0.0039	0.0088	0.3874	0.0259	61.5838	62.3715	70.0132	70.1294	----	----	-----	5.76	26.30	2.37	13.86	3:1	1.35:1	0.5300	43.5	59.1	Same as above. Very fine particle size.					
8-812-81 ^a	0.511	0.390	0.875	0.0081	0.0182	0.0041	0.0091	0.4339	0.0996	64.0505	64.8657	70.4552	70.5725	31.0	33.0	-----	28.60	8.76	13.86	4.62	3:1	1.34:1	0.5488	----	----	Gas evolved - black specks formed on anode.					
9-812-85 ^a	0.455	0.347	0.990	0.0072	0.0206	0.0036	0.0103	0.4773	0.0832	64.8657	65.5902	70.5725	70.7704	31.0	34.5	-----	31.80	9.70	13.40	2.68	5:1	1.75:1	0.6201	----	----	Same as above.					
10-812-89 ^a	0.498	0.376	1.111	0.0078	0.0232	0.0039	0.0116	0.7278	0.0699	65.5902	66.3846	70.7704	70.9737	31.5	34.5	4.47	44.7	7.16	13.40	2.68	5:1	1.69:1	0.9487	18.9	----	Same as above.					
3-812-56 ^a	0.405	0.337	1.095	0.0070	0.0228	0.0035	0.0114	0.8548	0.0249	60.9385	61.5838	69.6848	70.0132	31.0	----	5.43	53.8	4.81	13.50	1.35	10:1	3.07:1	1.0403	17.1	----	Same as above.					
7-812-76 ^a	0.393	0.330	1.025	0.0069	0.0214	0.0034	0.0107	0.4381	0.0055	63.4243	64.0505	70.1267	70.4552	30.0	32.0	-----	28.1	1.25	13.50	1.35	10:1	3.21:1	0.5034	----	----	Same as above.					
16-812-110 ^a	0.322	0.278	1.192	0.0058	0.0249	0.0029	0.0124	0.3565	0.0452	67.5543	68.0573	76.7750	77.1069	29.0	30.0	4.50	25.9	15.30	13.40	0.67	20:1	4.66:1	0.4514	26.0	----	Same as above.					
17-812-114 ^a	0.575	0.526	1.548	0.0110	0.0322	0.0055	0.0161	1.4705	0.0499	68.0573	68.9737	77.1069	77.7892	28.5	31.0	2.74	56.5	13.06	13.40	0.67	20:1	6.82:1	1.6539	12.0	----	Same as above.					
20-812-168 ^a	0.315	0.273	0.443	0.0057	0.0092	0.0028	0.0046	0.5462	0.0375	64.4000	64.9025	74.7516	74.9017	31.0	33.5	11.50	51.4	6.53	13.86	4.62	3:1	1.85:1	0.5760	32.3	51.1	Same as above. Very coarse product.					
21-812-172 ^a	0.302	0.271	0.461	0.0056	0.0096	0.0028	0.0048	0.6253	0.0299	64.9025	65.3843	74.9017	75.1383	31.5	33.5	6.75	53.5	7.48	13.40	2.68	5:1	2.93:1	0.8461	19.5	63.4	Same as above.					
22-812-176 ^a	0.270	0.248	0.488	0.0052	0.0093	0.0026	0.0047	0.7855	-0.0060	65.3843	65.8153	75.1383	75.4263	31.0	32.5	7.08	67.1	d	13.50	1.35	10:1	5.02:1	0.8487	18.3	58.7	Same as above.					
23-812-180 ^a	0.258	0.245	0.520	0.0051	0.0108	0.0026	0.0054	0.8497	-0.0077	65.8153	66.2264	75.4263	75.7583	30.5	33.5	5.46	70.0	d	13.40	0.67	20:1	9.40:1	0.9401	12.1	85.0	Same as above.					
24-812-202 ^b	0.355	0.240	0.500	0.0050	0.0104	0.0025	0.0052	0.4679	-0.0043	74.9501	75.4366	68.7670	68.8557	29.0	32.0	8.80	50.0	d	13.86	4.62	3:1	1.45:1	0.4600	47.3	73.1	No gas evolved. Reddish-orange product.					
25-812-209 ^c	0.343	0.284	0.524	0.0067	0.0124	0.0034	0.0062	0.5848	-0.0016	75.4366	75.9841	68.8557	68.9870	26.5	27.5	25.10	52.8	d	13.86	4.62	3:1	1.63:1	0.9077	77.0	51.7	Gas evolved. Fine, dark, yellow product.					
26-812-213 ^c	0.315	0.253	0.502	0.0058	0.0114	0.0029	0.0057	0.5533	-0.0041	75.9841	76.4865	68.9870	69.0900	27.5	28.5	28.25	56.0	d	13.86	4.62	3:1	1.52:1	1.0092	71.5	52.6	Same as above.					
28-812-224 ^c	2.375	2.295	2.800	0.0359	0.0437	0.0180	0.0219	7.7426	0.0399	76.4969	80.2859	68.7062	71.0069	29.0	35.5	57.25	77.9	1.66	13.40	2.68	5:1	4.10:1	12.2636	90.0	63.2	Same as above. Yellower product obtained.					
29-812-228 ^c	0.328	0.279	0.626	0.0058	0.0131	0.0029	0.0065	0.8027	-0.0181	80.2859	80.8088	71.0069	71.1969	31.5	30.5	41.25	69.4	d	13.40	2.68	5:1	2.17:1	1.2181	90.0	59.7	Same as above.					
30-812-230 ^c	0.290	0.249	0.746	0.0052	0.0156	0.0026	0.0078	0.9529	-0.0186	80.8088	81.2711	71.1969	71.4627	30.5	30.5	60.00	82.5	d	13.50	1.35	10:1	3.27:1	1.5052	93.7	53.3	Same as above.					
31-812-232 ^c	0.257	0.234	0.719	0.0049	0.0150	0.0024	0.0075	1.0489	-0.0079	81.2711	81.6815	71.4627	71.7638	30.0	30.0	66.75	90.5	d	13.40	0.67	20:1	6.50:1	1.6672	93.9	55.4	Same as above.					

^aElectrolyte composition — mixture of 6.80 grams K₂CrO₄/1000 grams distilled water and 8.14 grams NaNO₃/1000 grams distilled water.

^bElectrolyte composition — mixture of 3.60 grams K₂CrO₄/1000 grams distilled water and 11.62 grams NaNO₃/1000 grams distilled water.

^cElectrolyte composition as described under "b", and bath pH was held constant at 6.0 throughout test by addition of 2.0 weight per cent solution of CrO₃.

^dReverse cycle corrosion efficiency is meaningless for these tests since two outer electrodes gained weight.

^eCurrent efficiency = $\frac{(\text{weight of product})(\% \text{CrO}_3 \text{ as PbCrO}_4)(\text{M. W. of Cu})}{(\text{gain in weight of coulometer cathode})(\text{M. W. of PbCrO}_4)} \times 100$.

^fBased on total coulometer.

Note: 500 milliliters of electrolyte were electrolyzed for 4840 seconds in all tests.

TABLE IV
Operating Conditions, Data and Results Obtained From the
Electrolytic Production of Lead Chromate Using
Alternating Current Superimposed
on Direct Current

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Operating Conditions, Data and Results Obtained From the Electrolytic Production of Lead Chromate Using Alternating Current Superimposed on Direct Current

Test No	Electrolyte Volume	Current			Direct Current Voltage	Alternating Current Densities ^a		Direct Current Densities		Loss in Weight		Corrosion Efficiency %	Current Efficiency ^c %	Frequency cy/sec	Bath Temp		Weight Crude Product grams	CrO ₃ as PbCrO ₄ %	Yield ^e gm/D. C. amp-hr
		Direct ^d amp	Alternating RMS Peak amp			Middle Electrode amp/sq cm	Outer Two Electrodes amp/sq cm	Middle Electrode amp/sq cm	Outer Two Electrodes amp/sq cm	Middle Electrode grams	Outer Two Electrodes grams				°C	°C			
			ml	amp															
35-812-252	500	0.214	0.038	0.054	1.45	0.00113	0.00057	0.00444	0.00222	0.7534	-0.0014	67.9	64.5	60	27.5	28.5	1.1844	94.1	3.87
33-812-242	500	0.213	0.044	0.062	0.90	0.00141	0.00071	0.00484	0.00242	0.7414	-0.0063	67.0	63.7	60	29.0	28.0	1.1713	93.8	3.83
36-812-256	500	0.214	0.10	0.14	1.50	0.00292	0.00146	0.00444	0.00222	1.4657	-0.0023	84.5	60.2	60	28.5	29.5	1.1076	94.2	3.62
34-812-248	880	0.458	0.50	0.71	1.25	0.00690	0.00345	0.00440	0.00220	0.9944	-0.0032	41.8	38.2	60	28.5	26.0	1.5746	90.0	2.30
32-812-239	500	0.213	0.44	0.62	0.30	0.01410	0.00705	0.00484	0.00242	0.1235	0.0026	11.2	11.0	60	28.0	29.0	0.2141	88.6	0.66
38-812-269	700	0.464	0.10	0.16	2.00	0.00160	0.00080	0.00464	0.00232	2.4381	-0.0053	101.0	94.4	504.5	27.5	28.0	3.6476	97.2	5.69
39-812-272	700	0.480	0.50	0.78	2.00	0.00780	0.00390	0.00480	0.00240	2.4973	-0.0154	100.0	97.8	494.7	28.0	32.5	3.8237	99.4	5.89
37-812-266	500	0.240	0.44	0.68	2.50	0.01546	0.00773	0.00545	0.00273	1.1411	-0.0048	91.7	89.7	500.0	27.5	31.0	1.7850	97.6	5.40
40-812-276 ^b	700	0.415	0.10	0.16	1.50	0.00160	0.00080	0.00415	0.00208	1.0255	-0.0124	103.1	97.6	510.0	28.0	30.0	1.6233	93.0	5.87

^aBased on peak values of alternating current.

