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The Effect of Additives on Electrodeposition And Electrodisolution of Metals

TECHNICAL DOCUMENTARY REPORT NO. ASD-TDR-63-212

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Directorate of Materials and Processes
Aeronautical Systems Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

Project No. 7353, Task 735305

(Prepared under Contract No. AF 33 (657)-7485 by Baylor
University, Waco, Texas; Thomas C. Franklin, Jerry Barrett,
Robert E. Graves, Fred Tibbals and John Bowman, authors.)

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FOREWORD

This report was prepared by Baylor University, Waco, Texas, on Air Force Contract No. AF 33 (657)-7485, under Task No. 735305, "Interactions and Reactions Occurring at Interfaces," of Project No. 7353, "Characterization of Solid Phase and Interphase Phenomena In Crystalline Substances." The contract efforts were accomplished under the cognizance of the Metals and Ceramics Laboratory, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. The technical work was directed by Lt. J. W. Reishus as project engineer.

ABSTRACT

A preliminary investigation was made of the effect of additives on the electrodeposition of cadmium and on the electrodisolution of nickel.

The electrodeposition study was primarily limited to a study of techniques. These techniques included constant current pulses, cyclic voltammetry, microvolumetric measurement of hydrogen evolved, and hydrogen embrittlement. It was found that the current efficiency for the deposition of cadmium varied with concentration of additive in a regular pattern. Using different plating times, different base metals, different current densities, and in stirred and unstirred solutions the additive effects on current efficiency were similar.

The electrodisolution study indicated that under some conditions an oxidizing additive acted on the metal in a first order corrosion reaction. This reaction was accelerated by the application of the anodic potential.

This technical documentary report has been reviewed and is approved.

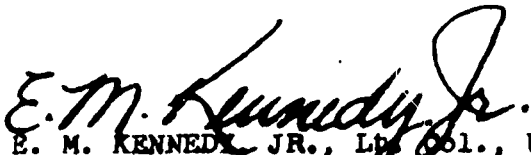

E. M. KENNEDY, JR., Lt. Col., USAF
Chief, Advanced Metallurgical Studies Branch
Metals and Ceramics Laboratory
Directorate of Materials and Processes

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Introduction

This project was undertaken to investigate the role of so-called "non-participating" substances on anodic dissolution and cathodic electrodeposition processes. These substances are very important in commercial electropolishing and electroplating baths for such things as grain refiners and brighteners. Such a study is of major magnitude and this report is only over the initial phases of the study. The process selected for the electrodeposition study was cadmium plating from a cadmium sulfate bath. The process selected for the anodic dissolution study was the anodic dissolution of nickel. In order to study the role of the additives in the dissolution studies it was felt that it was necessary to study the mechanism of dissolution of the nickel to see whether nickel went through a nickel (I) state or not. Then, it could be established whether the additives affected the nickel metal or nickel (I).

I. The Effect of Additives on the Electrodeposition of Cadmium

Introduction

The electrodeposition studies followed up the previous studies on the effect of additives on the codeposition of hydrogen and nickel (1,2). In the present study an investigation was made of the effect of the additive on the codeposition of cadmium and hydrogen. The study for this year was limited to a survey of available experimental techniques and some preliminary experiments.

Historical Section

The effects of addition agents on both the deposition of cadmium, or any metal, and the codeposition of hydrogen necessitates the investigation of the variable conditions governing deposition and the existing theories explaining these processes.

Electrodeposited cadmium has for a great number of years found importance in its use as a protective coating against corrosion. The protective coatings also give an attractive appearance to the various basis metals, and have found especial use on iron and steel, and also on copper, copper-rich alloys, aluminum, and on other metals and alloys. The specific usefulness of cadmium coatings to provide anodic protection has been extensively investigated under outdoor and indoor conditions, in normal, industrial, and salt spray atmospheres by a number of investigators (3-17). It has been shown that on iron and steel, corrosion protection afforded by cadmium coatings is similar to that provided by zinc coatings (whether electrodeposited, or otherwise applied). (18,19)

A universal acceptance of the cyanide plating bath for cadmium deposition has resulted from the fact that fine, closely grained and bright crystalline deposits result without the use of special addition agents, as is necessary in most acid baths.

Cadmium plating baths will be broken into the following three groups: (1) cyanide baths, (2) sulfate baths, and (3) all other types. These are listed in order of relative importance.

Although cadmium cyanide solution formulas were published as early as 1845 (20), cadmium plating was not used commercially

prior to 1915 (21). The early literature has been surveyed by Mathers and Marble (22) in a rather detailed investigation of a large number of plating baths.

The work of Udy (23) produced a solution in 1919 that aroused interest in commercial cadmium plating. His solution was composed of a mixture of cadmium hydroxide, sodium cadmicyanide and sodium hydroxide but no free sodium cyanide. (21)

C. H. Humphries (24) introduced the first brightening agent, a caustic solution of wool or other proteins, into cadmium cyanide solutions in 1922. C. M. Hoff (25) presented a detailed discussion of the properties of cadmium plate and cadmium plating solutions in 1926. (21)

In recent years investigations in cyanide solutions have been directed along four principle lines which are given below. (21)

1. The bright plating range has been evidenced by the introduction of new brightening agents for the cyanide baths.

2. The use of bright dips has brought about increased and more uniform luster of cadmium plates on recessed articles.

3. Detailed studies of anode conditions during dissolution have led to new anode designs and construction.

4. Improved bath formulas and better control of plating conditions has been brought about by an understanding of the functions of the bath constituents and of the effect of foreign materials in the bath, notably metallic impurities and oxidizing agents.

The second grouping of baths, i.e. the sulfate baths, have been studied with great interest for several reasons: (1) the sulfate solution is more convenient to use from the electroplater's point of view (26); (2) the low pH cadmium sulfate solution can provide a very thin but highly adherent undercoating for heavy coatings from cyanide cadmium baths (27); and (3) codeposition of hydrogen can best be studied in sulfate solutions. Some of the examples of the studies performed in sulfate solutions are given here to represent the developments made using this plating bath.

In 1876, Wrightson (28) found that the electrolysis of a solution of cadmium sulfate was not suitable for quantitative analysis. The cadmium was found to deposit easily and quickly from an acid bath, but not in a compact, weighable condition.

The investigation of Luckow (29) in 1880 led him to the conclusion that cadmium can be completely precipitated from dilute neutral sulfate solutions.

It was even concluded by Smith (30) in the same year that the best quantitative results for cadmium could be attained through the use of cadmium sulfate solutions. In his work the separation of cadmium from copper, by electrolysis took place in a bath which had been acidified with nitric acid. The cadmium remaining in solution after electrolysis was deposited after the nitric acid had been removed by evaporation with sulfuric acid.

Wieland's (31) investigations in 1884 revealed that cadmium could be deposited from weak sulfuric acid solutions.

Smith and Frankel (32) developed a method in 1889 for separating copper from cadmium, in that cadmium was not deposited from a solution containing 10 ml. of sulfuric acid at low applied currents (0.03 amp.) while copper was.

In analytical investigations in the same year Kollock (33) studied cadmium deposition from sulfate baths and attained complete separation of the cadmium, but it required quite long deposition times and the deposits weighed more than theoretically predicted.

The first brightening agent appears to have been used in sulfate baths by Balcahowsky (34) in 1900. He obtained bright deposits from sulfate cadmium baths with the addition of urea and formaldehyde, or urea and acetaldehyde.

A number of investigators have studied the effects of electrode rotation on the deposition of cadmium from sulfate baths. Medway (35) (1904) studied the effect of rotating the cathode during deposition while the rotating anode effect was studied by Exner (36) (1903), Ashbrook (37) (1904), Davison (38) (1905), Flora (39) (1905), and Holmes (40) (1908). Other experimentors have investigated the effects of rotating electrodes but the studies have more or less followed the same lines as outlined by those listed here.

Mercury cathodes were first used in cadmium deposition from sulfate baths by Carhart (41) in 1904 and by Stoddard (42) in 1909.

Stirring of the electrolyte solution was achieved by Stoddard (42) and by Benner (43) (1910) through the utilization of gas evolution at the electrode surface and heat produced by the current.

Hulett and Perdue (44) and Laird and Hulett (45) determined the atomic weight and the electrochemical equivalent of cadmium by deposition from sulfate solutions.

Analytical investigations by Breyer (46) in 1912 produced a method of analysis for small amounts of cadmium using a sulfate bath and employing electrochemical precipitation. Accuracy within 0.2 percent was attained.

A large number of other investigators have used the sulfate plating bath for both theoretical and practical purposes. (47-64)

The use of the third and final group of baths, i.e. all types other than cyanide or sulfate, has been rather limited and they will only be mentioned briefly here. Mathers and Marble (22) have made a rather complete study of the early work done in cadmium plating from a number of different baths.

Desch and Vellan (48) investigated several electrolytes, including the fluosilicate, oxalate, and chloride, for the deposition of cadmium.

Senn (65) investigated the use of fluoboric and perchloric acid solutions, with and without added colloids.

Planner's (66) studies dealt with a number of acid baths and particularly perchloric and fluosilicic acids.

Electrolytic deposition of cadmium from its pyrophosphate solution has been studied by Koyanagi. (67)

As mentioned previously, in order to obtain smooth, bright cadmium deposits from sulfate solutions it is necessary to use brightening addition agents. Investigations have been conducted where bright cadmium was plated without addition agents, but special techniques or multi-component baths are usually necessary to accomplish this.

The work of Balcahowsky (34) in 1900, adding either urea and formaldehyde or urea and acetaldehyde, has already been referred to as the first attempt at using brighteners in the cadmium sulfate bath. Since that time extensive work has been carried on in this respect and a host of organic compounds have been used to produce brightening in the sulfate solution. Some of the organic compounds which have been used are: glycine (68); cresolsulfonic acid (69); soap (Lipofar), licorice, and saponin (70); gelatin, glue, and aniline (71); heliotropin (72); sullosalicylic acid, anthranilic acid, trilon, 2-naphthol, camphor, diphenylamine, and triethanolamine (73); condensation products of ethylene oxide containing aliphatic or

aromatic radicals (74); tribenzylammonium sulfate (75); dextrin (76); peptone, and creosol (77); furfurole (78); sulfitecellulose wastes (79); agar-agar, and caramelized sugar (80); acetaldehyde, aldol, crotonaldehyde, and paraldehyde (81); oxidized amketaldoresin (82); reaction products of aldehydes or ketones with amines (83); hydroxy-aliphatic amines, and ether derivatives of alkylene glycole (84); polyvinyl alcohol (85); acetic acid, propionaldehyde, benzene, vanillin, anisaldehyde, ethylether, methylpropyl ether, biacetyl and cyclohexanone (86); tung oil, cod-liver oil (87); an alkyl aromatic sulfonic acid compound of the benzene series (88); ethylenediamine (89); 1-naphthylamine gluconate plus nickel gluconate, and gluconic acid plus 1-naphthylamine (90); coffee extract concentrate (91); sulfonated marine animal oils (92); sodium carboxymethyl-cellulose (93); methyl oleate, and sulfated ethylene glycol oleate (94); polyglycol esters of fatty acids, and alkali metal zanthates (95); polyvinylpyrrolidinone (96); a higher aliphatic amine plus one or more of dextrose, levulose, sucrose, and lactose (97); an alkali metal salt of an alkylnaphthalenesulfonic acid (98); potassium salt of ethylenediaminetetraacetic acid (99); and formyl-substituted phenyl ethers of polyhydroxy alcohols (100). This list of additives is by no means complete, but it does serve to illustrate the various types of organic compounds that have been used effectively.

