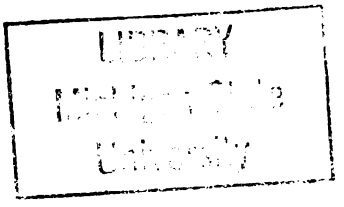

THE ELECTROLYTIC DEPOSITION OF CADMIUM.

THE ELECTROLYTIC DEPOSITION OF CADMIUM.

A THESIS

SUBMITTED TO THE FACULTY OF

MICHIGAN STATE COLLEGE

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

MASTER OF SCIENCE

BY

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1925.

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INTRODUCTION.

The electrolytic deposition of cadmium is by no means a recent discovery. Smee appears to have been one of the first, if not the first, to deposit cadmium electrolytically. Since the publication of his results, the matter has received very little attention.

About this time, Woolrich and Russell were granted a patent in England in 1849, or nine years after the discovery of silver plating. Their solution was made by dissolving cadmium in HNO_3, precipitating $Cd\ CO_3$, with Na_2CO_3, washing with water, and redissolving in KCN.

Within the last few years, there has been a marked activity in the electrolytic deposition of cadmium. The reason for this is quite apparent when one considers that in cadmium, there is, to a very high degree, the protective value of zinc and the pleasing appearance of nickel.

It might be well at this time to review a few of the properties of this metal. Cadmium is always found in nature associated with zinc. In the extraction of the zinc, the cadmium distills first, since its boiling point (778°C) is considerably less than that of zinc (930°C). The distillate is collected, mixed with coke or charcoal, and distilled at about 800°C. In this way a metal of over 99.5% purity is obtained. The chief source of cadmium is America. It is estimated that production could be brought up to 500 tons or more a year if necessary to supply the

market.

Cadmium has a silver white color with a bluish tinge and a bright luster, which dulls somewhat on exposure to air. The cast metal is crystalline which when etched reveals polygonal crystals. It has a specific gravity of 8.65 at 20°C. Cadmium has a Brinnell hardness of 29.0. It can be easily cut with a knife and is very flexible, ductile, and malleable.

Cadmium is strongly electro-positive as shown by the following table of electrode potentials at 25°C.

Zinc ----------	+.758
Cadmium -------	+.398
Iron ----------	+.441
Nickel --------	+.220
Hydrogen ------	.000

The relative position of iron and cadmium are in question. Altho, according to the electromotive force, cadmium should be below iron in the series, its chemical and electrochemical behavior and its position in the periodic system would lead one to correctly place it above iron. Unless cadmium is above iron, it can hardly be expected to protect iron against corrossion. That it does protect iron has been shown by Blassett, (1).

However, since it lies so close to iron it cannot be expected to give as much intrinsic protection as zinc, and consequently will not protect as large areas as will zinc. It follows that a deposit of cadmium must be nearly impervious in order to furnish continued protection.

However, cadmium will not corrode as rapidly as zinc, will preserve a better appearance, and will protect the iron longer than will a similar plate of zinc, provided the iron is not exposed because of porosity or abrasion.

As the potential of cadmium is much closer to nickel than is zinc, it is more advisable to plate nickel over cadmium than zinc, since there would be less tendency to deposit nickel by immersion and if the cadmium is subsequently exposed, there would be less tendency for it to corrode and cause peeling of the nickel. By plating successively with cadmium and nickel it may be possible to materially increase the protective value of the nickel without sacrificing its desirable properties.

Whether the theoretical advantages of cadmium as compared with zinc can be realized commercially, and whether they will justify the added cost of the cadmium, can only be determined after more experience.

REVIEW OF LITERATURE.

A review of the literature showed that altho there has been some investigation, the majority of this has been of an analytical nature only. In any investigation in electroanalysis, the problem is to remove all of the desired metal quantitatively, and in an adherent form. No reference to this kind of work will be made as it was deemed of little value in relation to electroplating. Mathers and Marble (2), give a complete abstract of the electrolytic deposition of cadmium. Mathers and Marble investigated cadmium deposition using a very low current density (0.4 amperes per square decimeter), and allowing the deposition to continue over a long period of time. Their work, consequently, was in reality one of the refining of cadmium rather than that of plating. They used a great number of different solutions among which were the sulphate, chloride, nitrate, acetate, ammoniacal, cyanide, bromide, iodide, fluosilicate, fluoborate, fluoride, and the perchlorate. In the case of the sulphate bath, they obtained only crystalline deposits after a few different addition agents had been used and so abandoned it as hopeless.