^bElectrolyzed for 2229 seconds, all others electrolyzed for 4840 seconds.

^cCurrent Efficiency = $\frac{(\text{weight of product})(\% \text{ CrO}_3 \text{ as PbCrO}_4)(\text{M. W. of Cu})}{(\text{gain in weight of coulometer cathode})(\text{M. W. of PbCrO}_4)} \times 100.$

^dBased on copper coulometer.

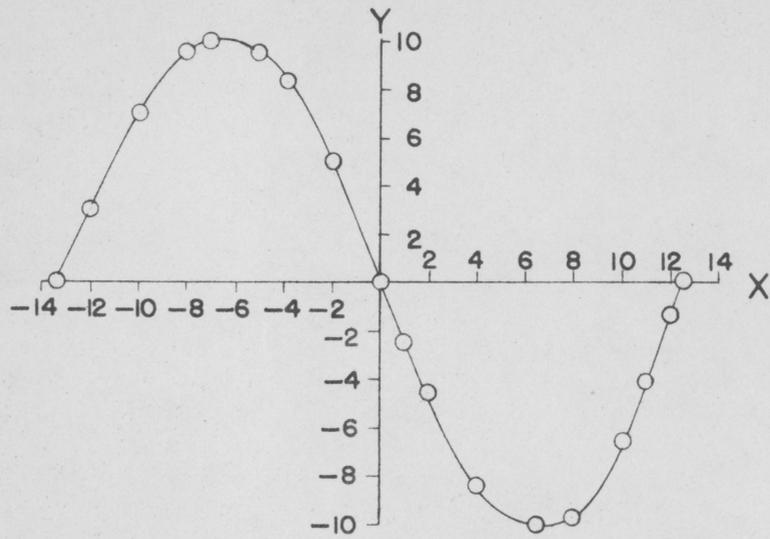
^eTheoretical is 6.07 grams/direct current ampere-hour.

Note: Electrolyte composition — mixture of 3.60 grams K₂CrO₄/1000 grams distilled water and 11.62 grams NaNO₃/1000 grams distilled water. Bath pH was held constant at 6.0 by addition of 2.0 weight per cent solution of CrO₃.

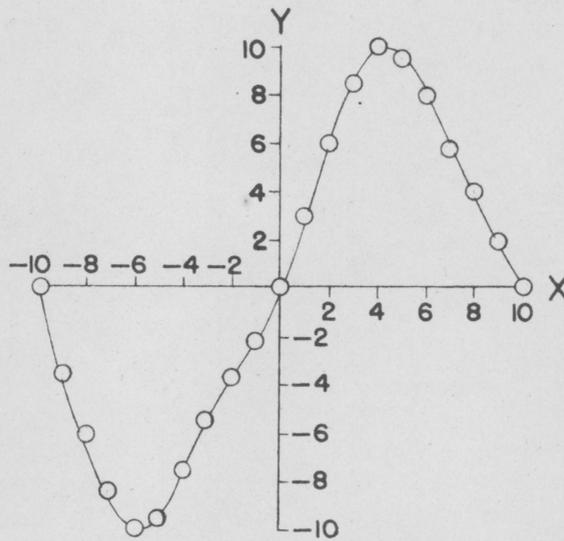
TABLE V

Data From Oscilloscope Used for Plotting Wave Forms
of Alternating Currents of 60 and 500 Cycles Per Second

Frequency			
<u>60 cy/sec</u>		<u>500 cy/sec</u>	
x-component	y-component	x-component	y-component
divisions	divisions	divisions	divisions
-13.5	0.0	-10.0	0.0
-12.0	3.0	-9.0	-3.5
-10.0	7.0	-8.0	-6.0
-8.0	9.7	-7.0	-8.4
-6.5	10.0	-6.0	-10.0
-5.0	9.5	-5.0	-9.5
-4.0	8.2	-4.0	-7.5
-2.0	5.0	-3.0	-5.4
-1.0	2.5	-2.0	-3.8
0.0	0.0	-1.0	-2.2
1.0	-2.5	0.0	0.0
2.0	-4.5	1.0	3.0
4.0	-8.4	2.0	6.0
6.5	-10.0	3.0	8.5
8.0	-9.5	4.0	10.0
10.0	-6.5	5.0	9.5
11.0	-4.1	6.0	8.0
12.0	-1.4	7.0	5.8
12.5	0.0	8.0	4.0
		9.0	2.0
		10.0	0.0



(A) 60 CYCLE WAVE FORM.



(B) 500 CYCLE WAVE FORM.

FIGURE 13. WAVE FORMS OF ALTERNATING CURRENT.

Sample Calculations

Samples of the calculations performed with the data obtained during the experimental portion of this thesis are given in this section. Included in this section are samples of calculations performed with the data obtained from direct current, periodically reversed direct current and alternating current superimposed on direct current tests. The data used to illustrate these calculations are those obtained from test 31-812-232, except where otherwise specified. Also included in this section are calculations dealing with number of poles in the alternator, and the determination of a factor for converting root-mean-square values of 500 cycle alternating current to peak values.

Total Current. The total current flowing through the electrolytic cell was calculated on the basis of the gain in weight of the cathode of a total copper coulometer connected in series with the cell. The following formula was employed:

$$I = \frac{(F)(G_t)}{(E_{Cu})(T)}$$

where:

- I = total current passed, amp
- F = Faraday's constant, 96,500 amp-sec/equivalent
- T = length of time of test, sec
- G_t = gain in weight of cathode of total copper coulometer, gm
- E_{Cu} = equivalent weight of copper, or 31.8 gm

$$I = \frac{(96,500)(0.4104)}{(31.8)(4,840)} = 0.257 \text{ amp}$$

Weight of Copper Deposited on Cathode of Net Coulometer

During Either Direct or Reverse Cycle. This calculation was performed by the simultaneous solution of two equations.

$$w_1 + w_2 = W_1$$

and

$$w_1 - w_2 = W_2$$

where:

w_1 = weight of copper deposited on cathode of net coulometer during direct cycle, gm

w_2 = weight of copper deposited on cathode of net coulometer during reverse cycle, gm

W_1 = weight of copper deposited on cathode of total coulometer, gm

W_2 = weight of copper deposited on cathode of net coulometer, gm

$$w_1 + w_2 = 0.4104$$

$$+ w_1 - w_2 = 0.3011$$

$$2w_1 = 0.7115$$

$$w_1 = 0.3558 \text{ gm}$$

$$w_2 = 0.0546 \text{ gm}$$

From these weights were calculated the respective number of amperes that flowed through the cell during either the direct or reverse cycle of the electrolysis.

Direct to Reverse Current Ratio. The direct to reverse current ratios for the periodic reverse tests were calculated according to the following formula:

$$R = \frac{w_1}{w_2}$$

where:

R = direct to reverse current ratio, gm/gm or amp/amp

w₁ = weight of copper deposited on cathode of net coulometer during direct cycle, gm

w₂ = weight of copper deposited on cathode of net coulometer during reverse cycle, gm

$$R = \frac{0.3558}{0.0546} = 6.5 \text{ gm/gm or amp/amp}$$

Anode and Cathode Current Densities. These values were calculated by means of the following formula:

$$CD_a = \frac{I_d}{A_a}$$

where:

CD_a = anode current density, amp/sq cm

I_d = current that flowed through cell during direct cycle, amp

A_a = total surface area of anode, sq cm

$$CD_a = \frac{0.234}{48} = 0.0049 \text{ amp/sq cm}$$

Current densities for the reverse cycles were calculated by the same formula. Cathode current densities for either direct or reverse cycle were merely half that value obtained for the direct cycle since two electrodes were used for cathodes.

Anode Corrosion Efficiency. The anode corrosion efficiencies for both direct and reverse cycles of periodic reverse direct current were calculated according to the following formula:

$$ACE_d = \frac{L_a}{(w_1) \left(\frac{MW_{Pb}}{MW_{Cu}} \right)} (100)$$

where:

ACE_d = anode corrosion efficiency for direct cycle, per cent

L_a = loss in weight of anode, gm

w_1 = weight of copper deposited on cathode of net coulometer during direct cycle, gm

MW_{Pb} = molecular weight of lead, gm

MW_{Cu} = molecular weight of copper, gm

$$ACE_d = \frac{1.0489}{(1.3558) \left(\frac{207.21}{63.6} \right)} (100) = 90.5 \text{ per cent}$$

Current Efficiency. The current efficiency was calculated on the basis of pure lead chromate produced. The following formula was used:

$$CE = \frac{(W_{cp})(P_{PbCrO_4})}{(W_1) \left(\frac{MW_{PbCrO_4}}{MW_{Cu}} \right)} (100)$$

where:

- CE = current efficiency, per cent
- W_{cp} = weight of crude product, gm
- P_{PbCrO_4} = per cent lead chromate in crude product, per cent
- W_1 = weight of copper deposited on cathode of total coulometer, gm
- MW_{PbCrO_4} = molecular weight of lead chromate, gm
- MW_{Cu} = molecular weight of copper, gm

$$CE = \frac{(1.6672)(0.939)}{(0.4623) \left(\frac{323.22}{63.6} \right)} (100) = 66.75 \text{ per cent}$$

Calculation of Number of Poles in Alternator. The number of poles in the alternator was calculated from the data given on the name plate. These data are as follows:

frequency output of alternator = 400 cycles/sec

velocity of alternator for rated frequency = 4800 rev/min

The formula used is given as follows:

$$f = \frac{p r}{2}$$

where:

f = frequency output of alternator, cycles/sec

p = number of poles in alternator

r = velocity of alternator at rated frequency, rev/min

$$p = \frac{(2)(60 \text{ sec/min})(400 \text{ cycles/sec})}{4800 \text{ rev/min}}$$

p = 10 poles

Frequency of Alternating Current Used in Tests Performed
With High Frequency Alternating Current Superimposed on Direct
Current. This calculation was performed in connection with the
following formula:

$$f = \frac{pr}{2}$$

where:

f = frequency of alternating current, cycles/sec

p = number of poles in generator

r = velocity of generator, rev/sec

For test 37-812-266 the calculation gave the following results:

$$f = \frac{(10)(6,000 \text{ rev/min})}{(2)(60 \text{ sec/min})}$$

$$f = 500 \text{ cycles/sec}$$

Determination of Factor for Converting Root-Mean-Square
Values of High Frequency Alternating Current to Peak Values.