Although the above list indicates something of the number and variety of additives that have been used, nothing has been said concerning the theories of addition agents. Very little is known concerning the actual manner in which additives act, but at least four theories have been proposed to explain the mechanism of bright electrodeposition. These will not be considered in order of their appearance in the literature.

1. Adsorption Theory. In his "Axioms of Electroplating," Bancroft (101,102) offered as his fourth axiom: "The crystal size is decreased when there are present at the cathode surface substances which are adsorbed by the deposited metal." In order to explain their data on the electrodeposition of copper in the presence of gelatin, Taft and Messmore (103) assumed that the copper deposited by the current adsorbed gelatin on the surface. Although Frolich (104) demonstrated that nickel deposited in the presence of gelatin containing organic matter, he found Bancroft's idea of an adsorbed film of the addition agent at the cathode highly hypothetical and suggested that experimental results were unavailable to corroborate the theory. Further, he pointed out that Holmes and Child (105), using gelatin and an emulsifying agent, which represented optimum conditions for film formation, were unable to establish any concentra-

tion of gelatin at solution interfaces. In recent work Gritsan and Tsvetkov (106) have postulated that the additive is adsorbed and desorbed at the electrode surface producing cathodic potential oscillations.

2. Reducing Agent Theory. Kern (107) observed that reducing agents such as polyhydroxyphenols, tannins, and aromatic amines refined the grain deposits of copper, lead, and silver. Oxidation anions such as nitrate and perchlorate did not, however, yield such favorable results. He was thus led to suggest that "the function of an addition agent in an electrolyte is to maintain a reducing menstrum around the cathode which, in turn, causes the deposit to form denser and smoother."

Hendricks (108) has maintained that this reducing agent theory is untenable. He based his decision on the observation that fine grained metal deposits can be obtained from acid copper baths containing nitrates and from chromic acid baths used for chromium plating.

3. Complex Ion Theory. This theory was first proposed by Mathers (109) in 1916, and elaborated by him (110) in 1939. He suggested that effective addition agents form complex ions with the depositing metal. He was led to this concept by investigations on refining silver deposits to give smooth and adherent deposits from baths containing silver nitrate, nitric acid, and tartaric acid. It was found by Fuseya et. al. (111,112) that silver and copper formed positively charged complex ions with metaphosphoric acid, tartaric acid, and glycocoll. They also observed that these substances entered into the cathode deposits, increased the weight of the deposits, and caused the grain size to be smaller. Sugars and higher alcohols, which did not form significant complexes with silver and copper, had little or no effect on the cathode deposit.

Matula and Matsumura (113) concluded from some of their work that protein had the property of forming complex cations with metal ions, and Isgarischew (114) found evidence which indicated the existence of complex cations when gelatin was added to copper or zinc baths. The latter worker attributed the favorable effect of gelatins as an addition agent to its complex-forming property. According to his view, the velocity of separation of free metallic ions from the complex ions was not great and the growth of coarse crystals was retarded. This view of Isgarischew differs from that of Fuseya et. al. (111,112), who held that the codeposition of the complex cations with metallic ions would be the principal cause of hindrance to crystal growth.

4. Cathode Interference Theory. In papers on the structure of electrodeposited metals, Hunt (115) concluded that:

The crystalline structure of an electrodeposited metal will be governed by the relation of the metal ion concentration of the other constituents of that film. If the proportion of metal ions to inert particles is comparatively high, there will be little interference with crystal growth, and coarsely crystalline deposits will result. If, however, the proportion is low, due to low degree of dissociation, complex ion formation, high hydration of the metal ions, or the presence of colloid matter that has migrated cataphoretically into the film, . . . there will be considerable interference with crystal growth, with the consequent formation of many nuclei.

Hendricks (108) gave an interpretation of the mechanism of bright electroplating which extended the cathode interference theory to include some of the tenets of the adsorption theory. He suggested that the brightening process might be compared with the Liesegang phenomena which is often explained as a periodic supersaturation and precipitation. For bright deposition, an alternating adsorption of the additive and deposition of the metal could explain the production, of a striated deposit.

Perhaps of more significance, Hendricks emphasized the inhibitor-like properties of brighteners or the reduction products of the brighteners. He outlined the following mechanism by which a brightener might work.

1. A cadmium crystal at an active center attains a higher potential than the surrounding crystals.
2. The higher potential causes electrolytic reduction of adjacent brightener to form an inhibitor which is adsorbed to form an insulating layer which temporarily halts crystal growth.
3. The adjacent crystals, uninhibited, continue growth until the potential increases to the reduction potential of the brightener and likewise become filmed with the inhibitor.
4. When the entire surface has been filmed in this manner, the cathode reaction shifts to cadmium deposition, after which the adsorption cycle is repeated.

Support for the mechanism proposed by Hendricks can be found in the literature. Frolich (104), and Hotersall and Gardom (116) found that carbon was present in nickel deposits obtained in the presence of organic compounds, and Zentner et. al. (117), in an exhaustive study of the effect of plat-

ing variables on the structure and properties of electrodeposited nickel, found that sulfur was present in nickel deposits obtained when organic brighteners containing sulfur were present. Sutyagina (118) was able to show that sulfur was occluded in the deposit by using as the additive thiourea which contained radioactive sulfur.

Other investigations that support Hendrick's theory have been conducted by several investigators. (119-122)

Many techniques have been used in attempts to understand electrode properties and electrode processes. Notable among these are (1) capacitance methods, (2) chronopotentiometry, (3) radioactive tracer methods, and (4) polarization studies.

Experimental Section

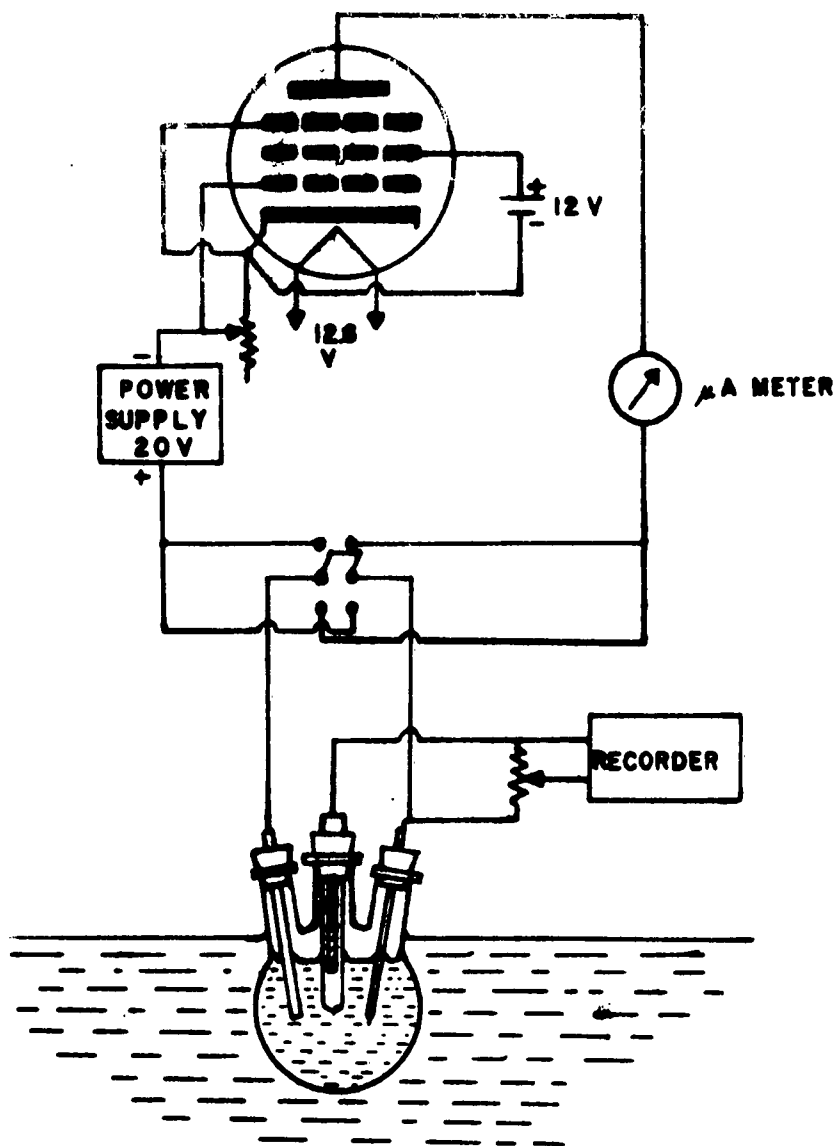
The techniques investigated were:

1. Constant current pulses, automatically plating and dissolving cadmium, while the potential of the electrode was followed automatically with a recording potentiometer.
2. Cyclic voltammetry, sweeping the voltage back and forth, linearly increasing and decreasing it, passing through both regions of plating and dissolving of the cadmium. Current voltage curves were recorded for these processes.
3. A microvolumetric technique, used to measure the volume of hydrogen evolved during the plating process.
4. The embrittlement of iron wires, measuring the relative amount of hydrogen codeposited with cadmium on iron electrodes.

1. Constant Current Pulse Technique.

A schematic diagram of the apparatus is shown in Figure 1. This shows a diagram of the constant current source that was designed and built for use to furnish the low constant current pulses needed. The square pulse function generator was constructed from a piece of surplus equipment formerly used for programming the taking of pictures during a bomb run. The series of timed impulses were used to activate a stepping relay. The relay (the switch shown in the diagram) reversed the polarity of the pulses applied to the cell. The cell consisted of a micro electrode (primarily platinum and in a few cases iron), a large non polarizable 99.9% cadmium stick

FIGURE 1. SCHEMATIC DIAGRAM OF APPARATUS
USED FOR CONSTANT CURRENT PULSE
EXPERIMENTS.



electrode and a Beckman saturated Calomel reference electrode. The potential between the calomel reference electrode and the micro electrode was followed as a function of time using a Varian G-11 recorder. Figure 2 is a typical curve. The ratio of the length of the line for anodic dissolution of the cadmium to the length of the line for plating is the current efficiency for the plating of the cadmium.

2. Cyclic Voltammetry.

Figure 3 shows a block diagram for the apparatus used in these experiments. The Model 202A Function generator was used to apply a linearly varying voltage function across a micro platinum electrode and a large non polarizable cadmium stick electrode. The current voltage curves were plotted with an Offner Dynograph recorder.

3. Microvolumetric Technique.

Figure 4 shows the cell for the measurement of the volume of hydrogen evolved during the deposition of cadmium on cadmium. This apparatus is the same as that described by Franklin and Goodwyn (2).