As far as could be determined the only bath in use at the present time for depositing cadmium is the cyanide solution.

The Udylite Process Company (3), covers the electrolysis of iron, steel, and other metals in a neutral or basic solution of cadmium cyanide with anodes of graphite, carbon, or other insoluable and non-polarizing materials.

The articles are then washed in water and baked for some hours at a temperature of 150°C to 200°C, or up to 250°C, if the plates are imbedded in $Ca(OH)_2$. The electrolyte may contain from 1.25 to 15% cadmium and 1 - 25% Na CN. The cadmium is precipitated as $Cd(OH)_2$ and redissolved in NaCN or KCN. A slight excess of cyanide is allowable. Cadmium is added to the solution in the form of $Cd(OH)_2$. With an electrolyte containing 10.5% cadmium, a current density of 25 - 100 amperes per square foot may be used.

Wm. A. Wissler and C. H. Humphreys (4), control a patent for practically the same process.

The Udylite Process Company, of Kokomo, Indiana, have developed a commercial method for depositing cadmium and are prepared to grant licenses for its industrial use.

The writer was of the opinion that cadmium could be deposited from a slightly acid solution of cadmium sulphate by means of suitable addition agents.

Blum and Hagaboom in their recent book, "Principles of Electroplating and Electroforming", say "It is possible to deposit cadmium from slightly acid chloride or sulphate solutions, but the deposits are coursely crystalline and entirely unsuited for electroplating unless some suitable addition agents are present.

This investigation was undertaken to determine the effect of various addition agents on the electrolytic deposition of cadmium from a sulphate solution.

THE PRINCIPLES OF ELECTRODEPOSITION.

It might be well to review some of the theoretical considerations in regard to the character of deposits as influenced by various factors. In electroplating as in other lines of work, there are a good many factors entering whose effects are not known.

There is no single case where one factor governing electrodeposition can be changed without changing quite a number of other factors. For instance, if we have a solution of a metallic salt in water and we add some acid, we now have changed the acidity, both actual and total, the conductivity, and the metal ion concentration slightly, as well as other factors. It can be readily seen that the problem of addition agents is a very complex one, and a consideration of principles, in so far as they are known, is of the utmost importance. These principles have as yet not been proven to be absolutely true in all cases but they are merely advanced as an aid to the electrodeposition of metals.

If the process of electrodepositing metals depends upon the formation of crystals, it seems reasonable that the principles or ordinary crystal growth must apply in some degree to the formation of crystals by electrodeposition. A consideration of these principles led W. D. Bancroft (5), to state certain "axioms" regarding the structure of electrodeposited metals.

These "axioms" were stated by Dr. Bancroft in the following terms:

1. Bad deposits are due to excessive admixtures of come compounds or to excessively large crystals.

2. Excessive admixture of any compound can be eliminated by changing the conditions so that the compound cannot precipitate.

3. Increasing the current density, increasing the potential difference at the cathode, or lowering the temperature, decreases the size of the crystals.

4. The crystal size is decreased when there are present, at the cathode surface, substances which are absorbed by the deposited metal.

5. If a given solution will give a good deposit at any current density, provided the conditions at the cathode surface are kept constant.

6. Treeing is facilitated by a high potential drop thru the solution and by conditions favorable to the formation of large crystals.

No time will be taken for a discussion of these "axioms" but they will be referred to in the conclusion and discussion of the experimental work.

Wm. Blum, of the Bureau of Standards (6), discusses and gives experimental evidence of these axioms and also advances a theory of crystal formation.

Mathers and Marble in the discussion of their paper say, "that a good deposit is the result of the

additive properties of the acid ion and the additive substance. A stronger statement of the theory is that any metallic salt will give a good deposit for the proper addition agent is used." They attempt to prove this statement by the experimental work of their paper.

The above principles are just some of the theories concerning the character of electrolytic deposits and will be referred to later in this thesis.

METHOD OF PROCEDURE.