This calculation was performed for the purpose of determining the relationship between root-mean-square and peak values of 500 cycle alternating current. The calculation was based on data obtained from the graphical integration given in Figure 14, page 98.

Area Under Curve. The area under the curve in Figure 14, was obtained as follows:

$$A = \sum XY^2$$

where:

- A = area under curve, square divisions
- X = x-component, division
- Y² = y-component, division

$$A = 416.1 \text{ square divisions}$$

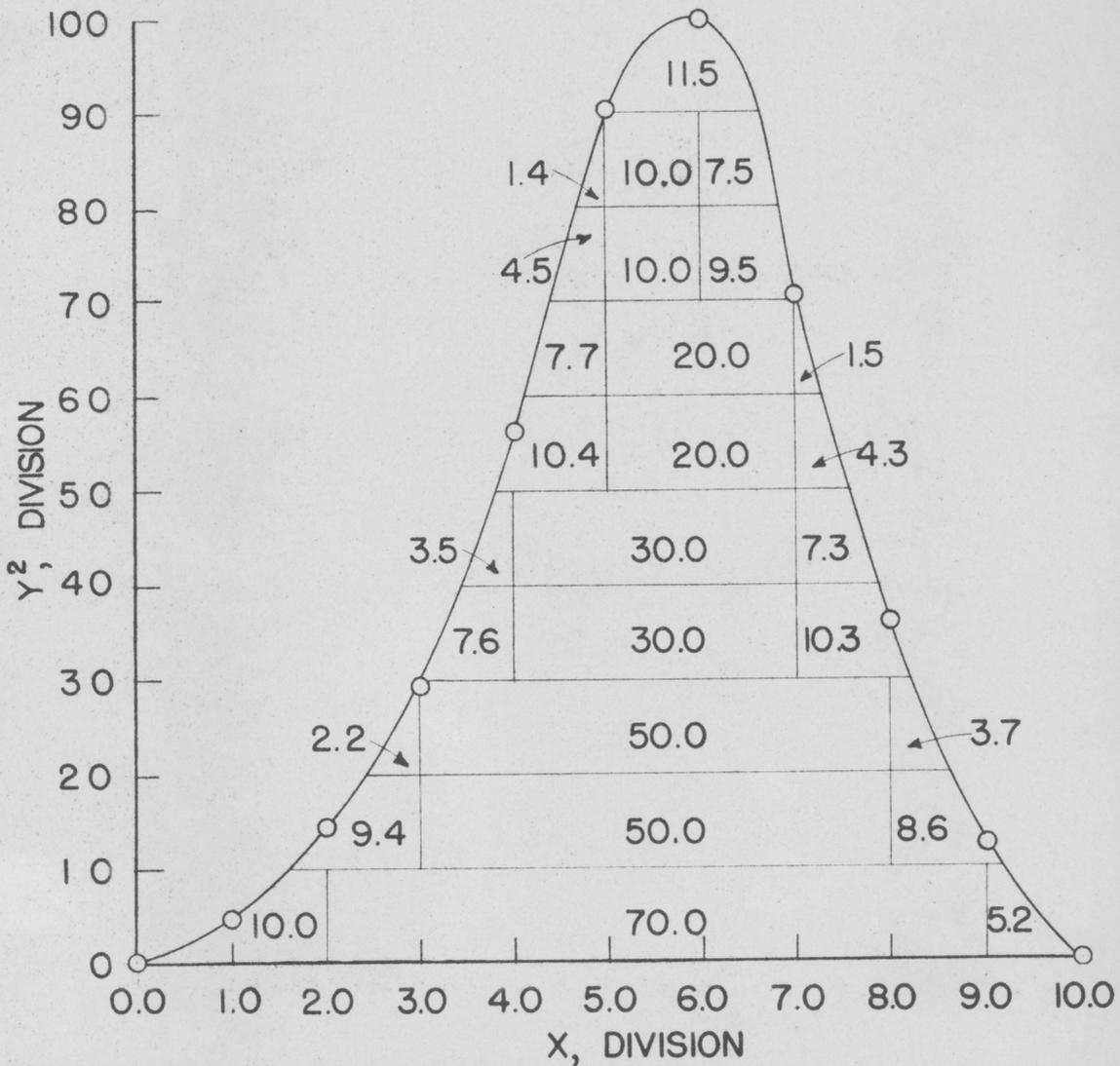


FIGURE 14. GRAPHICAL INTEGRATION USED FOR DETERMINING THE RELATIONSHIP BETWEEN ROOT-MEAN-SQUARE AND PEAK VALUES OF 500 CYCLE ALTERNATING CURRENT.

Evaluation of Root-Mean-Square Value of y-Component.

This calculation was performed by use of the following:

$$Y = \sqrt{A/X_m}$$

where:

Y = root-mean-square value of y-component,
division

A = area under curve, square divisions

X_m = maximum value of x-component, division

$$Y = \sqrt{416.1/10.0}$$

$$Y = \sqrt{41.6}$$

$$Y = 6.45$$

Calculation of Conversion Factor. The conversion factor is defined as the ratio of the peak y-component, or peak current, to root-mean-square of y-component, or current.

$$\frac{Y_p}{Y_r} = \frac{I_p}{I_r} = F$$

where:

Y_p = peak value of y-component, divisions

Y_r = root-mean-square value of y-component, divisions

I_p = peak alternating current, amp

I_r = root-mean-square alternating current, amp

F = conversion factor, dimensionless

$$F = \frac{10.0}{6.45}$$

$$F = 1.55$$

The final equation relating root-mean-square and peak alternating current for 500 cycles becomes:

$$I_p = 1.55I_r$$

$$I_p = (1.55)(0.10)$$

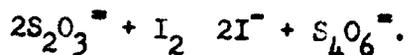
$$I_p = 0.155 \text{ amp}$$

A similar calculation was performed with 60 cycle alternating currents, but the conversion factor used was 1.414 instead of 1.55.

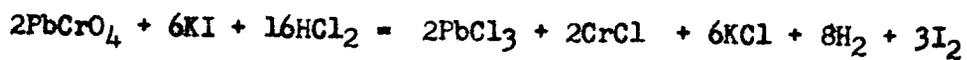
Lead Chromate Analysis. Arenson⁽¹⁰⁾ gives the reaction between sodium thiosulfate and iodine as follows:



or in ionic form as presented by Hamilton and Simpson⁽⁹⁾:



The oxidation-reduction reaction for the analysis is:



This calculation was performed according to the last reaction by means of the following equation:

$$\frac{(V)(N)(mew)}{S}(100) = \text{per cent PbCrO}_4$$

where:

N = normality of sodium thiosulfate solution

V = volume of standard sodium thiosulfate solution required for titration, ml

S = weight of sample analyzed, gm

mew = milliequivalent weight of lead chromate, gm =

$$\frac{\text{M. W. PbCrO}_4}{3000} = \frac{323.22}{3000} = 0.1077$$

$$\frac{(21.9)(0.10)(0.1077)}{0.2512}(100) = 93.9 \text{ per cent PbCrO}_4$$

Since the change in valence of chromium for the oxidation-reduction reaction is three, the milliequivalent weight of lead chromate is equal to its molecular weight divided by 3,000.

Lead Analysis. The per cent lead in the crude products was calculated by means of the following formula:

$$\frac{(MW_{Pb})(W_{PbSO_4})}{(MW_{PbSO_4})(W_s)}(100) = \text{per cent Pb}$$

where:

MW_{PbSO_4} = molecular weight of lead sulfate, gm

MW_{Pb} = molecular weight of lead, gm

W_{PbSO_4} = weight of lead sulfate, gm

W_s = weight of sample analyzed, gm

$$\frac{(207.21)(0.1789)}{(303.27)(0.2193)}(100) = 55.4 \text{ per cent Pb}$$

IV. DISCUSSION

The first portion of this section deals with a discussion of the more general aspects of the investigative work, particularly the observations made during various tests. The final portion is more specifically concerned with the calculated results obtained from the data recorded during the experimental portion of the study.

General Discussion

The paragraphs presented here discuss previous work pertaining to the investigation, and various observations in regard to the procedures employed during the experimental work.

Previous Work. Duplication of some direct current electrochemical methods for preparing lead chromate found in the literature^(52,54) was attempted in an effort to become familiar with known methods. Also, these experiments yielded results which could be compared with results obtained from later tests using periodically reversed direct current and alternating current superimposed on direct current.

To the author's knowledge, there has been no work done in connection with the electrochemical production of lead

chromate using periodically reversed direct current or alternating current superimposed on direct current.

Formation of Lead Dioxide. Many of the products obtained from the electrolyses carried out with direct current and periodically reversed direct current were spoiled by the formation of black specks at the anode along with the crude product. Although the black material was not analyzed in every case, it is assumed that it was probably lead dioxide.

Importance of Careful Cleansing of Lead Electrodes. Careful removal of adhering crude product from the lead electrodes was of importance in two respects. In the first place, it was imperative to remove all of the product so as to obtain an accurate measure of the yield. Secondly, it was important not to scrape off any lead metal from the electrodes. In the event that lead metal should be scraped from the electrodes along with the products, high values of current efficiency and low values of corrosion efficiency would be obtained. As was described in the method of procedure, the lead electrodes were scrubbed lightly with a soft toothbrush after each experiment. This procedure was found to clean the electrodes of all product and still leave the unreacted lead metal intact.