4. Embrittlement Studies.

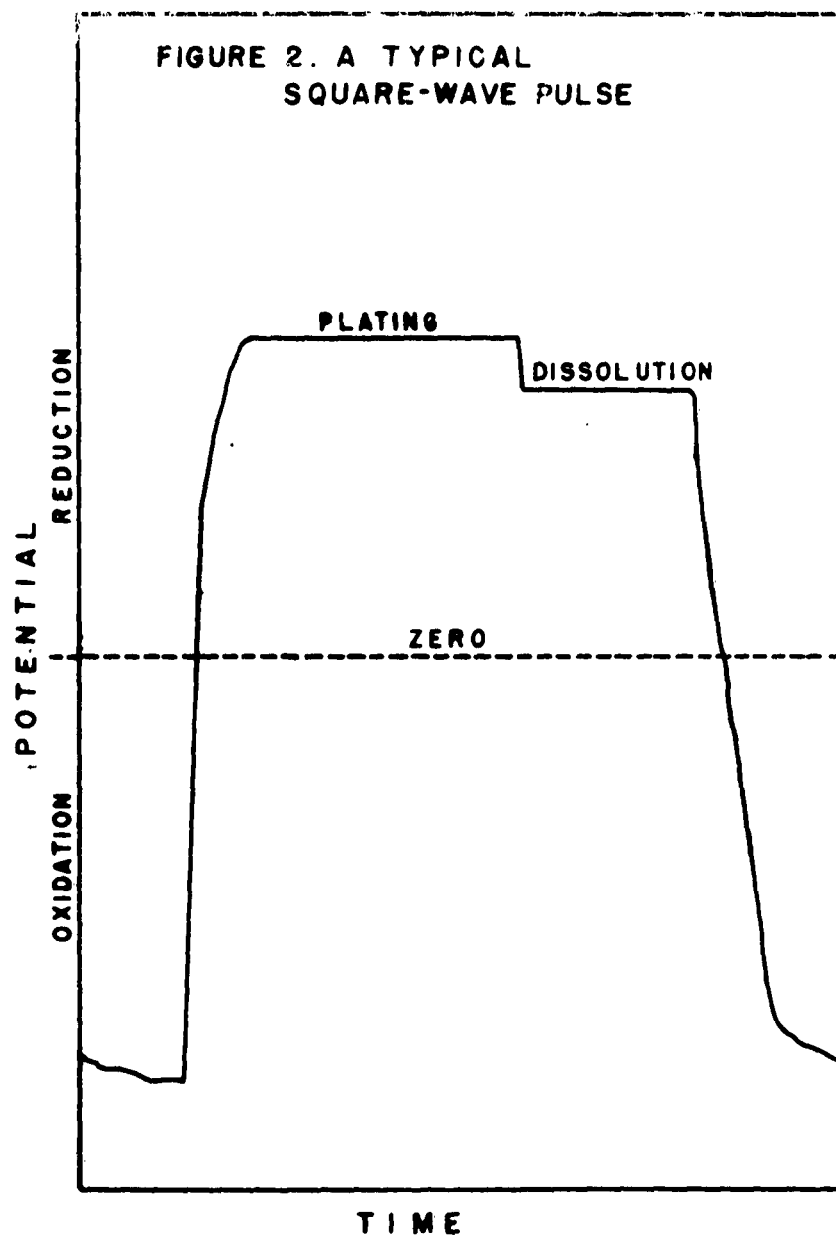
The iron electrodes used in the embrittlement measurements were prepared from the B & A reagent grade iron wire used for standardization. The embrittlement was measured with the commonly used bend test. The reproducibility was quite good with the same operator. Each electrode could be used for about three embrittlement tests and the results used had an average deviation within plus or minus one-third of a bend.

The solutions were prepared with different concentrations of cadmium sulfate. The pH usually was buffered at 4.85 with boric acid. The additives used were the sodium salts of propane and propene sulfonic acid. Variations were made in time of plating, rotation of the electrode, current density pH, concentration of cadmium, metal substrate and concentration of additives.

Results and Discussion of Results

1. Constant Current Pulse Technique.

Figures 5, 6, 7, 8, 9, 10, and 11 show typical curves



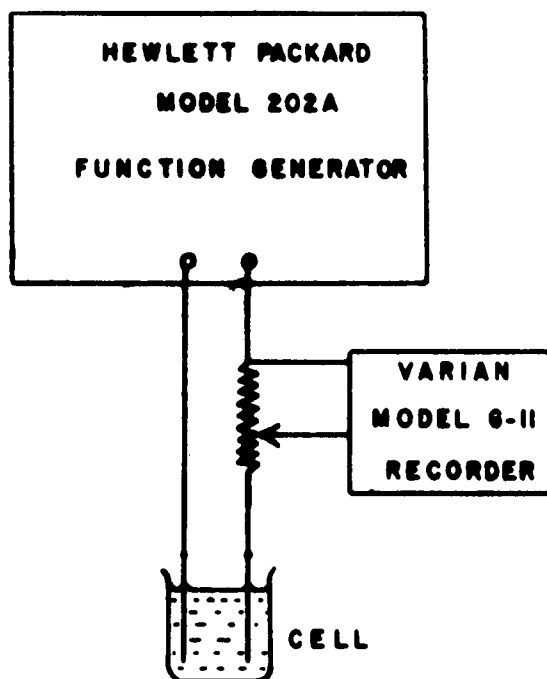


FIGURE 3. CELL AND
BLOCK DIAGRAM OF APPARATUS FOR
CYCLIC VOLTAMMETRY

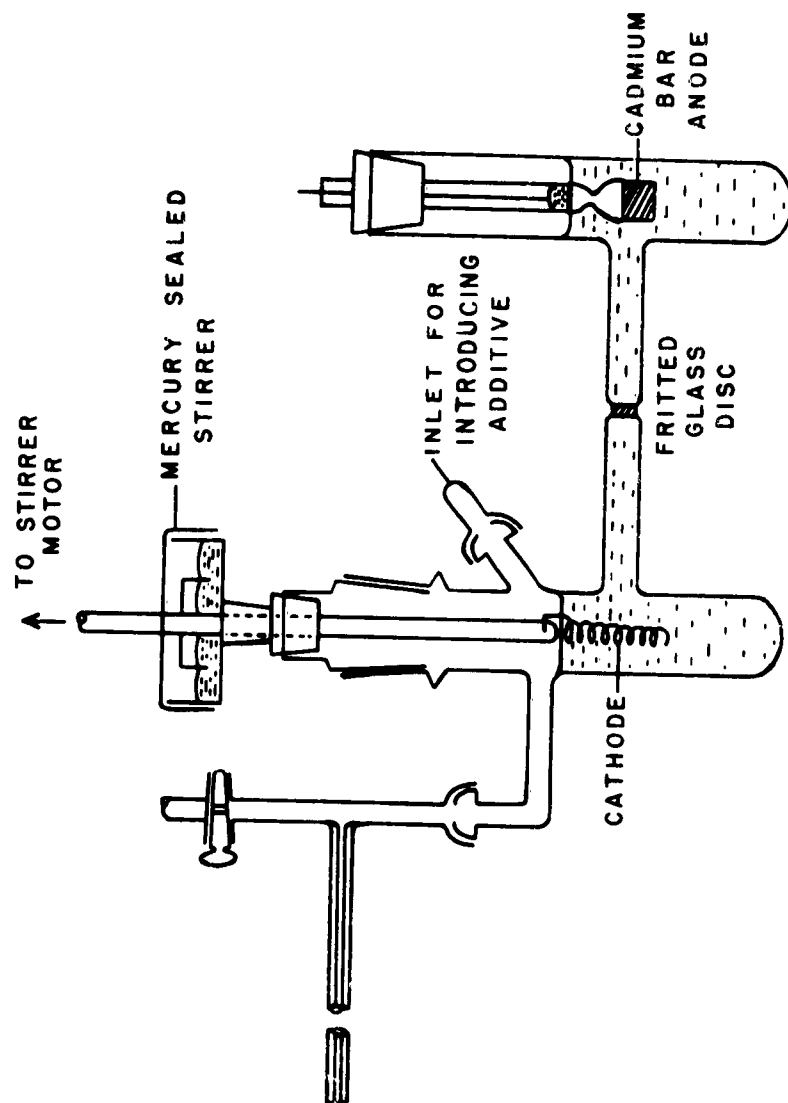


FIGURE 4. APPARATUS FOR MEASURING THE HYDROGEN EVOLVED DURING THE PLATING PROCESS

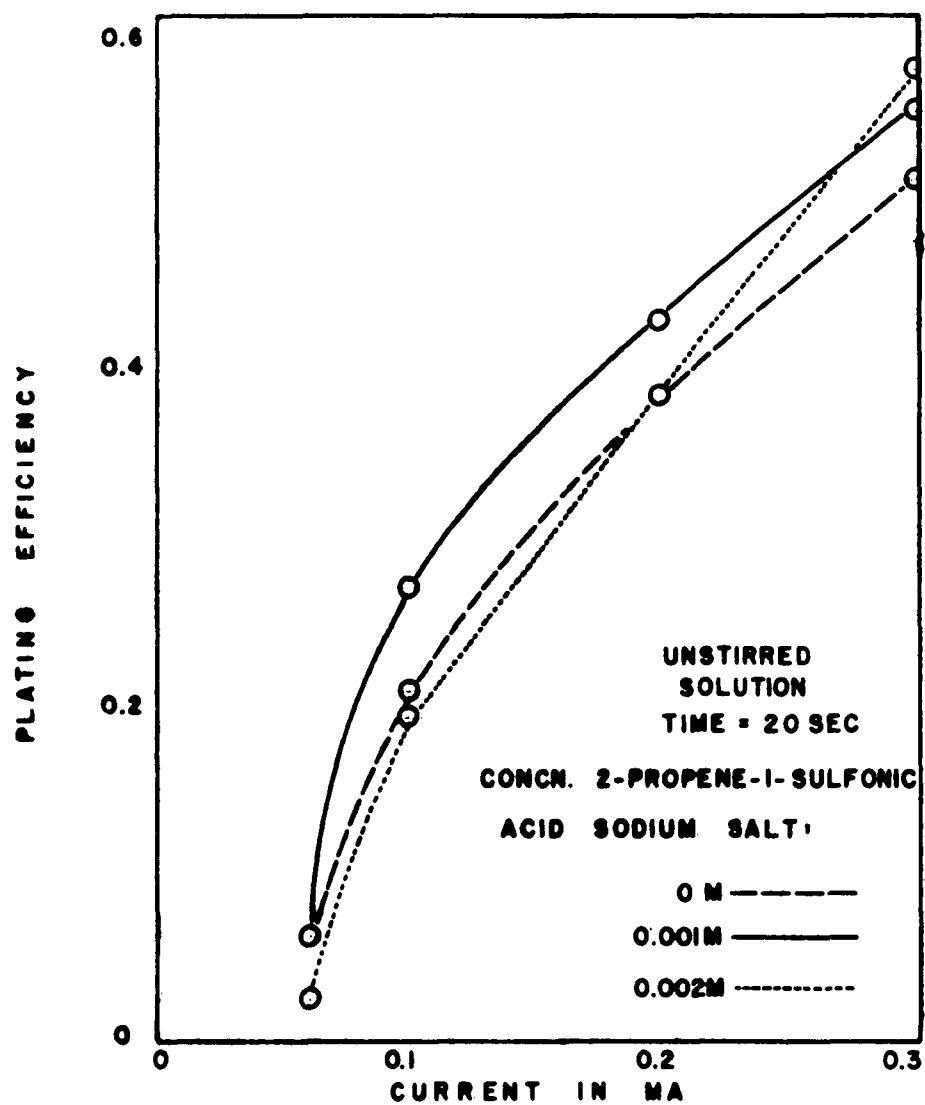


FIGURE 5. EFFECT OF ADDITIVE CONCENTRATION ON THE PLATING EFFICIENCY IN AN UNSTIRRED SOLUTION.