Solutions of various concentrations of Cd SO_4 were made and electrolytic deposits obtained from each of them at various conditions. Then to these solutions were added various salts at different concentrations and the results noted. Finally, the commonly called organic colliods and reducing agents were added and their effects noted.

After cleaning and washing, which method will be described in detail later, the specimen to be plated was placed in the solution under observation. The current was always on before any plate touched the solution; thereby preventing to a great degree any tendency to deposit by immersion. The voltage of the cell and amperage flowing thru the cell was regulated as desired by means of a rheostat. As a means of comparison a fixed time of 15 minutes was allowed for each plate. The current density was varied for different plates to observe that effect. Some plates were made to show the effect of agitating the solution with air or by stirring mechanically. The temperature was the same as room temperature and varied from 18° to 27° as maximum limits. After plating, the plates were rinsed in cold water and filed in a rack to dry. The crystal size and surface of the plates were compared by means of a microscope using a direct illumination from a 150 watt electric light. The magnification was set at

100 diameters. For the purpose of demonstration, photo micrographs of various plates were made but the method is included elsewhere in this thesis.

APPARATUS AND MATERIALS.

APPARATUS.

The apparatus used in this investigation consisted of a 250 cc beaker, two anodes of cadmium and a support for the cathode. All solutions used were made up to 250 cc volume.

CHEMICALS.

All chemicals used were of the purity commonly called "C.P." except in the case of some of the organic addition agents.

ANODES.

The anodes used were of cast cadmium in the form of rods and were of high purity.

CATHODE MATERIALS.

Two different kinds of sheet metal were used. One was what is known as blue steel because of the blue scale on the surface and the other was known as Russian Iron. The former was 24 gauge in thickness and the latter was 28 gauge. Very little difference was noticed in plating with these two kinds of metal. The metal was cut

into strips approximately 4 cm. wide by 15 cm. long. All plates were numbered for record.

SOURCE OF CURRENT.

The current was obtained from a 6 - 12 volt motor generator set thru a switchboard provided with an ammeter and voltmeter. The current was varied by means of a resistance in series with the bath.

PRETREATMENT OF CATHODE MATERIAL.

The pretreatment of the cathode material is of very great importance since all oil, grease, rust or any other kind of foreign matter must be thoroughly removed before attempting to electroplate, or a complete failure will be the inevitable result.

All specimens, before plating, were given the following preliminary treatment:- If specimen was covered with a heavy layer of oil, this was removed by $C Cl_4$ or $CH Cl_3$, then wiped with cloth. To remove the black scale, or in numerous cases to reuse plates previously plated with cadmium, the specimens were placed in a hot solution of the following composition: $Sn Cl_2$, 50 gm.; Tartaric Acid, 2 gm.; H_2O, 1000 cc. The specimens were allowed to remain in this solution until thoroughly cleaned, rinsed in cold water, and wiped dry with a cloth. This treatment was used to quite a number of plates at a time so that before they were finally used they became covered with rust again.

Just before plating the following procedure was used: The plates were first boiled in a strong alkaline solution to remove any remaining oil or grease, rinsed in hot water, and wiped dry. They were given a thorough cleaning with a fairly fine scratch brush on a motor driven buffing lathe to remove any rough spots and also any adhering loose material. The plates were immersed in a 10% solution of H_2SO_4, to remove the thin layer of rust

accumulated, rinsed in cold water, and given a 10 second dip in the following bright dip solution; HNO_3 conc.; 25% by volume; H_2SO_4 conc.; 50% by volume; and H20, 25% by volume. The plates were washed clean in water. The surface of the metal then had a very bright color and was clean.

The plates were next placed in a hot alkaline solution for about 5 minutes, washed in hot water, cold water, and were then ready for plating. The alkaline solution was of the following composition:

Na_2CO_3, 165 gms. per liter; NaOH, 15 gms. per liter.

METHODS FOR MAKING PHOTOMICROGRAPHS.

The apparatus used was a Bosch and Lomb Photo-Micrographic camera. The illumination was obtained from a high power electric lamp focused directly on the plate rather than the usual method of using an illuminator. It was found that by using the direct method of illumination a better picture was obtained. A magnification of twenty diameters was used. All exposures were for 15 seconds, and developed for about 8 minutes.

EXPERIMENTAL WORK.