Foaming of Electrolyte Due to Gas Evolution. At high current densities the fast rate of gas evolution due to the electrolysis of water usually obscured the electrodes from view, making it impossible to observe the electrodes during the tests. The value of current density which caused foaming of the electrolyte varied from 0.0130 to 0.0239 ampere per square centimeter. Temperature rises of 5 to 10 °C accompanied the high rate of gas evolution.

Selection of Electrolytes. The electrolytes used during the experimental portion of this investigation were styled after those given by Le Blanc and Bindshedler⁽⁵²⁾. Direct current electrolysis of these electrolytes yielded current efficiencies of 55.0 per cent. Other electrolytes⁽⁵²⁾ yielding current efficiencies of 100.0 per cent were described, but the ones yielding low current efficiencies were chosen so that the effects of periodically reversed direct current and alternating current superimposed on direct current could be readily observed.

Discussion of Results from Direct Current Electrolyses

Although the preparations of lead chromate using direct current were performed primarily for comparative purposes, they deserve some discussion pertaining to results.

Electrolysis of Water. Water, the solvent in the electrolyte, was decomposed during many of the tests yielding hydrogen at the cathodes and oxygen at the anode. The rate of gas evolution, although not measured, increased as the voltage drop across the cell increased. The potential difference across the cell varied from 5.0 to 6.5 volts for the direct current tests. Foaming of the electrolyte occurred during the tests operating at anode current densities of 0.0130 and 0.0239 ampere per square centimeter; the voltage drops being 5.5 volts in both cases. The foaming was due to the high rate of gas evolution from the electrodes.

Formation of Lead Dioxide. In tests 1-812-46, 2-812-60, 11-812-93, 12-812-97, 13-812-100, 14-812-104, 18-812-154, and 19-812-157 the product formed at the anode was spoiled by the formation of a black substance. As was previously mentioned, this black substance was assumed to be lead dioxide. Luckow⁽⁵³⁾ reported the formation of lead dioxide at the anode when a similar electrolyte was employed in preparing

lead chromate. Therefore, the formation of lead dioxide is not a new observation.

Formation of Basic Lead Chromate. The anodic formation of the crude product in all tests except 27-812-218, resulted in the production of a reddish-orange powder. Since lead chromate is bright yellow, it was assumed that the product obtained was some other combination of lead and chromate ions. Basic lead chromate ($\text{PbCrO}_4 \cdot \text{PbO}$) is reddish-orange in color. Wagner⁽⁷⁰⁾ describes an inorganic method of preparing basic lead chromates of the formulas $\text{PbCrO}_4 \cdot x\text{PbO}$ and $\text{PbCrO}_4 \cdot \text{PbO} + y\text{PbO}$ where x and y are at least one. These compounds are also reddish-orange in color. Another verification of the formation of basic lead chromate rather than lead chromate is that subsequent pH measurements of the electrolyte before and after electrolysis indicated that the pH increased from 8.0 to 12.0 after 1.345 hours of electrolysis. Since the electrolyte was basic to start with and increased in basicity as the electrolysis proceeded, it follows that basic lead chromate was formed as the product. Luckow⁽⁵⁴⁾ pointed out that reddish lead chromate could be prepared by the electrolysis of a basic electrolyte, and that chrome yellows could be formed with an acidic electrolyte.

Test 27-812-218 was performed using an electrolyte acidified to pH 6.0 as a duplication of Luckow's method. The product formed was a rather dark yellow which analyzed 92.7 weight per cent lead chromate. A brighter yellow was not obtained since an excess of chromic acid was used in acidifying the electrolyte which darkened the color slightly. This particular test yielded higher current and anode corrosion efficiencies than all of the other direct current tests. Those values were 98.1 and 105.9 per cent, respectively. The electrolyte used consisted of a mixture of 3.60 grams of potassium chromate and 11.62 grams of sodium nitrate per 1000 grams of distilled water.

Effect of Current Density. Increasing the anode current density caused an increase in the crude product yield, and a slight increase in the weight per cent lead chromate in the product. Increasing amounts of lead dioxide were formed at the cell anode at current densities of 0.0130 and 0.0239 ampere per square centimeter. It was impossible to weigh the lead dioxide actually produced since its formation occurred simultaneously with that of the basic lead chromate.

Discussion of Results from Periodically
Reversed Direct Current Electrolyses

A series of twenty-two electrolyses were performed to determine the effect of using periodically reversed direct current on the production of lead chromate. It should be noted that the potential drop across the cell was not reported for any of the tests. This value was not measurable since a voltmeter could not be placed in the circuit without incurring damage to the instrument when current was reversed.

Formation of Product During Periodically Reversed Direct Current Electrolyses. The tests performed using a direct to reverse time ratio of 1.0 were the only ones in which crude product was formed on all three lead electrodes. Although some small particles were observed forming on the three electrodes during tests performed using time ratios of 3.0, 5.0, 10.0, and 20.0, the amounts were not appreciable, and were not measured. It should be readily understood that the formation of product on all three electrodes in the tests performed using unit time ratios may be attributed to the fact that 50.0 per cent of the time the outer two electrodes were anodic. The weight yield in all cases was very low. This point will be discussed later. It is also believed that the failure of product to form at the outer two electrodes in the electrolyses

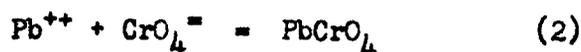
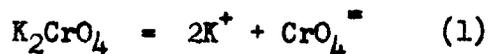
carried out at high time ratios was due to the shortness of time of the reverse cycle. The reverse cycle time varied from 0.67 to 4.62 seconds.

The two outer electrodes in the cell, when cleaned after electrolysis, were found to be coated on their surfaces facing the middle electrode with a black substance. The deposit was rather porous and adhered to the electrodes. These deposits were assumed to be either lead or lead dioxide or both. The formation of these substances was so great in some cases that the outer two electrodes gained weight.

pH Measurements of Electrolytes. Measurement of the pH of the electrolyte used in test 24-812-202 with Fisher alkacid test paper indicated that the pH increased from approximately 7 at the beginning of the test to approximately 10 at the end of the test. This observation led to a series of tests in which the pH of the electrolytes was maintained slightly acidic at a value of 6.0. During these tests, a pH meter was employed to obtain a more accurate measure of that value. The periodic addition of 2.0 weight per cent chromic acid to the electrolyte served to stabilize the pH.

As was mentioned previously, during tests performed using unacidified electrolytes, the solution became more and more basic as the electrolysis proceeded. Explanation of the

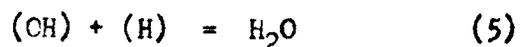
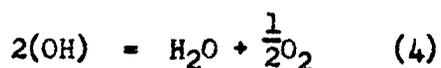
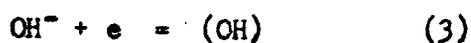
progressive increase of the basicity of the electrolytes may be aided by reference to the following chemical equations:



Equations (1) and (2) show the ionization of potassium chromate and the formation of lead chromate, respectively. Equations (3) and (4) indicate the ionization of water and the formation of gaseous hydrogen from hydrogen ions or nascent hydrogen, respectively. It is easily seen that, with the evolution of hydrogen gas and the precipitation of lead chromate, potassium ions from equation (1) and hydroxyl ions from equation (3) react to give potassium hydroxide as is shown in equation (5). The formation of water soluble potassium hydroxide caused the electrolytes to become basic upon continuous electrolysis. Analogous reasoning may be given for the formation of sodium hydroxide from sodium nitrate.

Ammeter Fluctuations During Current Reversal. A rather interesting phenomenon was observed during current reversal in regard to the ammeter, A₂, shown in Figure 7, page 67. Test 23-812-180 will serve to illustrate the action even though it was observed in all tests. At the beginning of the test, the rheostat, R, was adjusted so that a reading of 0.25 ampere was obtained from ammeter, A₂. Under this condition, the middle electrode was anodic and the outer two electrodes were cathodic. Hydrogen gas was evolved at the cathodes. Upon current reversal the reading of ammeter, A₂, increased rapidly to approximately 0.50 ampere, and hydrogen gas was still seen being given off at the cathodes. A few seconds later all gas evolution ceased. Then, the current was reversed to its original polarity, and ammeter, A₂, slowly decreased its reading to 0.25 ampere. Hydrogen gas evolution from the two outer electrodes did not begin until a few seconds later, when the cycle was at its original point. The time intervals for these ammeter variations were not measured during these tests.

In explanation of the phenomenon, the following equations may be helpful.



The first two equations illustrate the reaction taking place at the cathode during the current cycle in which the middle electrode is anodic. Equations (3) and (4) show the reactions taking place at the outer two electrodes during the current cycle in which the middle electrode is cathodic. During the reverse cycle, on the former electrode, the reaction of equation (2) is terminated since no more nascent hydrogen is supplied. Instead, hydroxide ions are neutralized and react with the residual hydrogen according to equation (5). This serves to account for the time lag of hydrogen evolution when the current reverses to its original polarity.

The up-scale fluctuation of the ammeter, A_2 , on current reversal is an indication that an overvoltage exists in the

cell circuit. When current is first reversed, nascent hydroxyl ions react with nascent hydrogen absorbed on the surface of the electrode. This absorbed nascent hydrogen, cause of the so-called hydrogen overvoltage, is used up. Then the current drops back as the hydroxyl overvoltage builds up. The opposite reactions take place at the electrode which changed from anode to cathode.