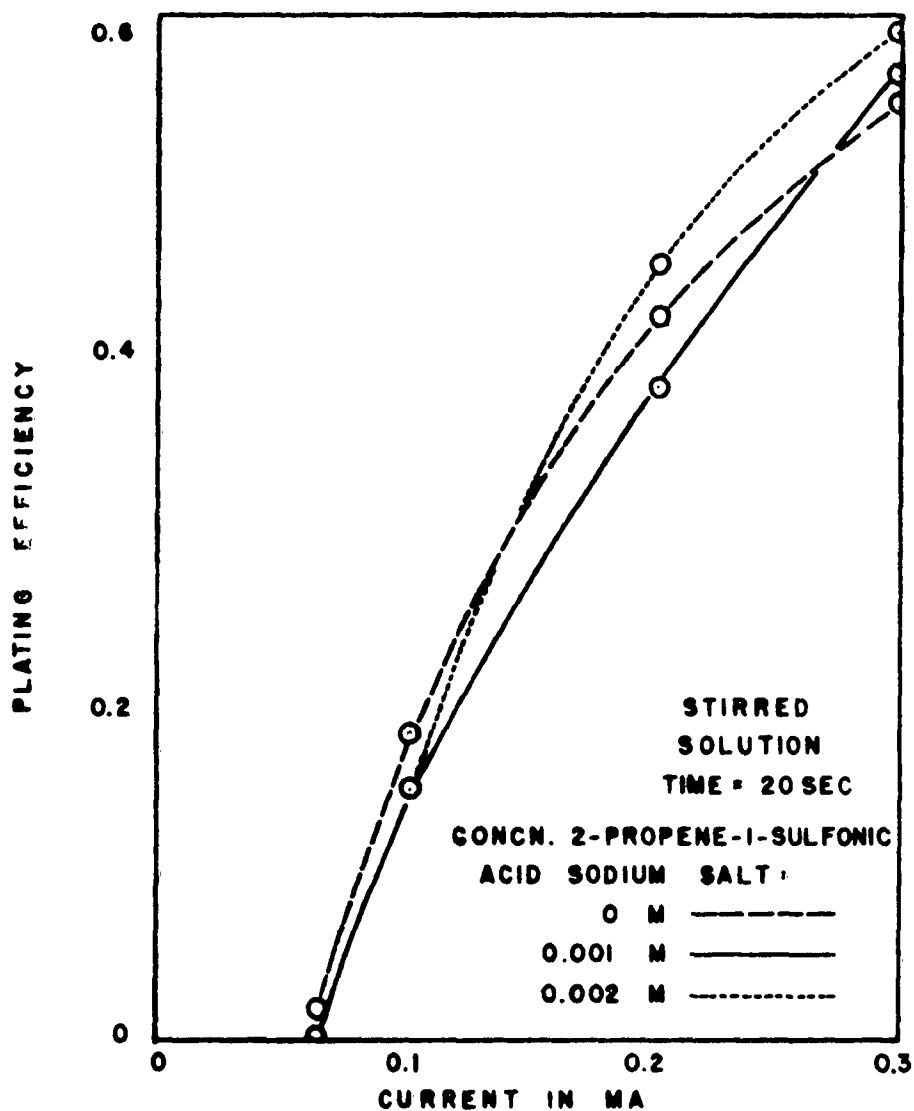


FIGURE 6. EFFECT OF ADDITIVE CONCENTRATION
ON THE PLATING EFFICIENCY IN A
STIRRED SOLUTION.

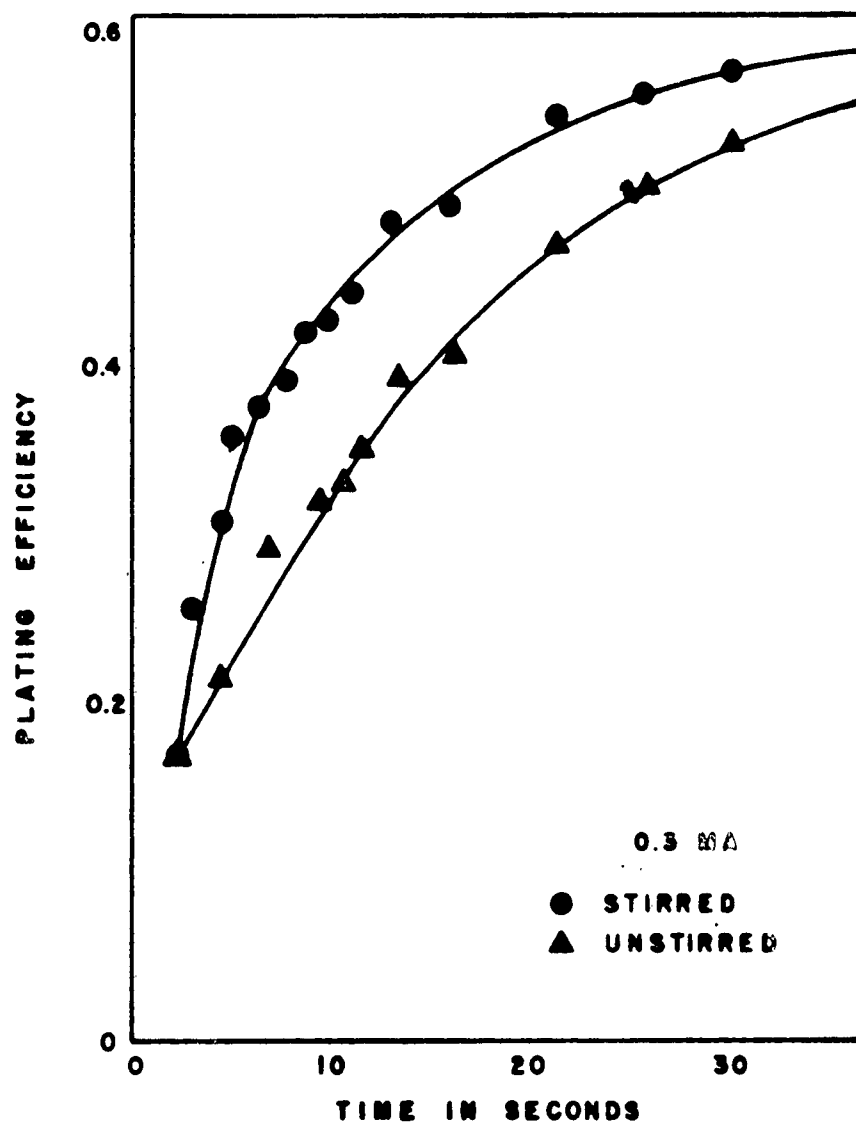


FIGURE 7. EFFECT OF PLATING TIME ON THE PLATING EFFICIENCY.

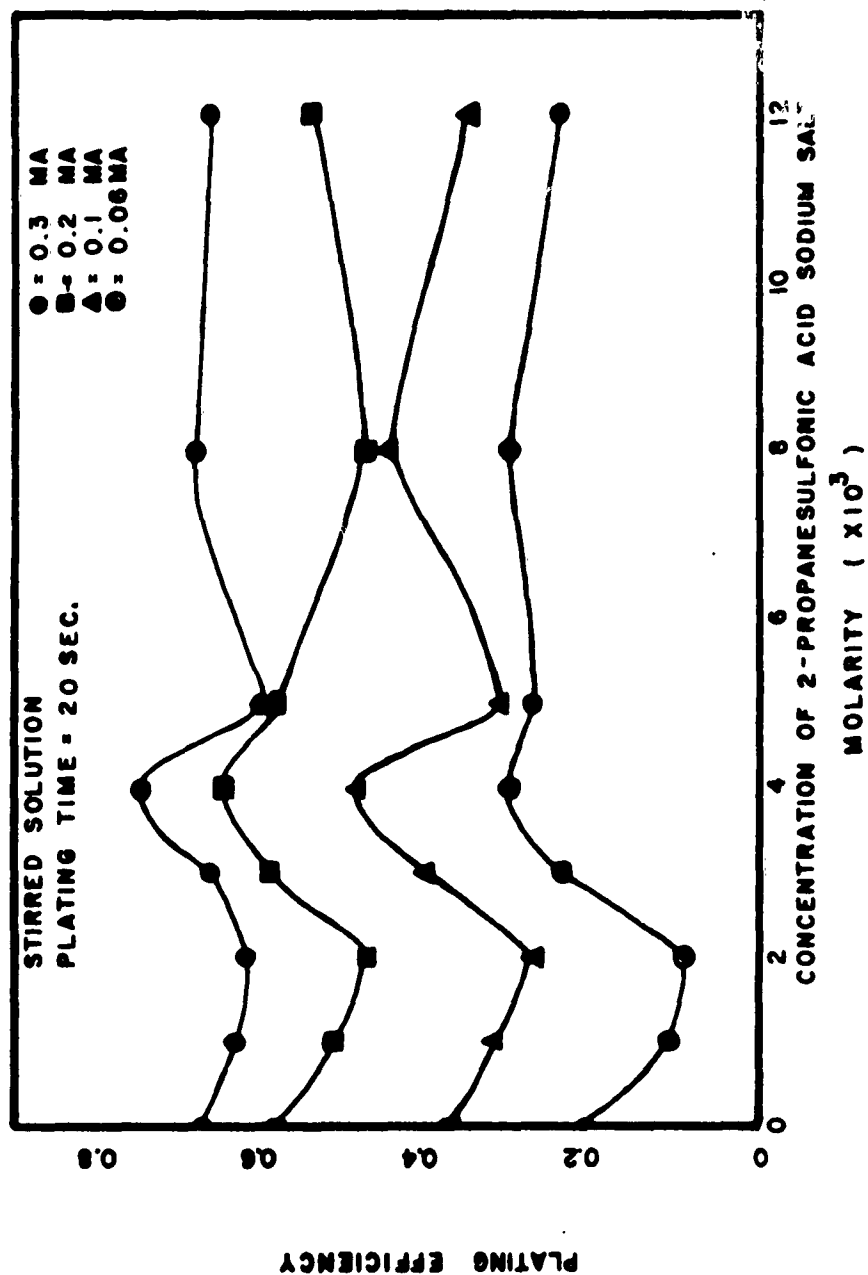


FIGURE 8. EFFECT OF CURRENT DENSITY ON THE PLATING EFFICIENCY ON PLATING WIRE WITH 2-PROPANESULFONIC ACID SODIUM SALT ADDED.