In order that the experimental work of this thesis might be presented in as clear a manner as possible, the work has been divided into several parts, each of which will be presented and discussed separately. The photo-micrographs found elsewhere are of value in getting a clearer insight into some of the subject matter. Whenever possible, concentrations have been expressed in terms of normality. In some cases, however, it was deemed advisable to express the additions in terms of the quantity added for bath of 250 cc. In the case of liquids, these additions are expressed in terms of cc of addition agent for 250 cc of solution.

In presenting the effects of a bath on the deposit, it should be remembered that the comparison is always drawn from a bath which does not contain the addition agent under consideration.

EFFECT OF ADDITION OF NON-METALLIC SALTS WITHOUT FREE ACID.

The standard for comparison was a bath containing simply Cd SO_4 (1.0N). The deposit was coarsely crystalline. The color was fair; the cover poor; and the adhesion very poor. There was considerable treeing on the edges.

$(NH4)_2$ SO_4 (0.25N). The deposit was coarsely crystalline with larger crystals than those of the Cd SO_4 (1.0N). The color was improved some. The cover was poor, and adhesion was very poor. This bath was also tried

giving the sample a preliminary dip for about 5 seconds in the following arsenic dip; 60 gms. As_2O_3 per liter of concentrated HCl. The crystal size was decreased considerably. The color and cover were about the same as was the adhesion.

$(NH_4)_2$ SO_4 (0.50N). The crystal size was decreased somewhat. The color was darker; the cover and adhesion were poor. The amount of treeing was decreased considerable but there was still a tendency for the edges to get rough. There was also a decided tendency for the surface of the plate to become rough which was more pronounced if the time was increased to 30 minutes.

(NH_4) Cl (0.25N). The deposit was crystalline with a slight increase in the size of the crystals. The color was darker; the cover and adhesion were poor. There was an excessive treeing on the edges.

NH_4 Cl (0.50N). There was an increase in the crystal size. The color was darker than with (0.25N). The cover and adhesion were poor.

Na_2 SO_4 (0.25N). A crystalline deposit with practically no change in crystal size was obtained. The color was slightly darker; the cover was fair and the adhesion was improved. There was considerable treeing.

Na_2 SO_4 (0.50N). The crystal size was decreased slightly. The color was improved; the cover was fair and the adhesion was better but still poor. The treeing was only slight but the edges were rough.

Na Cl (0.25N). The crystal size was increased

slightly. The color was darker; the cover was poorer, and the adhesion was also poor. Considerable treeing was observed.

Na Cl (0.50N). The crystal size was decreased slightly. The cover was poor; the color was slightly darker, and adhesion was poor.

$K_2 SO_4$ (0.25N). The crystal size appeared about the same; the color darker; the cover and adhesion were poor. There was a decided tendency to sponge. There was some treeing and the edges were rough.

$K_2 SO_4$ (0.50N). The crystal size decreased. The color was slightly darker; the cover and adhesion were poor. There was still a tendency to sponge, but there was no treeing.

K Cl (0.25N). The crystal size did not appear to be changed; the color was slightly darker; the cover was poor and the adhesion was poor. Treeing was excessive.

K Cl (0.50N). The crystals appeared to increase in size with a rougher surface. The cover was poor; the color slightly darker, and the adhesion was poor. A slight treeing was observed.

SUMMARY.

Practically all of the above addition agents gave treeing to a more or less degree. The crystal size was not changed to any great extent. The cover and adhesion were poor in all cases. It appeared that the SO_4-ion is better

than the Cl-ion as an addition agent. $Na_2 SO_4$ +$(NH_4)_2 SO_4$ are the best addition agents of this class.

DISCUSSION.

In the first case without addition agents the deposit was crystalline with considerable treeing. Reasoning from Bancroft's sixth "Axiom" by increasing the conductivity we should decrease treeing. Altho the conductivity was increased by addition of the salts the tendency to tree was still quite pronounced. It is evident that treeing in this case must be greatly influenced by the second part of the sixth "axiom". We might further increase the concentration of the salts but this was thought inadvisable. However, we can increase the concentration of the $Cd SO_4$. This will be discussed later.

EFFECT OF $H_2 SO_4$ AND NON-METALLIC SALTS.