Comparison Between Direct to Reverse Time and Current Ratios. Inspection of the direct to reverse time and current ratios in Table III, page 84, shows that there is little agreement between corresponding values. In most of the tests the ratio of direct to reverse time was found to be two or three times greater than the corresponding current ratio. This discrepancy may be attributed to the fact that the reverse current flowing through the cell was usually two or three times greater than that current flowing during the direct cycle. This being true, more copper would be plated onto the coulometer cathode during the reverse cycle than would be deposited during the direct cycle for the same time interval. The true cause of the discrepancy is that the overvoltage on the reverse cycle, as was discussed in the previous section, caused the increased reverse current which, in turn, caused the ratio of direct to reverse

current to be smaller than the ratio of direct to reverse time. A plot of the ratios of direct to reverse time and current is given in Figure 15, page 117, to illustrate the disagreement between the two values. The data plotted were obtained from tests 20-812-168 to 23-812-180, inclusive.

A point of interest in regard to the direct to reverse time and current ratios is that they more closely approach each other at high current densities. To illustrate the point, tests 28-812-224 and 29-812-228 will be compared. In both experiments the ratio of direct to reverse time was 5.0, but their respective ratios of direct to reverse current were 4.10 and 2.17. The current density on the middle electrode during the direct cycle was 0.0359 ampere per square centimeter in test 28-812-224, and the corresponding value for test 29-812-228 was 0.0058 ampere per square centimeter.

Effect of Electrolyte Composition. During the investigative studies with periodically reversed direct current, two different electrolytes were employed. The compositions of these electrolytes were: Type I, a mixture of 6.80 grams of potassium chromate and 8.14 grams of sodium nitrate per 1000 grams of distilled water, and type II, a mixture of 3.60 grams of potassium chromate and 11.62 grams of sodium nitrate per 1000 grams of distilled water. The original use of these

NOTES: AVERAGE TOTAL CURRENT = 0.286 AMP
AVERAGE DIRECT CURRENT DENSITY = 0.0054 AMP/SQ CM

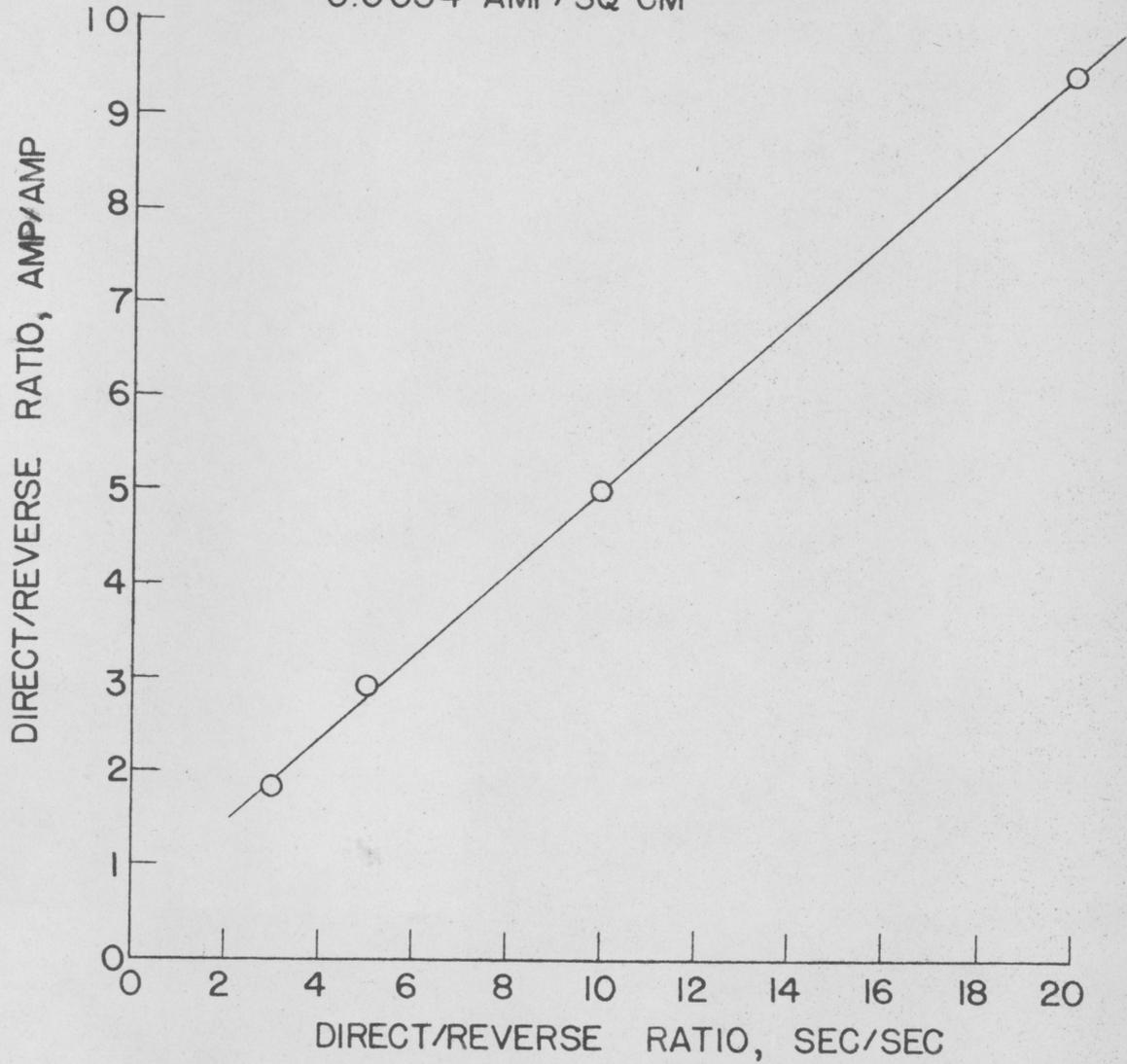


FIGURE 15. RELATIONSHIP BETWEEN THE RATIOS OF DIRECT TO REVERSE TIME AND CURRENT

electrolytes may be found in the publication of Le Blanc and Bindshedler⁽⁵²⁾. Type II was found to give higher yields in direct current experiments. Comparison between tests 20-812-168 and 24-812-202 performed with type I and type II electrolyte, respectively, indicates that, for the same ratio of direct to reverse time, the electrochemical yield increased from 0.51 to 0.67 grams of lead chromate per ampere-hour and the purity increased from 32.3 to 47.3 per cent. The current efficiencies based on pure lead chromate were 11.5 and 8.8 per cent, respectively. These figures indicate that better electrochemical yields and purer products are obtainable from the more dilute electrolyte.

Test 25-812-209, performed with acidified electrolyte, is comparable to test 24-812-202, using unacidified type II electrolyte. The former test yielded a current efficiency of 25.1 per cent, an electrochemical yield of 1.83 grams of lead chromate per ampere-hour, and a purity of 77.0 per cent. The results of the latter test are given above. The results of this comparison indicate that the results were best when type II electrolyte was acidified. Figure 16, page 119, and Figure 17, page 120, show the relationship between the purity of lead chromate and the ratio of direct to reverse time. The results plotted in Figure 16 were obtained from tests performed

NOTES: DATA FROM EXPERIMENTS 20, 21,
22 AND 23 ARE PLOTTED

ELECTROLYTE COMPOSITION:

27.3 GM K_2CrO_4

32.7 GM $NaNO_3$

3940 GM H_2O

PH WAS NOT CONTROLLED

TEMPERATURE: $32^\circ C$

TIME: 1345 HOURS

DIRECT CURRENT DENSITY:

0.0057 TO 0.0051 AMP/SQ CM

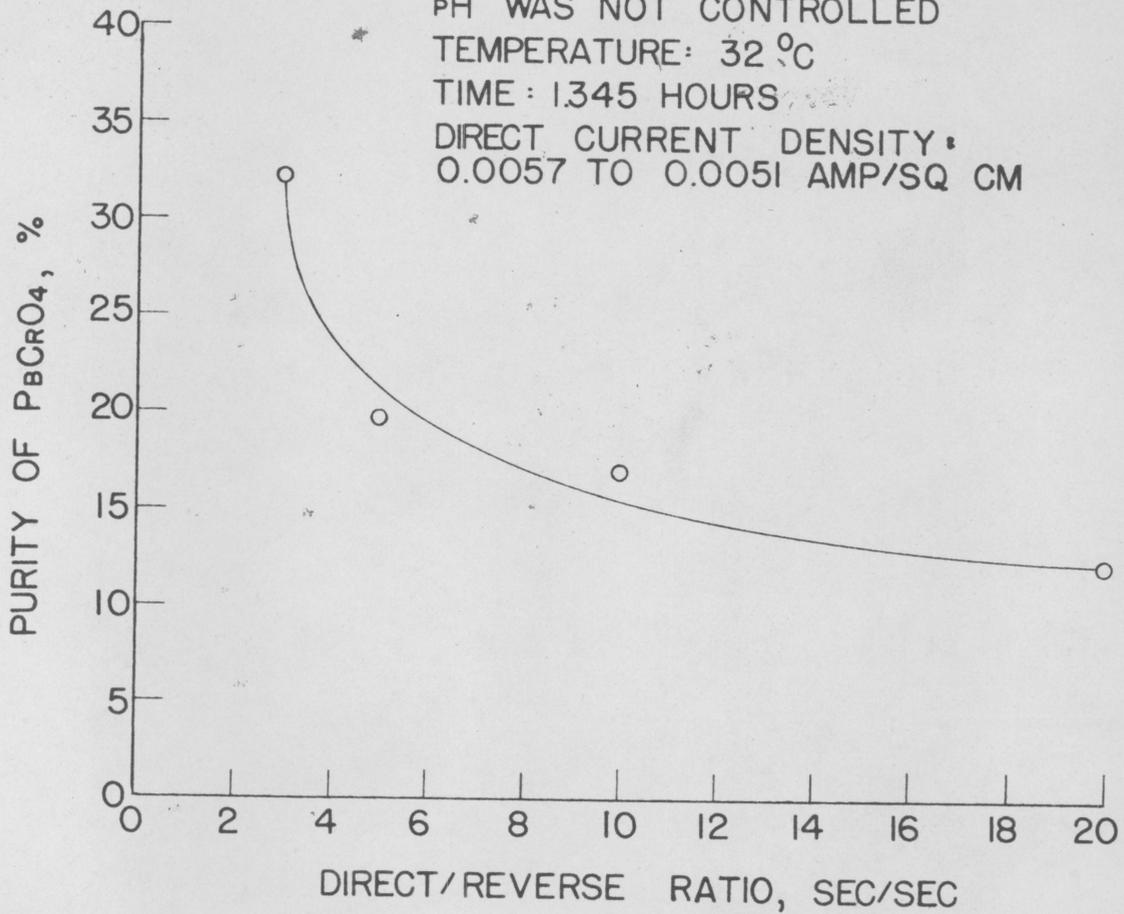


FIGURE 16. RELATIONSHIP BETWEEN PURITY OF LEAD
CHROMATE AND THE RATIO OF DIRECT
TO REVERSE TIME

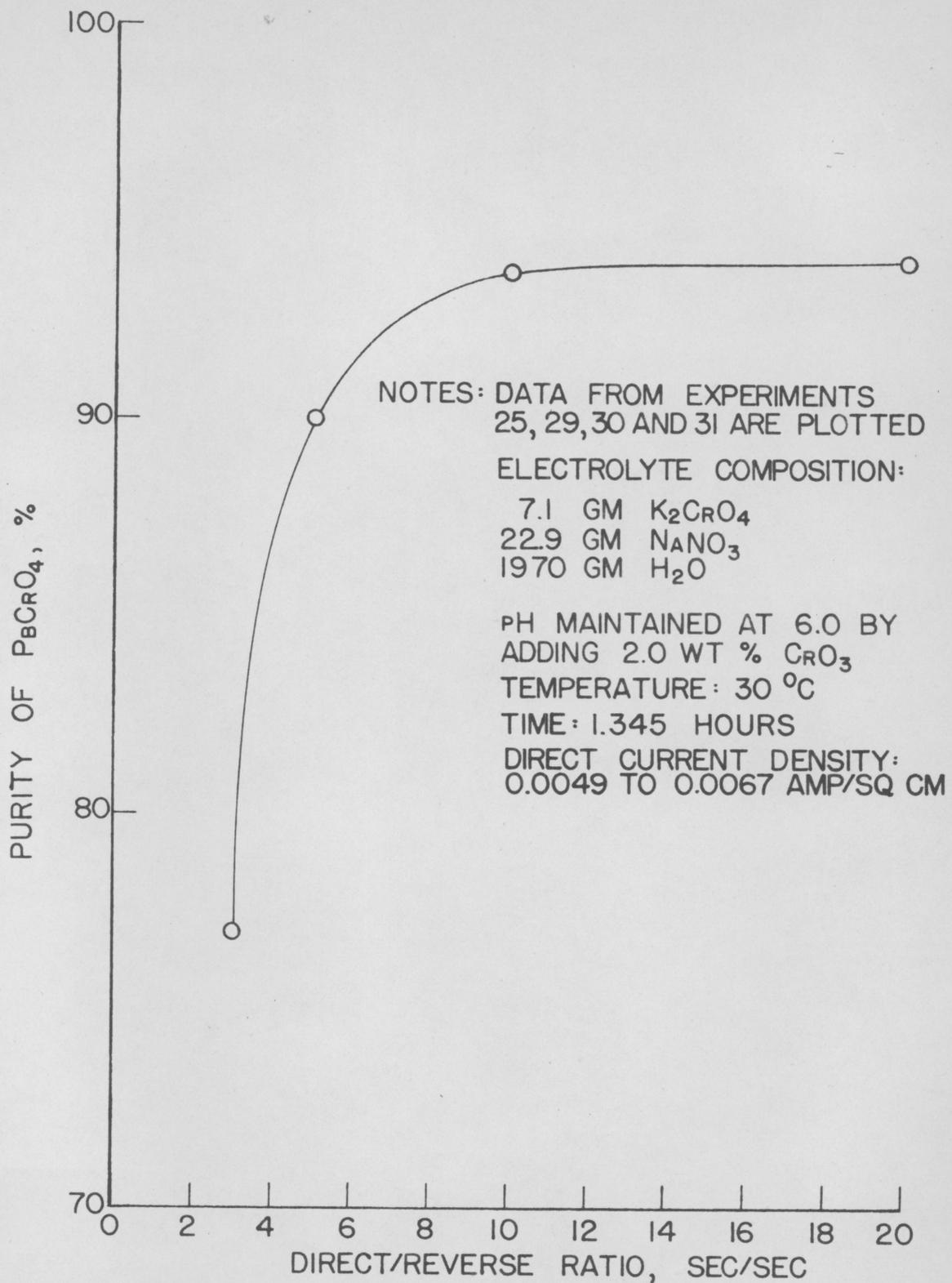


FIGURE 17. RELATIONSHIP BETWEEN PURITY OF LEAD CHROMATE AND THE RATIO OF DIRECT TO REVERSE TIME

using type I electrolyte, and Figure 17 results were obtained from tests performed using the acidified type II electrolyte. The production of purer lead chromate by using the acidified electrolyte is in agreement with the statements of Luckow⁽⁵⁴⁾, that the more acid the electrolyte, the less the possibility of producing basic lead chromate which contains less lead chromate than does normal lead chromate.

Corrosion Efficiencies. In general, the corrosion efficiencies of the electrodes during the direct and reverse cycles increased as the ratio of direct to reverse time increased. Also, the weight of crude product increased as the corrosion efficiencies increased, since the dissolved lead produced an increased amount of crude product. The corrosion efficiency during the reverse cycle was not calculated for tests 22-812-176 to 26-812-213 and 29-812-228 to 31-812-232, inclusive. For these tests, the outer two electrodes gained weight during the reverse time cycle as a result of the formation of an adherent layer of lead dioxide. Corresponding direct to reverse time ratios for corrosion efficiencies of 56.0, 69.4, 82.5, and 90.5 per cents were 3.0, 5.0, 10.0, and 20.0, respectively. Although no correlation existed between the two, the corrosion efficiencies obtained for the direct cycles were usually 20.0 per cent higher than the

corresponding current efficiencies. No explanation for this relationship is presented at this time.

Current Efficiencies. As was mentioned previously, the current efficiencies reported for the tests of the present investigation were calculated on the basis of calculated weight of pure lead chromate. A literature source⁽⁵⁵⁾ reported some current efficiencies as high as 98 to 100 per cent for the direct current electrolyses, but the basis of these calculations were not given. A 98 per cent current efficiency for direct current electrolysis of acidified, type II electrolyte was confirmed in test 27-812-218, but the purity was only 92.7 per cent. The best current efficiency obtained during the tests performed using periodically reversed direct current was 66.75 per cent from test 31-812-232 using acidified type II electrolyte and a direct to reverse time ratio of 20.0. Current efficiencies were noted to decline as the time ratio was decreased. It is interesting to note that test 28-812-224 performed using the same electrolyte, but employing a time ratio of 5.0, yielded a current efficiency of 57.25 per cent whereas, the next test gave a current efficiency of 41.25 per cent while employing the same time ratio. Products from both tests analyzed 90.0 per cent lead chromate, but the total

current flow for test 28-812-224 was approximately 7.2 times greater than that of test 29-812-228.

Product Yield and Analysis. As the time ratio was increased from 3.0 to 20.0, the electrochemical yield decreased from 0.51 to 0.35 grams of lead chromate per ampere-hour. In addition to this observation, the lead chromate purity decreased from 32.3 to 12.1 per cent and the lead content in the products increased from 51.1 to 85.0 per cent. These results were obtained from tests 20-812-168 to 23-812-180, inclusive. The tests were performed using type I electrolyte. These results indicate that progressively increasing the time ratio may have increased the production of basic lead chromate. Since the electrolyte was not acidified, it is likely that the electrolyte became more basic as electrolysis proceeded, as was discussed in a previous section. It should be re-emphasized that the formation of basic lead chromate was not verified experimentally.

Tests performed with acidified, type II electrolyte yielded increasing amounts of product of higher purity as the time ratio was increased. As the time ratio was increased from 3.0 to 20.0, the electrochemical yield and purity increased from 2.12 to 4.97 grams of lead chromate per ampere-hour and 71.5 to 93.9 per cent, respectively.

The lead in the products remained relatively constant at approximately 55.0 per cent. The results just mentioned correspond to tests 26-812-213 to 31-812-232, excluding test 28-812-224. These results prove again that a product of higher purity may be obtained by using the more dilute electrolyte slightly acidified. It should be noted that the electrochemical yield using periodically reversed direct current never exceeded the yield obtained for the direct current electrolysis in test 27-812-218, that being 6.07 grams of lead chromate per ampere-hour.

Test 28-812-224 yielded 3.57 grams of lead chromate per ampere-hour and test 29-812-228 yielded 2.92 grams of lead chromate per ampere-hour. Both tests were performed using a time ratio of 5.0 and acidified, type II electrolyte. The difference arises from the fact that the former test consumed 7.2 times the current consumed in the latter test, and the yield was increased by only 1.22 times. The purity of lead chromate of both of the products was 90.0 per cent.

Discussion of Results from Alternating Current
Superimposed on Direct Current Electrolyses

A series of electrolyses were conducted to study the effects of varying alternating current density and frequency of an alternating current superimposed on direct current on the production of lead chromate. During these tests, the direct current density was maintained at approximately 0.0049 amperes per square centimeter, since this was the approximate optimum current density found during tests performed with simple direct current. The electrolyte tested in all cases was composed of 3.60 grams of potassium chromate and 11.62 grams of sodium nitrate per 1000 grams of distilled water. The pH of the electrolysis baths was maintained at 6.0 throughout the duration of the tests.