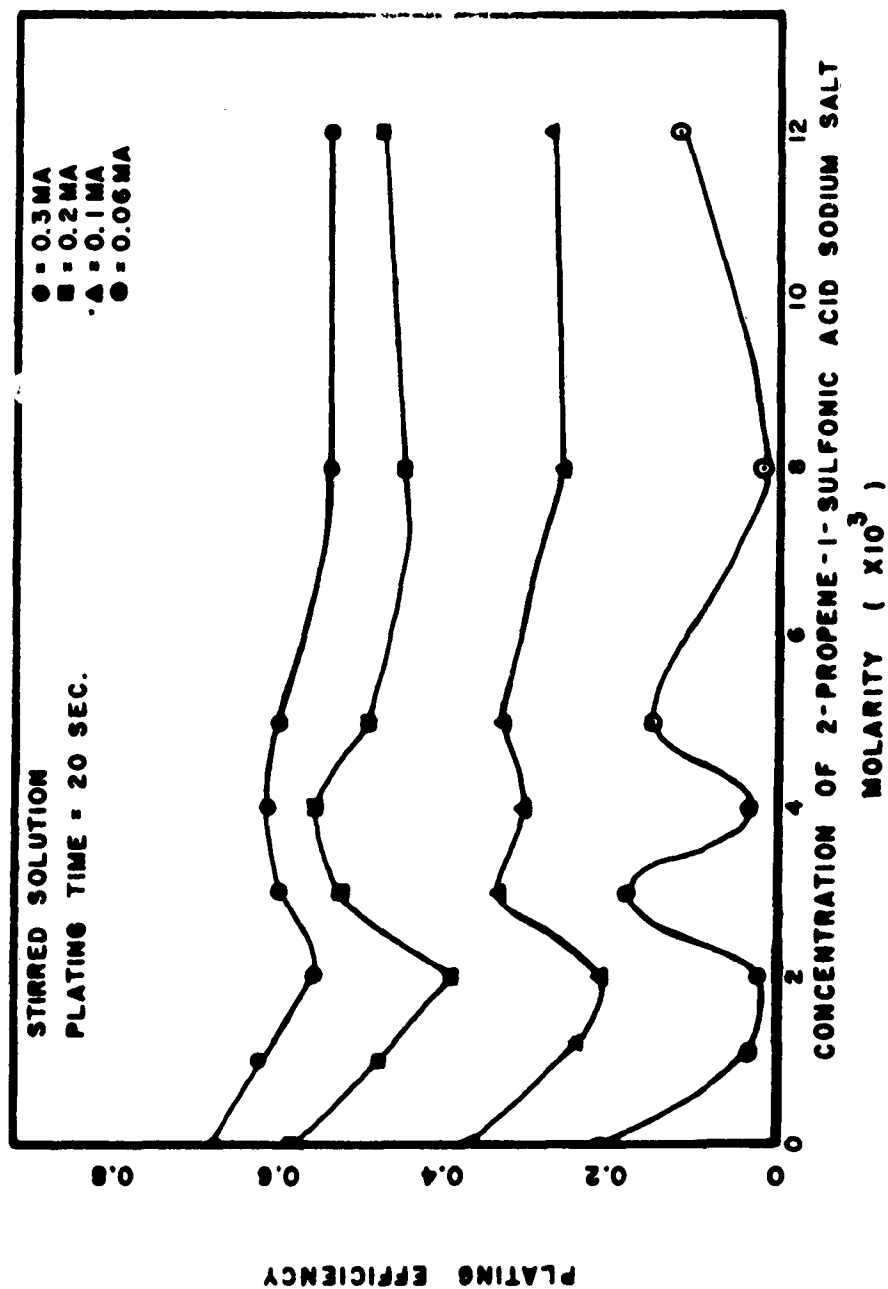


FIGURE 9. EFFECT OF CURRENT DENSITY ON THE PLATING EFFICIENCY ON PLATINUM WIRE WITH 2-PROPENE-1-SULFONIC ACID SODIUM SALT ADDED.

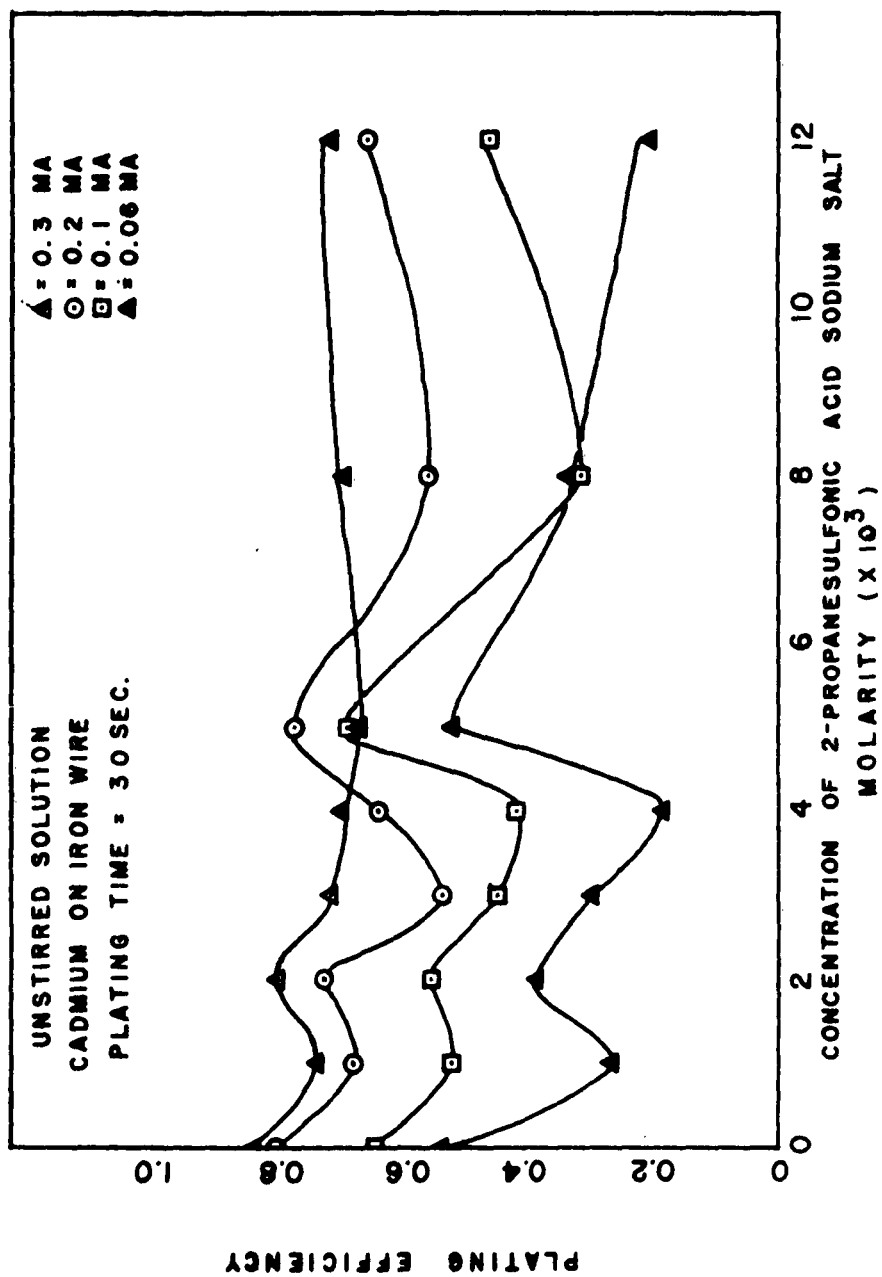


FIGURE 10. EFFECT OF CURRENT DENSITY ON THE PLATING EFFICIENCY ON IRON WIRE (FOR 30 SECONDS) WITH 2-PROPANESULFONIC ACID SODIUM SALT ADDED.

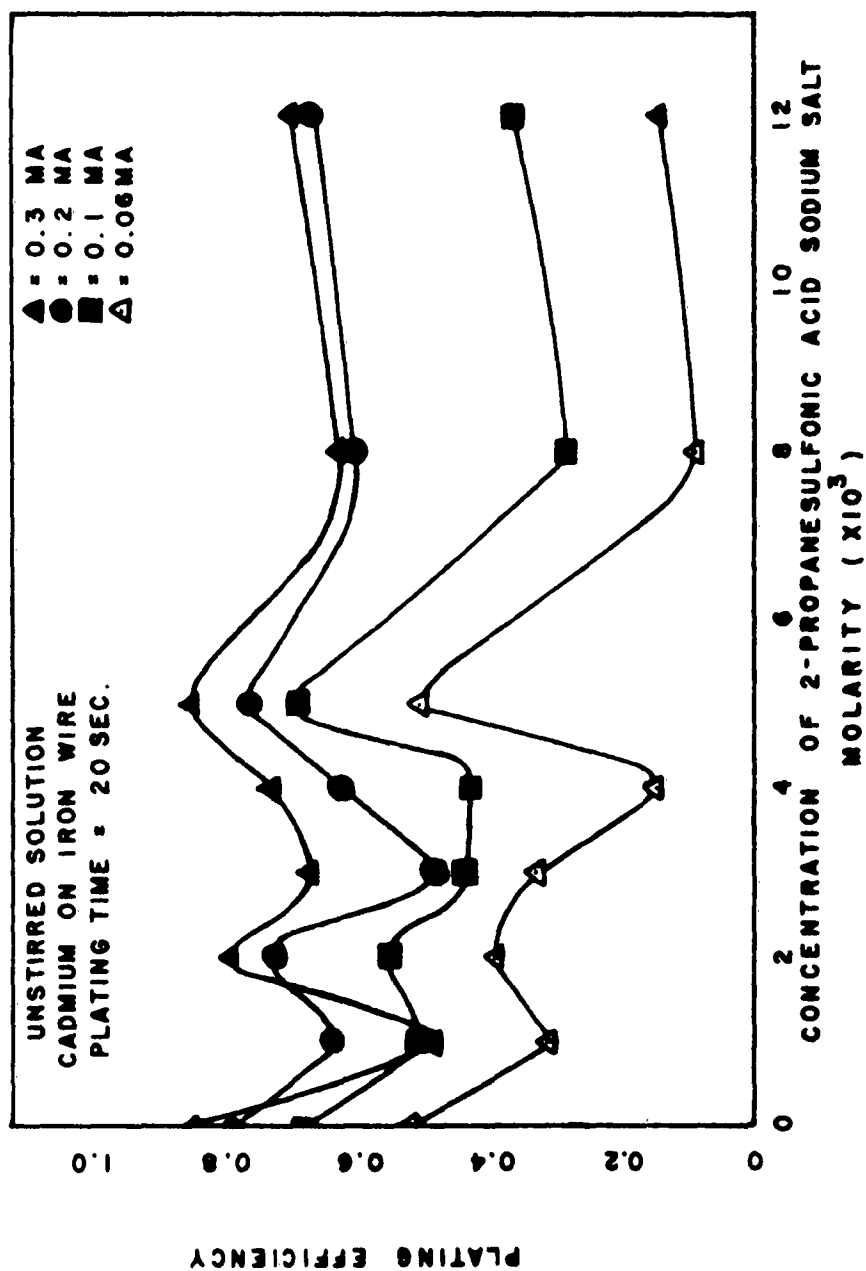


FIGURE 11. EFFECT OF CURRENT DENSITY ON THE PLATING EFFICIENCY ON IRON WIRE (FOR 20 SECONDS) WITH 2-PROPENE-1-SULFONIC ACID SODIUM SALT ADDED.

showing the variation of current efficiency for the deposition of cadmium on platinum with different variables. From Figures 5, 6, and 7 it can be seen that stirring the solution merely shifts the curves but it does not alter the general shape of the curves. This is true whether an additive is present or not. This indicates that these are not diffusion limited processes.

Figures 8 and 9 are for the deposition of cadmium on platinum and Figures 10 and 11 are for the deposition of cadmium on iron. It is seen that in spite of variations in the metal substrate, current density, additive, stirring of the solution and time of plating the general shape of the curves are quite similar to each other. They are in fact somewhat similar to the results of Franklin and Goodwyn (2) for the deposition of nickel on nickel. The cadmium results are somewhat more complex since the current efficiency for the deposition of cadmium on platinum is significantly lower than for deposition of cadmium on cadmium. Because of this it is noted that the current efficiency for the deposition of cadmium improved with longer plating times and higher current. These conditions produce a higher percentage of cadmium plated on cadmium.

2. Cyclic Voltammetry.

Figure 12 shows a typical current voltage curve for a cycle involving the electrodeposition and electrodisolution of cadmium on a platinum microelectrode in a solution containing the sodium salt of 2-propane sulfonic acid as an additive. On the oxidation side one first anodically dissolves the cadmium, then forms oxides on the platinum. On the reduction side the oxides are first reduced then the cadmium and hydrogen are deposited. The shaded area seems to be present only when an organic additive is present and is probably due to the oxidation of the additive on the platinum. Figure 13 shows a plot of this shaded area against the concentration. The current efficiency for the deposition of cadmium is plotted on the same page for comparison. It is seen that the curves are quite similar although they are displaced.

3. Microvolumetric Method.

The apparatus for this type study has been prepared; however, only preliminary runs have been completed. This method will be used to determine the current efficiency for the deposition of cadmium on cadmium.