With no non-metallic salt, as the acid was added gassing started at the cathode and increased with increased concentration of the acid. The tendency to tree, however, decreased with increased concentration. The crystal size appeared to decrease also. Sponginess was noticable on some of the plates. The color does not seem to stay constant as some plates are darker than others. The cover was about the same for all concentrations but only fair.

The adhesion was fair, improving slightly with concentration. The maximum acid concentration appeared to be about 8 cc. conc. $H_2 SO_4$ per 250 cc. solution as cadmium seems to redissolve as fast as it is plated out.

$(NH_4)_2 SO_4$ (0.25N). On increasing the concentration of acid, the crystal size appeared to decrease, but sponginess appeared. The adhesion improved with the concentration. The cover was fair. The color was about the same thruout. The treeing decreased with increased concentration of the acid. Cathode gassing increased with increase of acidity.

$(NH_4)_2 SO_4$ (0.50N). On increasing the concentration of the acid the crystal size appeared to decrease. The tendency to sponge was observed at concentrations over .2 cc. The tendency to tree decreased at the higher concentration until the edges were just rough. Adhesion improved with increase concentration of acid as did the color. Cathode gassing increased with increased concentration of acid.

$NH_4 Cl$ (0.25N). On increasing the concentration of acid, the crystal size decreased. In all cases the color was considerably darker than with the $Cd SO_4$ alone or with $(NH_4)_2 SO_4$. The adhesion was fair, improving with the concentration of acid. The cover was poor, and the treeing decfeased with increased concentration of acid. Rough edges were observed on all plates. Cathode gassing increased with acid concentration. Sponginess appeared at the higher concentrations of acid. The best condition appeared to be at an acid concentration of 1cc.

NH_4 Cl (0.50N). On increasing the acidity about the same results as above were noted. Increasing the concentration of NH_4 Cl appeared to have very little effect.

Na_2 SO_4 (0.25N). On increasing the acid concentration, the crystal size decreased. The color appeared to be slightly darker. Adhesion was fair, and treeing decreased with increasing concentration of acid. The edges were not very rough. The cover was poor without acid, but improved with concentration of acid. Maximum concentration of acid was less than 1 cc as deposit could be seen only on one side.

Na_2 SO_4 (0.50N). About the same effects as noted above were observed except that the maximum concentration was 2.00 cc. Increasing the concentration of Na_2 SO_4 from (0.25 to 0.50N), decreased crystal size and as well as treeing.

Na Cl (0.25N). Increased concentration of acid decreased the crystal size. The color was darker and the cover was fair. Considerable treeing was observed without acid but this decreased with increased concentration of acid. The adhesion was poor but improved with acid concentration.

NaCl (0.50N). Increased concentration of acid produced about the same effect as noted above except that the deposit appeared somewhat denser.

With K_2 SO4 (0.25N). Increasing the concentration of acid decreased the crystal size and improved the cover and adhesion. The color was darker. A slight treeing was

observed, decreasing with increased concentration of acid. The edges were rough, and sponginess was observed on some of the plates.

$K_2 SO_4$ (0.50N). Increased concentration of acid produced about the same effects as were noted above. The maximum concentration of acid was about 0.5 cc.

KCl (0.25N). Increasing the acidity decreased the crystal size but improved the adhesion and cover. The color was dark. Considerable treeing was noted but this decreased with increase of the acidity.

KCl (0.50N). Increased concentration of acid produced about the same effects as were noted above. The best concentration noted was .04 cc. Except for color, this was the best deposit in the series. Above this concentration there was a tendency to sponginess and rough edges.

SUMMARY.

In all cases, as soon as $H_2 SO_4$ was added, cathode gassing started and increased with increase of the acidity. In nearly all cases the crystal size was increased with the addition of a salt. There appeared to be a definite acidity for this type of bath and was approximately 0.1 - 0.2 cc. The color with $(NH_4)_2 SO_4$ was the best and with $Na_2 SO_4$ second. KCl (0.50N) gave the finest crystals with .04 cc acid but the color was dark.

DISCUSSION.

The addition of acid decreased the hydrogen overvoltage at the cathode so that hydrogen was more easily released. Altho the addition of salts of this type deminished the tendency to tree, the crystal size did not appear to be affected to a very great degree. There was also a more pronounced tendency to produce a spongy deposit. The effect of the addition of the non-metallic compounds used appeared to be of a detrimental nature, either alone or with a slight acidity.