Formation of Product. In all of the tests performed with alternating current superimposed on direct current, the product, lead chromate, formed solely on the middle electrode. The middle electrode in the electrolysis cell was the anode with respect to the direct current. Even during those tests in which current reversal was obtained, no product precipitated at the outer two electrodes. This may be explained by pointing out that, although the current was reversed,

the polarity of the electrodes was reversed for such a short time that the product did not have sufficient time to form. To clarify this concept further, before the current is reversed, the diffusion layer of solution surrounding the outer two electrodes is being depleted of chromate ions. After the current reverses, there are no chromate ions present in the diffusion layer to react with the lead ions. Before enough chromate ions can migrate to the electrode to combine with lead ions, the current reverses again, starting the cycle over.

Temperature of Bath During Electrolysis. Although no attempt was made to control the temperature of the baths during the electrolyses, the greatest rise in temperature recorded was 4.5 °C for test 39-812-272. In general, the temperature rise was less than 2.0 °C, since the addition of relatively cold chromic acid solution served to cool the electrolytes somewhat. The operating temperature for a large majority of the experiments was found to vary between 30.0 and 33.0 °C.

Effect of Alternating Current Density. Figure 18, page 127, gives the relationship between yield and the ratio of peak alternating to direct current density. The data plotted were obtained from tests performed using 60 cycle

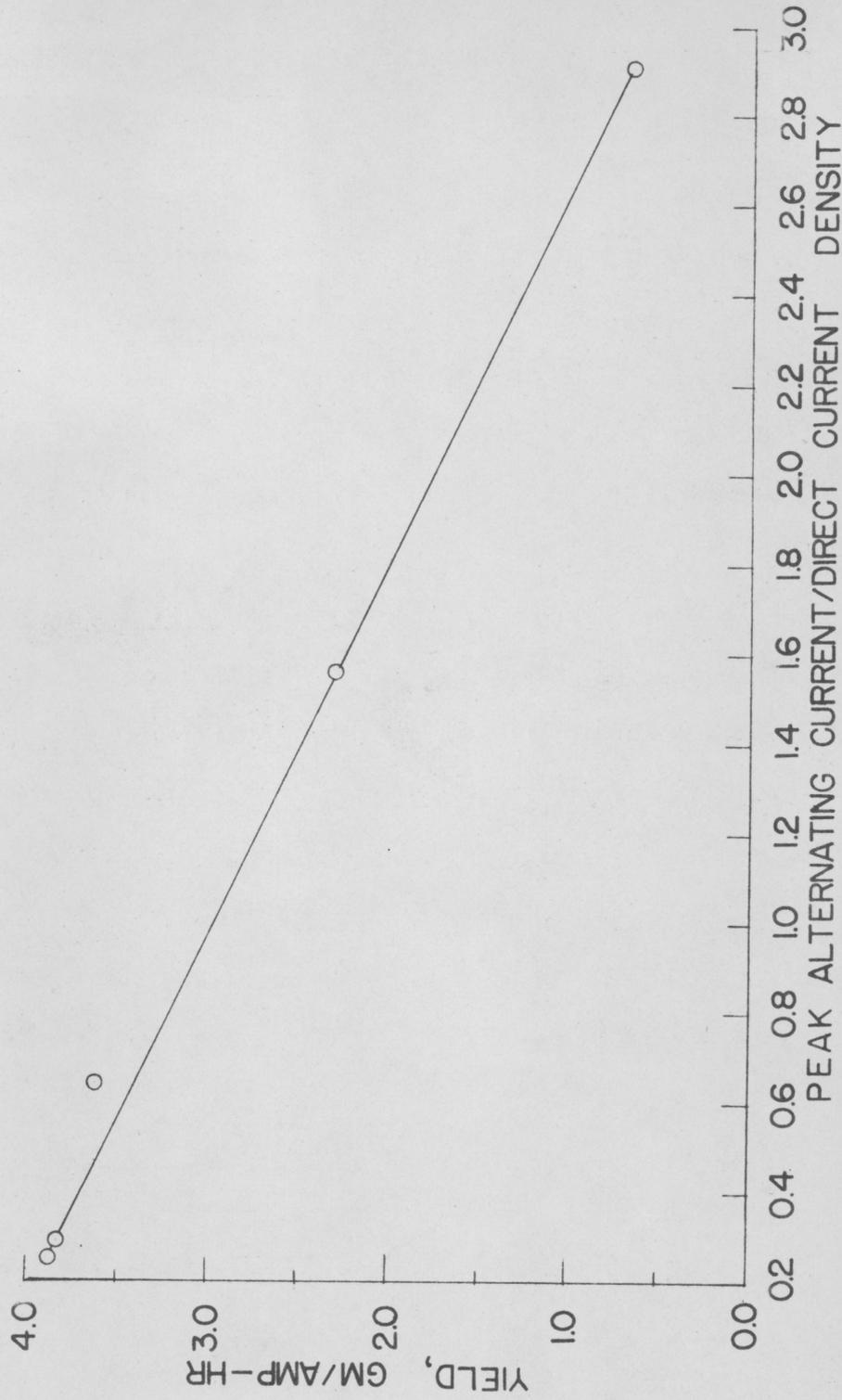


FIGURE 18. RELATIONSHIP BETWEEN THE RATIO OF ALTERNATING TO DIRECT CURRENT DENSITY AND THE YIELD OF LEAD CHROMATE USING 60 CYCLE ALTERNATING CURRENT

alternating current. The average direct current density for these tests was 0.00460 amperes per square centimeter. As can be seen from the curve, increasing the ratio of peak alternating to direct current density increased the yield in grams of pure lead chromate per ampere-hour. In other words, the yield of product decreased even without current reversal. This will be discussed further in a later section.

A series of four tests were performed employing high frequency alternating current superimposed on direct current. The average frequency used was 502.3 cycles per second. A plot of the electrochemical yield and the ratio of peak alternating to direct current density is not given since the yield varies so little. For test 37-812-266 the yield was 5.40 and for test 39-812-272 the yield was 5.89 grams of lead chromate per ampere-hour, using alternating current densities of 0.01546 and 0.00780 amperes per square centimeter, respectively. The average direct current density was 0.00476 amperes per square centimeter. The same reasoning may be applied to explain the results of tests performed with high frequency alternating current as was applied in explaining results obtained from tests performed with 60 cycle alternating current.

Effect of Alternating Current Frequency. Since only two values of alternating current frequency were investigated, no graphical relationship is presented. Comparison between tests 33-812-242 and 40-812-276 indicates that, for substantially the same operating conditions, 500 cycle alternating current yielded 5.87 grams of lead chromate per ampere-hour, while 60 cycle alternating current yielded 3.83 grams of lead chromate per ampere-hour. The direct current densities for these tests were 0.00484 and 0.00415 amperes per square centimeter, respectively. The peak alternating current densities for these tests were 0.00141 and 0.00160 amperes per square centimeter. In neither test was the current reversed. That is, the amplitude of the alternating current was not large enough to cause polarity to reverse for half of the cycle. Therefore, the wave form of the electrical energy employed was merely pulsed direct current. Apparently all tests performed with high frequency alternating current gave higher yields as compared to 60 cycle alternating current. The pulsed effect that is given to the direct current by the alternating current is thought to have a buffeting action on the diffusion layer of the anode. This could cause ionic mixing in that region of the anode diffusion film, thereby preventing impoverishment of the chromate ions.

Effect of Current Reversal. Tests 34-812-248, 32-812-239, 39-812-272, and 37-812-266 were run under such conditions that the pulsed direct current was allowed to reverse polarity. The first two tests were performed with 60 cycles per second of superimposed alternating current and the last two were performed with approximately 500.0 cycles per second of superimposed alternating current, respectively. Comparing other tests performed with 60 cycle alternating current, but without current reversal, with the first two above indicates that reversal of the current is detrimental to the production of lead chromate. Also, the purity of lead chromate obtained from a test performed under current reversal conditions was lower than that obtained from a similar test without current reversal. Polarization of the electrodes caused by the reverse current could explain these differences.

Comparing tests 39-812-272 and 37-812-266 performed at the higher frequency with similar experiments run without current reversal one observes hardly any difference between the yield or purities obtained under either conditions. This may be explained by reasoning that at the higher frequency of the alternating current the electrodes were not polarized during the reverse cycle. There appears to be a minimum frequency of alternating current below which there is a

marked effect produced by whether or not the wave form is such that the current is reversed. Further study would be required to determine this minimum frequency.

Current and Corrosion Efficiencies. In all of the tests performed with alternating current superimposed on direct current, the current and corrosion efficiencies were of the same order of magnitude, the former always being smaller than the latter. As a generalization, the current efficiencies obtained from tests performed with 60 cycle alternating current were about 3.0 per cent smaller than the corresponding corrosion efficiencies.

For the tests performed with 500 cycle alternating current, the corrosion efficiencies obtained were 100.0 per cent and more. The corresponding current efficiencies ranged from 89.7 to 97.8 per cent. Corrosion efficiencies greater than 100.0 per cent indicate that more lead is being removed from the anode than is being converted to lead chromate molecules, resulting in an increase in lead content in the product. This was not proven quantitatively by experiment. The current efficiencies approaching values of 100.0 per cent indicate that nearly the same number of equivalents of lead chromate are precipitated as there are

equivalents of copper deposited on the cathode of the copper coulometer.

Comparison with Production by Direct and Periodically Reversed Direct Current. Experiments 27-812-218, 31-812-232, and 39-812-272 yielded 6.07, 4.53, and 5.89 grams of lead chromate per ampere-hour, respectively. These three tests were performed with direct current, periodically reversed direct current, and 500 cycle alternating current superimposed on direct current, in that order, with the same electrolyte and operating conditions. The time ratio of the periodically reversed direct current test was 20.0 to 1.0. These figures indicate, on an overall basis, that direct current electrolysis yields are the highest with alternating current superimposed on direct current and periodically reversed direct current yields decreasing in that order. It is interesting to note that test 39-812-272, performed using superimposed alternating current, yielded a product of 99.4 per cent lead chromate, about 6.0 per cent better than when direct or periodically reversed direct current was used. This was the best purity obtained and was secured without appreciable sacrifice of yield.