4. The Embrittlement Technique.

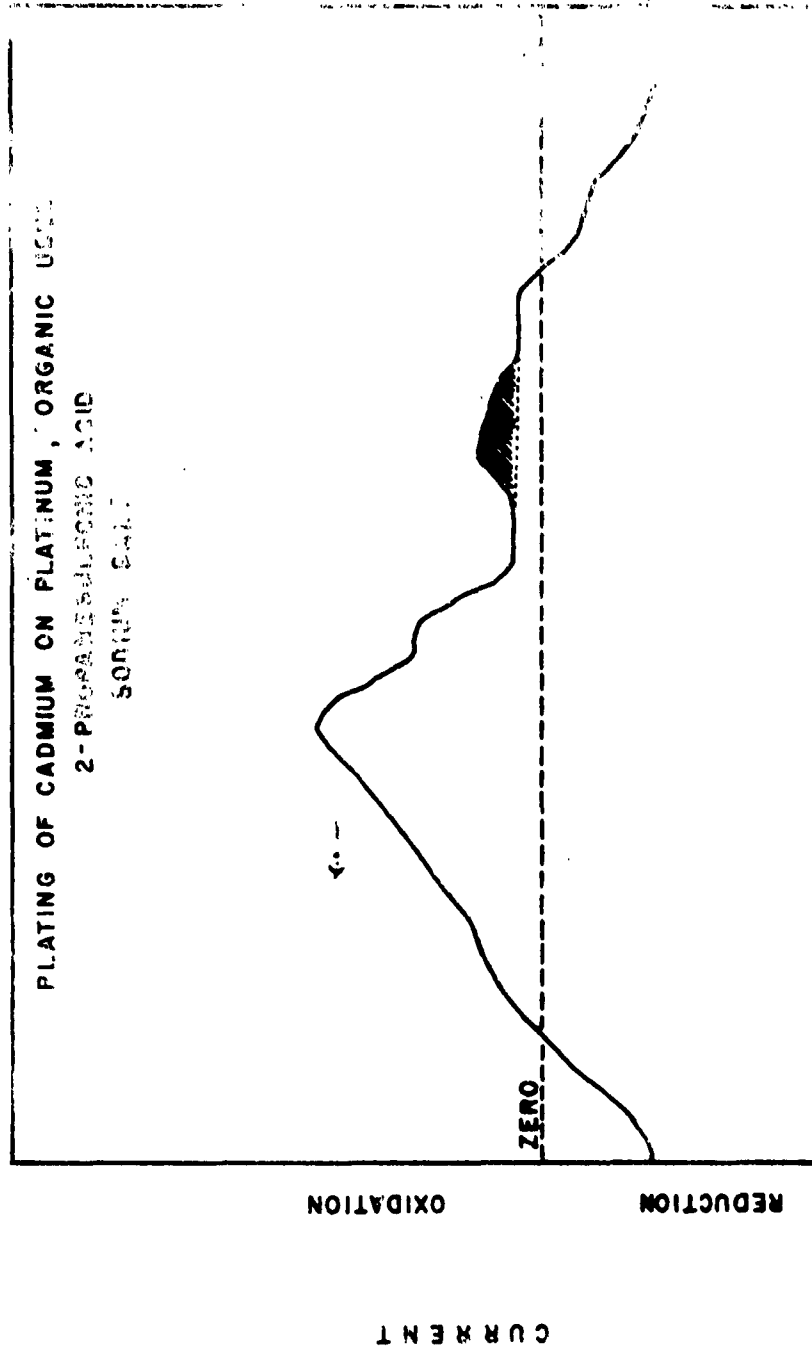


FIGURE 12. A TYPICAL CYCLIC VOLTAMMETRY CURVE

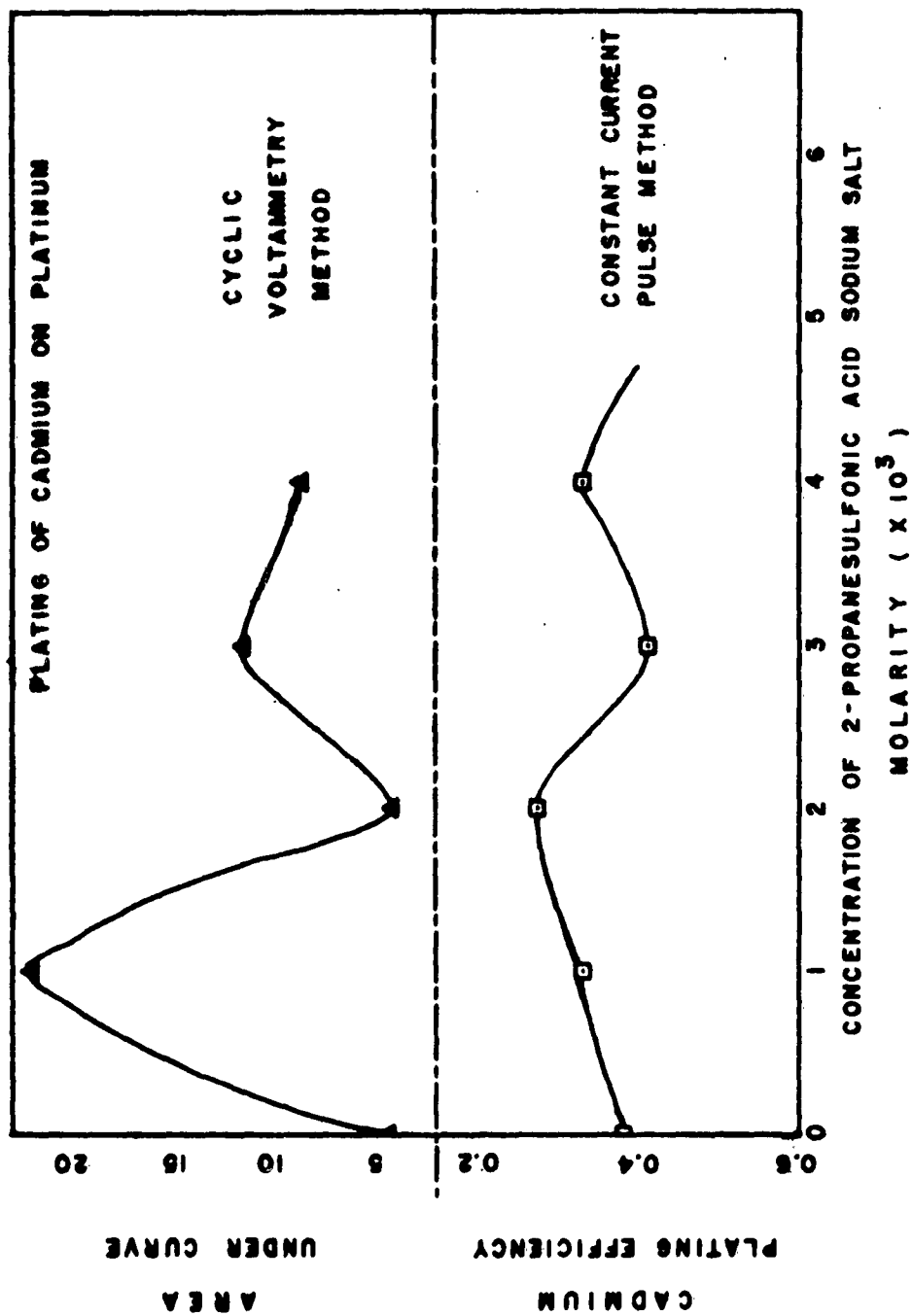


FIGURE 13. COMPARISON OF CYCLIC VOLTAMMETRY¹⁰ AND CONSTANT CURRENT PULSE RESULTS.

The electrolytic generation of hydrogen on iron wire electrodes, separately, or along with a metal in a deposition process, decreases the resistance of the iron wire to breaking. It was observed (Table I) that the hydrogen absorbed by iron wire can be removed, but it was observed that although this decreased the embrittlement it did not return the iron to its original strength probably because it did not heal the damage done by the hydrogen.

TABLE I

The Effect of Electrolytic Oxidation on the Embrittlement of the Iron Wire

<u>Sample</u>	<u>Number of Bends to Break</u>
Original iron wire	11.6
Iron wire plated with cadmium	9.6
Iron wire on which hydrogen has been electrolytically generated	7.3
Iron wire on which hydrogen has been electrolytically generated and then electrolytically oxidized	9.7

Conclusions

From the study to date it would seem that the organic additives affect the current efficiency for cadmium plating and the amount of codeposited hydrogen in a regular pattern. This is the same pattern as was previously observed for the codeposition of nickel and hydrogen. It would seem that this is a general type of curve that occurs with different electrodepositions, on different types of base metals, at different current densities, in stirred and unstirred solutions, and with different additives. The positions of the maxima and minima shift as conditions are changed but the general shape of the curve stays about the same.

It would seem that to understand the role of the additive it would be necessary to determine the cause of the curves obtained. It will be necessary to study the effect of the additive on both the hydrogen and cadmium deposition processes.

II. The Anodic Dissolution of Nickel

Historical Introduction

Nickel, as it is commonly encountered in compounds, is in the bivalent state although there are a number of instances where it is present in the monovalent state (123,124), and where it has been postulated as an intermediate in the electrodeposition and electrodisolution of nickel in various media (125-127).

This survey is the continuation of the brief survey given in references 126 and 127 and in which a study of the mechanism of anodic dissolution of nickel was made to see if nickel (I) is formed during the anodic dissolution process. Franklin and Goodwyn proposed the formation of nickel (I) in the anodic dissolution of a nickel anode in aqueous solutions and acetonitrile. This study was continued by Franklin and Parsons in acetonitrile and dimethylformamide (127). In both instances experimental results indicated that nickel dissolved with an oxidation number of less than two.

Results of a study of the valence of the ions produced during the electrolytic polishing of a large number of metals in the presence of ClO_4^- ions indicated that ions of lower than normal valence were produced (128). These ions were unstable and reacted with the ClO_4^- to produce stable ions and Cl^- ions. In these experiments the valence of nickel was found to be bivalent. Froment has published an article discussing the relationship between Faraday's law and electrolytic polishing (129). The discussion is preceded by a review concerning the difficulty of applying Faraday's law to anodic dissolution of metals. Froment found, that in the case of aluminum anodes, the study of which composed the main portion of the article, the process is influenced by concentration and composition of the bath, voltage, the electric field created by the anions at the metal-solution interface, and especially by the content of water in the bath (130).

The anodic attack on the metal may occur either directly by the admission of an ion from the metal or by a secondary chemical reaction (131). Christopher and King measured the solution rates of nickel cylinders rotated in acidified solutions of FeCl_3 and $\text{Ce}(\text{SO}_4)_2$ (132). The results were found to be transport-controlled, and first order constants were obtained for the process but only if a uniform degree of roughness was maintained during the experiment.

Dezider⁹ev studied the problems of anodic dissolution for high anodic current densities, at which densities it was found that chemical changes in the vicinity of the electrode considerably affect the anode process (133). The experiment consisted of measuring potentials in the solution immediately after the polarizing current was turned off. For anodic current densities up to 4 amp/dm², the potential measured reached values of 1.760 to 1.770 V. This indicated a relative constancy of the nickel concentration in the region surrounding the cathode. The values listed above were obtained in solutions of NiSO₄ · 7H₂O. It was found that addition of NiCl₂ · 6 H₂O reduced the measured potential.