Recommendations

The following recommendations are concerned with the whole investigation.

Bath Concentration. The use of more dilute electrolytes with respect to the chromate ion is suggested, since results of this investigation indicate that doing so would result in higher yields and better purities of lead chromate.

Temperature of Bath. The temperature of the baths used should be varied to ascertain whether or not this particular variable has any effect on the yield and purity of product.

Time of Electrolysis. A study to determine the effect of time of electrolysis on the product yield and purity is recommended.

Use of Other Acids. The effects of using other acids in the electrolytes should be investigated.

Physical Properties of Product. The determination of the physical properties of products obtained in subsequent investigations is recommended. The use of a high power microscope would facilitate such a study.

Statistics. It is suggested that further study in regard to the present investigation be based on some statistical design. A split-plot design could be employed

so as to include the investigative results of lead chromate production by use of direct current, periodically reversed direct current, and alternating current superimposed on direct current.

The following recommendations evolved from the observations made during the study of lead chromate production using direct current:

Current Density. Further study to determine the effect of high current densities, in the order of 0.0059 to 0.1000 amperes per square centimeter, is recommended.

The following recommendations evolved from the observations made during the study of lead chromate production using periodically reversed direct current:

Current Density. The effect of high current densities, as recommended for direct current electrolysis, should be determined. The current density referred to is that of the middle electrode or anode.

Time-current Relationship. It is recommended that a recording ammeter be placed in the circuit. This procedure would make it possible to obtain a time-current curve for the particular direct to reverse time ratios studied and would better indicate the operation of the periodic reverser.

The following recommendations are suggested after performing the experiments concerned with the electrolytic production of lead chromate using alternating current superimposed on direct current:

Current Density. It is recommended that experiments be conducted to determine the effect of varying the direct current density along with the alternating current density. This particular phase of the study could lend itself very well to a statistical analysis.

Electrical Circuit. The procedure of performing tests with equipment to which the alternating and direct currents would be connected in series is suggested as a means of comparing two different electrical systems.

Limitations

This investigation was limited to the use of periodically reversed direct current and alternating current superimposed on direct current as the sources of electrical energy. Other direct current experiments were performed for comparison purposes only.

Electrodes. Three lead electrodes, hung parallel to each, were used in all tests. The total submerged area of a single electrode ranged from 44.0 to 48.0 square centimeters.

Temperature. The temperature of electrolysis for the large majority of the tests was 33.0 ± 3.0 °C. No attempt was made to control this variable.

Time of Electrolysis. Electrolyses were carried out for 1.345 hours in all experiments except where otherwise specified.

Volume of Electrolyte Used. Five hundred milliliters of electrolyte were electrolyzed in all tests except where specifically noted otherwise.

Tests performed using periodically reversed direct current had the following specific limitations:

Direct to Reverse Time Ratios. The direct to reverse time ratios of periodically reversed direct current studied were 1.0, 3.0, 5.0, 10.0, and 20.0.

Current Density. The current density on the middle electrode during the direct portion of the time cycle was maintained at approximately 0.0059 amperes per square centimeter.

Electrolyte Composition. The majority of these experiments was performed with a bath consisting of 27.3 grams of potassium chromate, 32.7 grams of sodium nitrate, and 3,940 grams of water. A few of these tests, as noted, were performed with an electrolyte composed of 7.1 grams of potassium chromate, 22.9 grams of sodium nitrate, and 1,970 grams of water. These two baths are referred to as type I and type II, respectively. Type II electrolyte was maintained at a pH of 6.0 during the electrolyses by the periodic addition of a 2.0 weight per cent solution of chromium trioxide.

Bath Temperature. Although the bath temperature was not controlled, the average temperature rise during the tests was from 2.0 to 3.0 °C. The operating temperature averaged 33.0 °C.

The limitations placed on the tests performed using an alternating current superimposed on the direct current are given in the following paragraphs:

Frequency of Alternating Current. Superimposed alternating current frequencies of 60 and 502.3 ± 7.7 cycles per second were investigated during this phase of the study.

Direct Current Density. The direct current density on the middle electrode was maintained at an average of 0.00464 \pm 0.00020 amperes per square centimeter during these tests.

Alternating Current Density. The alternating current density was varied from 0.00113 to 0.01546 amperes per square centimeter in five steps.

Electrical Circuit. In this phase of the investigation the direct and alternating currents were connected in parallel with the electrolytic cell.

Meter Measurements. Direct current flow, being measured by means of a copper coulometer, was obtainable to \pm 0.001 ampere. Alternating current flow was read directly from the meters, and, consequently were accurate to only \pm 0.05 for 60 cycles per second and \pm 0.10 for 500 cycles per second.

V. CONCLUSIONS

A. From a study of the preparation of lead chromate using periodically reversed direct current from two baths described as follows: type I, 27.3 grams of potassium chromate, 32.7 grams of sodium nitrate, and 3,940 grams of water, and type II, 7.1 grams of potassium chromate, 22.9 grams of sodium nitrate, and 1,970 grams of water, at 33.0 ± 3.0 °C, using lead electrodes, it was concluded that:

1. As the current ratio or time ratio was increased, using the same total current and type II electrolyte, acidified to a pH of 6.0 by adding a solution of 2.0 weight per cent chromic acid, the purity of product was increased.

2. Compared to direct current electrolysis, periodically reversed direct current studies gave 4.53 grams of lead chromate per ampere-hour, while the former method gave 6.07 grams of lead chromate per ampere-hour, purities being 93.9 and 92.7 per cent lead chromate, respectively.

3. Use of more concentrated type I electrolyte, without pH control, resulted in larger yields, but lower purities (12 to 43 per cent lead chromate) than when type II was employed.

4. For type I electrolyte, at current densities from 0.0054 to 0.0076 amperes per square centimeter, decreasing the current ratio from 9.0 to 1.4 increased the purity from 12.0 to 42.0 per cent lead chromate.

5. Direct current production from type I electrolyte resulted in purities of lead chromate of 8.0 to 14.0 per cent, as compared to 12.0 to 30.0 per cent obtained by using periodically reversed direct current.

6. Maintaining the pH of type II electrolyte at a value of 6.0 by adding an aqueous solution of chromic acid resulted in an increase in purity of lead chromate from 47.3 per cent to 93.9 per cent.

7. The ratio of time of direct to time of reverse current was always greater than the ratio of the direct current to reverse current, the difference decreasing as the ratio decreased.

B. From a study of the preparation of lead chromate using alternating current superimposed on direct current as the energy source for the electrolysis of a bath containing 7.1 grams of potassium chromate, 22.9 grams of sodium nitrate, and 1970 grams of distilled water, the pH being maintained at 6.0 by the addition of a solution of 2.0 weight per cent chromic acid, at an

average temperature of 33.0 ± 3.0 °C, between lead electrodes, the following conclusions were drawn:

1. Increasing the ratio of peak alternating to direct current density from 0.255 to 2.915 resulted in a decrease in yield from 3.87 to 0.66 grams of lead chromate per ampere-hour.

2. Increasing the frequency of alternating current from 60 to 502.3 ± 7.7 cycles per second resulted in an increase in the yield of lead chromate from 2.30 to 5.89 grams per ampere-hour.

3. The conditions for the electrochemical production of maximum purity (99.4 per cent) lead chromate, using alternating current superimposed on direct current, were determined to be: peak alternating current density = 0.0078 amperes per square centimeter, direct current density = 0.0048 amperes per square centimeter, at an alternating current frequency of 494.7 cycles per second, at a temperature of 30.0 °C.

VI. SUMMARY

It was the purpose of this investigation to study the effect of varying the direct to reverse time ratio of periodically reversed direct current from 1.0 to 20.0 on the electrolytic production of lead chromate at an average anode current density of 0.0059 amperes per square centimeter, and to study the effect of 60 and 502.3 ± 7.7 cycles per second from 0.00113 to 0.01546 amperes per square centimeter of peak superimposed alternating current on direct current on the yield of lead chromate prepared by the electrolysis of a bath containing potassium chromate and sodium nitrate between lead electrodes.

Electrolysis of a bath containing 3.60 grams of potassium chromate, 11.62 grams of sodium nitrate, and 1000 grams of water with simple direct current yielded 6.07 grams of lead chromate per ampere-hour, the purity being 92.7 per cent lead chromate. The anode current density was 0.0049 amperes per square centimeter, and the current efficiency was 98.1 per cent. During the electrolysis, by maintaining the pH of the electrolyte at 6.0, by adding a solution of 2.0 weight per cent chromic acid, the purity of the product was increased.

Electrolysis of the same bath using periodically reversed direct current yielded 4.53 grams of lead chromate per ampere-hour, the purity being 93.9 per cent lead chromate. The time

ratio was 20.0, the anode current density was 0.0049 amperes per square centimeter, and the current efficiency was 66.75 per cent. Decreasing the direct to reverse time ratio gave lower yields and purities. Apparently, there is no advantage in using periodically reversed direct current over the use of direct current for this reaction under the above conditions.

Electrolysis of the same bath with alternating current superimposed on direct current yielded 5.49 grams of lead chromate per direct current ampere-hour, at a purity of 99.4 per cent lead chromate, when using 494.7 cycle alternating current. The alternating and direct current densities were 0.0078 and 0.0048 amperes per square centimeter, respectively. This was the purest product obtained in this investigation. Use of 60 cycle alternating current yielded 3.83 grams of lead chromate per direct current ampere-hour, at a purity of 93.9 per cent lead chromate. The alternating and direct current densities were 0.00141 and 0.00484 amperes per square centimeter.

Further experiments were made using direct current and periodically reversed direct current on a bath containing 6.80 grams of potassium chromate, 8.14 grams of sodium nitrate, and 1000 grams of water. Results from these electrolyses were much poorer than those obtained with the previous bath, so no experiments with superimposed alternating current on direct current were carried out with this latter bath.

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Addenda

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