Most of the work reported under the title of the mechanism of anodic dissolution deals with passivation effects. Trumpher and coworkers have studied nickel anode dissolution with respect to the effects of H₂SO₄ concentration, purity and pretreatment of the anodes and Cl⁻ concentration on the passivation of nickel electrodes (134-136). Pomosov and Gurevich studied the effect of the Cl⁻ concentration on the passivation of a nickel anode (137). They observed three effects corresponding to three regions of Cl⁻ concentration:

0.005 - 0.01 N Cl⁻ passivity occurred at higher current densities than in electrolytes without the Cl⁻.

0.02 - 0.1 N Cl⁻ periodic oscillations occurred.

0.5 - N Cl⁻ no passivation was observed up to current densities of 4.2 amp/dm².

Chih-Ping Chang, Kravstov and Durdin studied anodic polarization curves of nickel in H₂SO₄ (138). The experimental results were interpreted on the assumption that the anodic solution of nickel was accompanied by a change in the true surface and the activity of the electrode. Equations have been derived for the changes in the metal potentials when switching on and off the current for large and small polarizations (139).

Falicheva and Tsyfanova studied the rate of anodic dissolution of nickel in HNO₃ and found that the conditions for a maximum dissolution rate to be 40 degrees, 8.17N HNO₃ and an applied current density of 750 ma/cm² 140. They obtained a two branched polarization curve and listed as the processes occurring for the respective branches to be nickel (0) to nickel (II) for the first and oxygen evolution and nickel (III) formation for the second.

Piontelli and Serravalle investigated the anodic behavior of nickel in aqueous solutions of Cl⁻, F⁻, ClO₄⁻ and sulfamate at different values of pH, temperature and current density (141).

Shults and Tsyganov observed five regions on the polarization curves for nickel electrodes (142). The processes observed were (a) anodic solution of nickel with preserved surface activity, (b) gradual formation of a film, (c) formation of a phase oxide causing passivation, (d) dissolving the nickel through the film of passivating oxides and (e) evolution of oxygen. At sufficient concentration of Cl^- the last process is absent while the others are still present. The experimental results indicate that the presence of Cl^- ions does not retard the formation of the passivating oxide film on the nickel surface, but the depassivating effect of the chlorides is connected with their ability to facilitate the anodic solution of nickel through the passivating oxides.

Landsberg and Hollnagel postulated the anodic oxidation of the electrode surface for the passivation effects of a nickel anode in H_2SO_4 (143-145). According to these articles, only part of the electrode surface is anodically active, the remainder being covered by an oxygen containing compound. In very concentrated H_2SO_4 (85% H_2SO_4) the increasing passivity with increasing concentration is ascribed to the increase in viscosity which prohibits the diffusion process.

The effects of these conditions on various alloys of nickel have been studied (146,147).

Experimental Section

Figure 14 shows the apparatus used for the anodic dissolution studies. The rate of dissolution was followed with an Ainsworth recording balance. At the same time the potential was measured with respect to the saturated calomel electrode using a potentiometer circuit. The constant current was supplied by a 300 volt constant voltage power supply and a large resistor. The anode was made of 14 gauge nickel wire. The cathode was a large platinum gauze electrode. The solution was dilute sulfuric acid, normal in nickel sulfate. The additive studied most was potassium dichromate.

Results and Discussion of Results

As indicated in the Historical Introduction to this section some previous experiments have indicated that nickel dissolved anodically to form nickel (I). If this is true, then in anodic polishing baths the oxidizing agents very probably influence the reaction by reacting with the intermediate low valence state. In any study of the action of additives it seems profitable to see if the action is on the intermediate. Many previous studies on the anodic dissolution

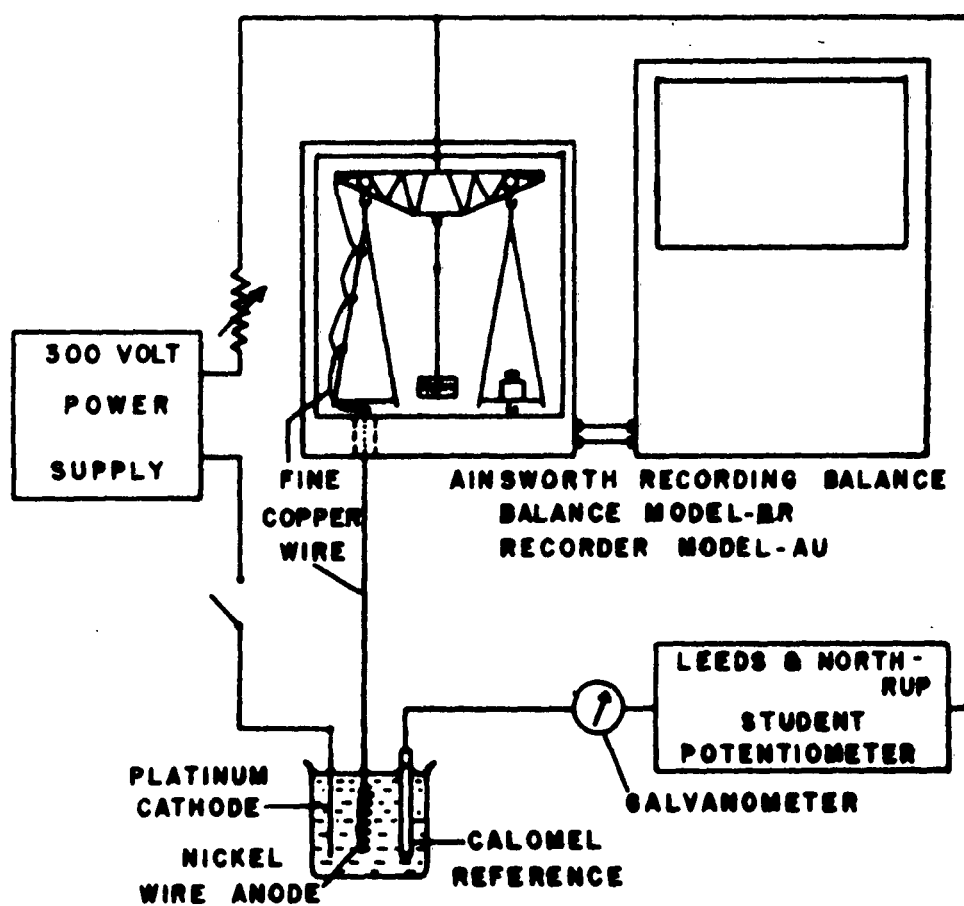


FIGURE 14. APPARATUS FOR ANODIC DISSOLUTION STUDIES.

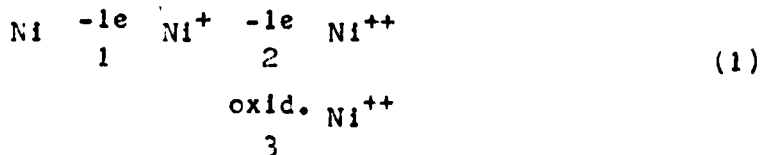
of magnesium and aluminum show that in the presence of oxidizing agents they apparently dissolve with a valence lower than the generally accepted valence. This has been attributed to:

(1) Corrosion of the metal by the oxidizing agent. In such cases the blank corrosion (without anodic current) did not vary much in the presence of the additive therefore it has been postulated that there is a so-called "difference" effect in which there is increased corrosion in the presence of the anodic current. Therefore the blank that is subtracted is lower than the blank should be.

(2) The Chunk effect. In some cases it was felt that the metal anode underwent intergranular corrosion because of the action of the oxidizing agent and chunks of unreacted metal fell off into solution.

(3) Low intermediate valences. If low intermediate valences are forming and reacting with the oxidizing agents then a study of the kinetics of the dissolution process might conceivably establish the mechanism of the dissolution process.

If we assume the mechanism to be:



The experiments were carried out at constant current therefore rate 1 + rate 2 = constant = k.

The experimental quantities measured were the rate of dissolving of nickel $\frac{-d\text{Ni}}{dt}$, and the potential of the dissolving electrode. They were measured as a function of the milliliters of oxidizing agent added.

Rate 1 is of course the measured quantity, $\frac{-d\text{Ni}}{dt}$. From this it is seen that rate 2 = constant - rate 1 = $k + \frac{d\text{Ni}}{dt}$. (2)

Rate 3 can be assumed to be a second order reaction (first order with respect to each of the reactants). Rate 3 = k_3 (concentration Ni^+) (concentration oxid. agent). Rate 3 = $k_3 (\text{Ni}^+) (\text{Oxid.})$ (3)

Since nickel (1) is a very short lived species

$$\frac{-d\text{Ni}}{dt} = \frac{d\text{Ni}^{++}}{dt} = \text{Rate 2} + \text{Rate 3} = k + \frac{d\text{Ni}}{dt} - k_3 (\text{Ni}^+) (\text{oxid.}) \quad (4)$$

Rearranging

$$\frac{-2dNi}{dt} = k - k_3(Ni^+)(\text{oxid.}) \text{ or } \frac{dNi}{dt} = \frac{k_3}{2} (Ni^+)(\text{oxid.}) - \frac{k}{2} \quad (5)$$

With no additive

$$\left(\frac{dNi}{dt}\right)_0 = -\frac{k}{2} \quad (6)$$

Subtracting this from the previous equation

$$\frac{dNi}{dt} - \left(\frac{dNi}{dt}\right)_0 = \frac{k_3}{2} (Ni^+)(\text{oxid.}) \quad (7)$$

If one takes the log of both sides of the equation one obtains

$$\log \left(\frac{dNi}{dt} - \left(\frac{dNi}{dt}\right)_0 \right) = \log \frac{k_3}{2} + \log (Ni^+) + \log (\text{oxid.}) \quad (8)$$

The first and last terms of this equation were measured experimentally. The (Ni^+) term can be evaluated from the Nernst equation.

$$E = E^\circ - \frac{RT}{nF} (Ni^+). \text{ At } 30^\circ \text{ C}$$

$$E = E^\circ - 0.06 \log (Ni^+) \text{ or } \log (Ni^+) = -\frac{E - E^\circ}{0.06} \quad (9)$$

Substituting this for $\log (Ni^+)$ and rearranging one obtains

$$\log \left(\frac{dNi}{dt} - \left(\frac{dNi}{dt}\right)_0 \right) - \log \text{oxid.} = \log \frac{k_3}{2} - \frac{E - E^\circ}{0.06} \quad (10)$$

If this approach is correct a plot of the left hand side of the equation against E should give a straight line. Experimentally it has been difficult to obtain a long series of runs of the same electrode to check this equation. Figure 5 shows a sample of the data obtained for the anodic dissolution of nickel using bromate as an additive. As can be seen the data followed the predicted straight line for three points then for some reason the blank on the electrode increased sharply and upon plotting the curve a different straight line was obtained. The slopes of the two lines were approximately the same. However, they do not fit the theoretical slope.

The difference in slope is possibly due to the fact that the nickel dissolution is activation limited.

The data shows that the observed low valences cannot be due merely to increased corrosion caused by cleaning off of oxide films because the corrosion blanks immediately before and after the current was passed through the electrodes were identical and were so small as to be negligible in the calculations.

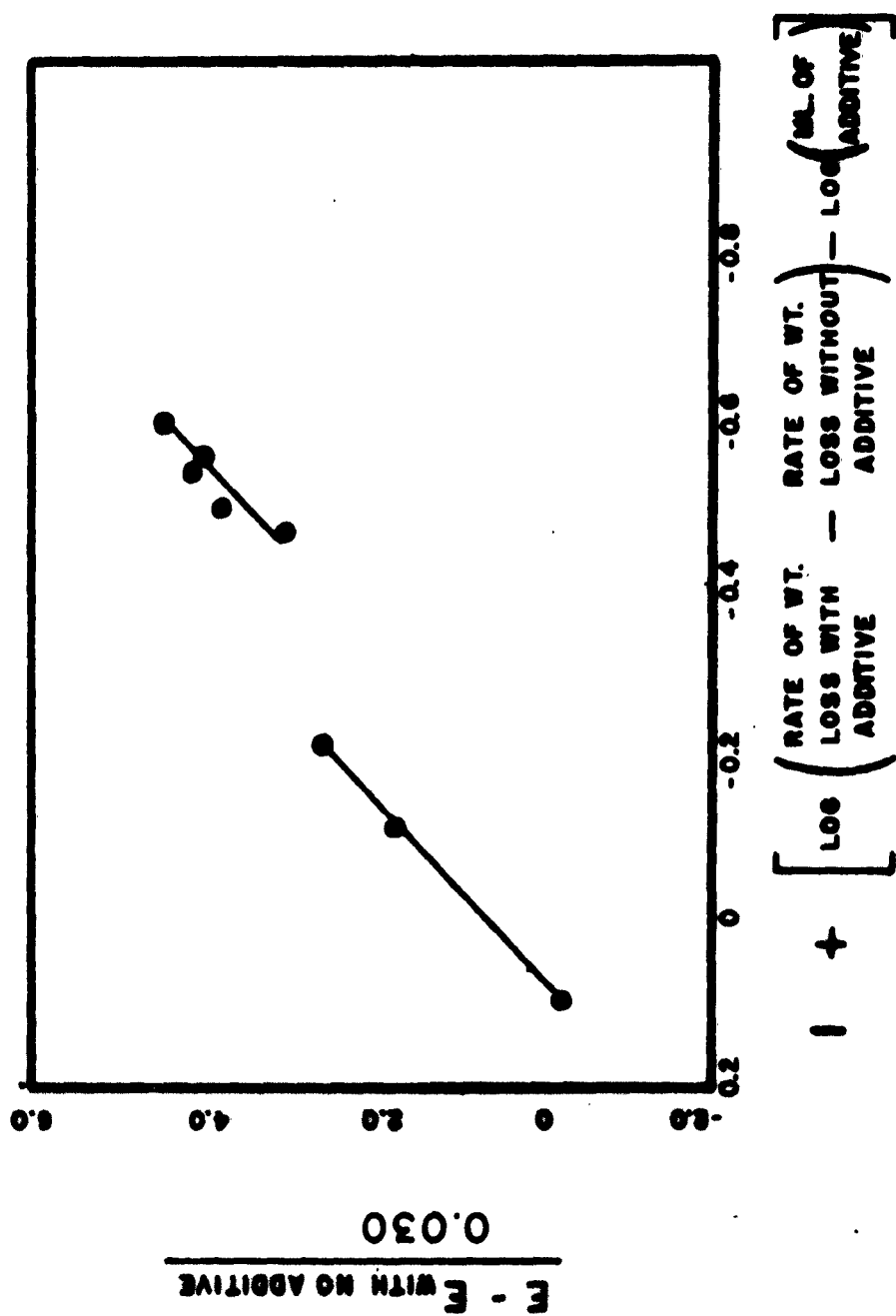
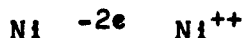


FIGURE 15. ANODIC DISSOLUTION OF NICKEL USING POTASSIUM BROMATE ADDITIVE.

Several series of experiments (different from previous results in the potential of operation gave results similar to those shown in Figure 16. It is seen that in these experiments with constant current the rate of dissolution increases linearly with the concentration of the oxidizing agent in the solution. The most logical explanation of these results is the following corrosion mechanism:



(11)



in which the corrosion reaction is first order with respect to the oxidizing agent concentration. In order for this to be true there must be a "difference" effect. In this case the cause of the difference effect can best be illustrated by a potential energy diagram such as is shown in Figure 17. The solid line indicates the potential energy diagram for the metal electrode without any applied potential and the dotted line indicates the potential energy curve of the metal with an applied potential. It is really seen that the energy of activation is markedly lowered and therefore the rate of oxidation of the nickel should increase correspondingly.

From these preliminary results it would seem that under some conditions the oxidizing agent affects the anodic dissolution by action on an intermediate nickel (I) and under other conditions the oxidizing agent directly attacks the metal in a first order reaction at an enhanced rate because of the applied potential. It remains for further experiments to establish the conditions of operation for each mechanism.

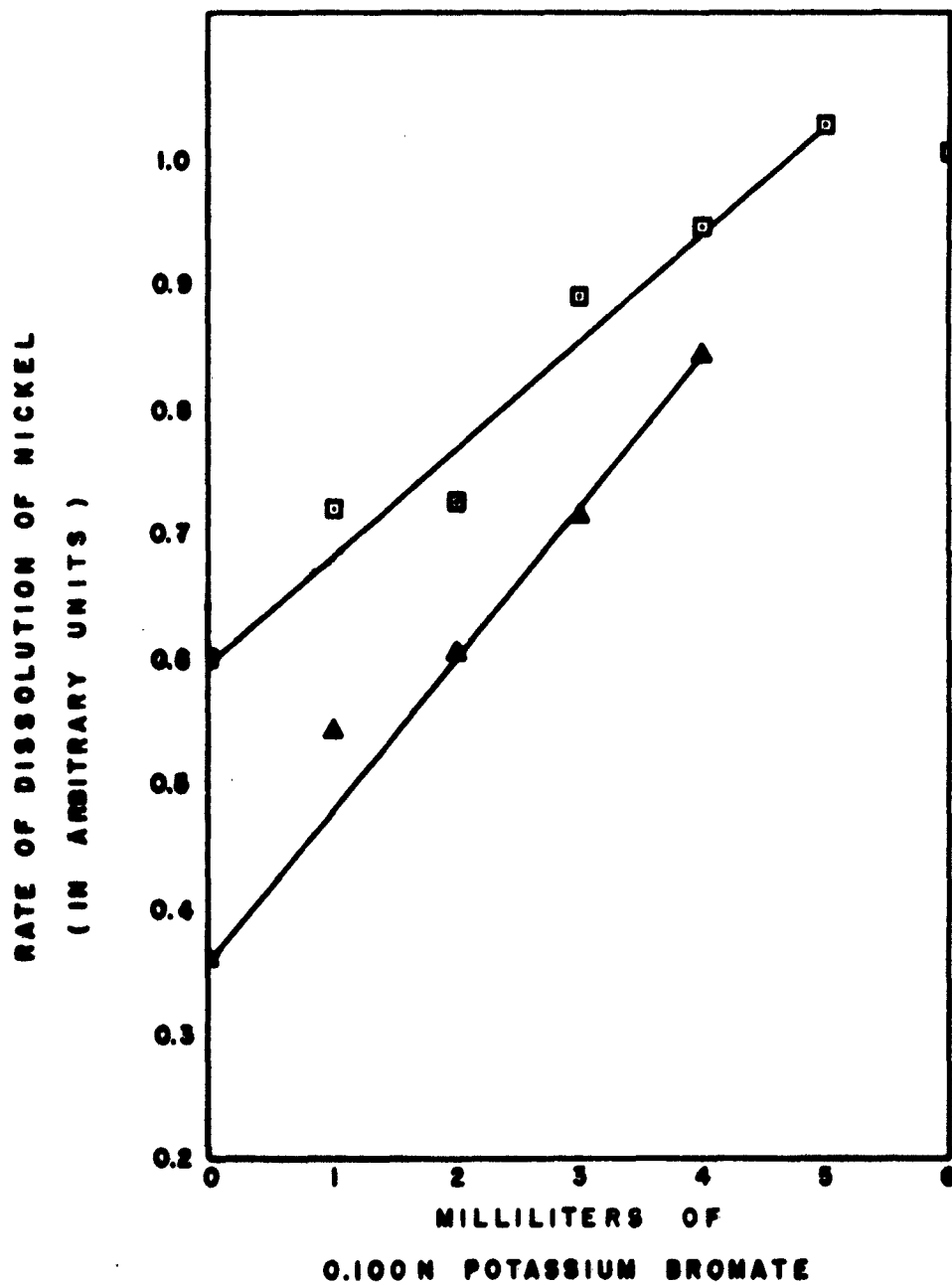
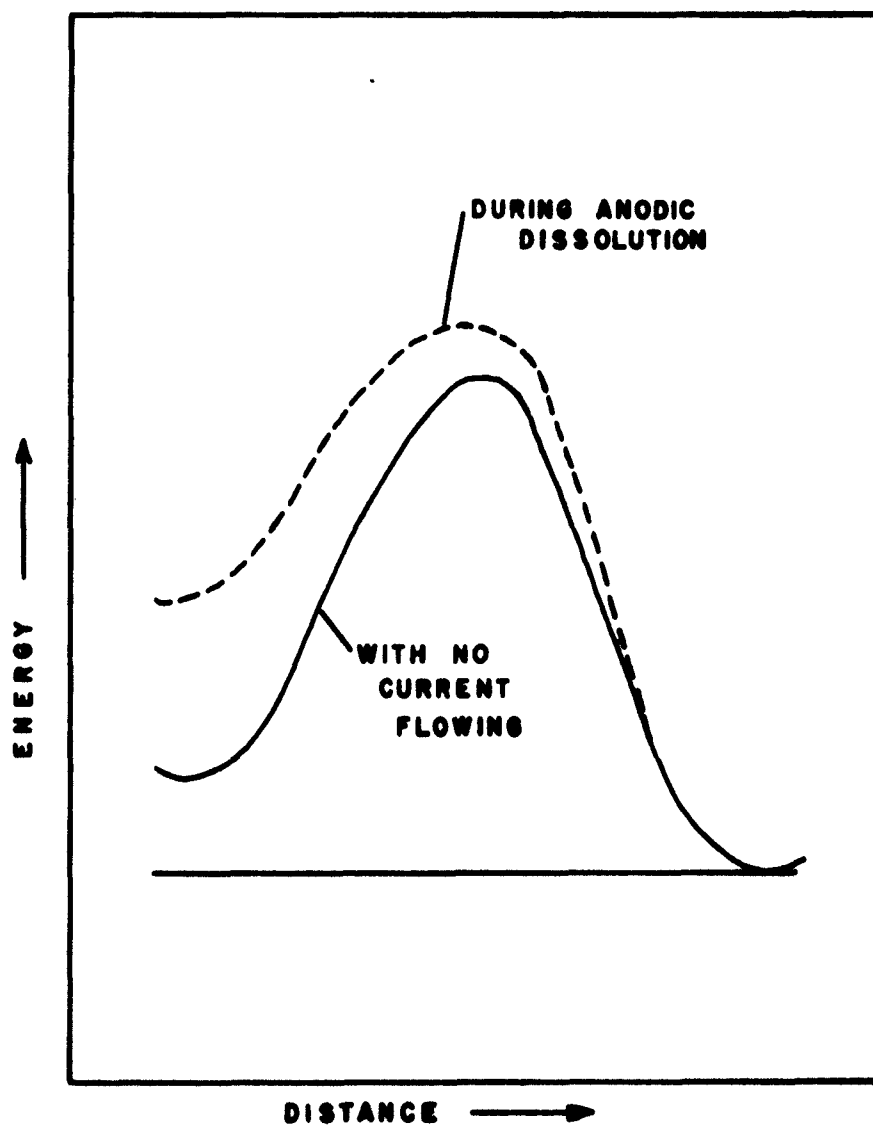


FIGURE 16. RATE OF NICKEL DISSOLUTION WITH POTASSIUM BROMATE ADDITIVE.



**FIGURE 17. ENERGY-DISTANCE RELATIONSHIPS
AT THE METAL-SOLUTION INTERFACE**

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