ADDITIONS OF METALLIC COMPOUNDS WITH ADDITIONS OF H_2SO_4 TO Cd SO_4 (1.0N).

$Al_2 (SO_4)_3$ (0.25N). Without the addition of acid or with not over 0.1 cc, H_2SO_4 was only slightly crystalline and of a fine texture. The adhesion was good and the color was very good with a high luster. Increasing the acidity the crystal size increased. Gassing started with an acid concentration above 0.1 cc. Treeing was observed but slightly without acid and gradually decreased with increased concentration of acid. The edges were slightly rough. With 5 cc of acid the deposit showed no marked attack by the acid.

Mg SO_4 (0.25N). The color was about the same as with $Al_2 (SO_4)_3$. The crystal size was slightly finer than

without Mg SO_4. The cover was not very good and there was a tendency for the surface to be rough with protruding crystals. There was a slight treeing and the adhesion was poor. On adding acid the crystal size decreased considerably for the first .04 cc. but then the decrease was slight. There was also an improvement in cover and a slight treeing. Increasing the concentration of acid above 1.0 cc, there was a tendency to produce sponginess and also an indication of excess acidity.

$Al_2 (SO_4)_3$ gave finer crystals than Mg SO_4 and better cover.

Mn SO_4 (0.1N). The crystal size was decreased and the cover was improved. The color was slightly lighter, and a good adhesion was noted, but there was considerable treeing. Increasing the concentration of acid decreased the crystal size slightly, as well as decreasing the tendency to treeing.

$Cr_2 (SO_4)_3$ (0.1N). The crystal size was fine and the cover was good giving a more even deposit. The color was lighter and the adhesion was poor until the acid concentration was 0.2 cc. Increasing the acidity decreased the crystal size but appeared to give a less even deposit.

Cr Cl_3 (0.1N). The deposit was very finely crystallined. The cover was good but the deposit was uneven or rough with considerable voids. The color was about the same as without Cr Cl_3 and the adhesion was good. Increasing the current density seemed to increase the

roughness of the surface. Increasing the concentration of acid appeared to increase the crystal size. The cover was good in all cases but the surface appeared to get rougher and more uneven with increased acidity, while sponginess was observed on some plates.

Increasing the concentration of Ce Cl_3 to(0.2N) tended to increase the crystal size slightly and gave a more uneven deposit.

Further increase of concentration to (0.4N) increased the crystal size more.

Fe SO_4 (0.1M). No change in the crystal size was observed. The color was considerably darker; the cover was poor; the surface was uneven, and the adhesion was poor. Increasing the acidity seemed to increase the crystal size but the adhesion was poor thruout and the surface was rough, with a fair cover. All deposits were somewhat spongy but this tendency increased with the acidity.

SUMMARY.

Arranging the addition agents in order of their increasing effect on the crystal size we get

Cr Cl_3 $Cr_2(SO_4)_3$ $Al_2(SO_4)_3$ Mg SO_4

Mn SO_4 Fe SO_4.

The cover was good with $Al_2(SO_4)_3$, fair with $Cr_2(SO_4)_3$, but poor in the rest. The color was excellent

with $Al_2(SO_4)_3$, not as good with the chromium salts, and darker with $FeSO_4$, $MgSO_4$, and $MnSO_4$. The surface with the $Al_2(SO_4)_3$ and chromium salts was slightly rough but the rest are very rough with a tendency of grouping crystals. In all cases of the addition of acid, cathode gassing was evident, and the crystal size decreased. The color and cover remained about the same as noted above. The surface showed a marked improvement with Aluminum, and both chromium salts while the rest were rather rough, but the crystals were less grouped or rather there were more crystals. $Al_2(SO_4)$ appeared to be of some value as an addition agent.

DISCUSSION.

In using $Al_2(SO_4)_3$ after the salt has dissolved the usual apoleseence was observed, due to hydrolysis, but this disappeared upon standing, probably due to an equilibrium being established. The aluminum sulphate seemed to possess that additive property which when used with $CdSO_4$ produced more nearly the condition required for a good deposit. $Al_2(SO_4)_3$ is the first addition agent that appears to have any marked tendency to give a good deposit.

EFFECT OF CONCENTRATION OF Cd SO_4 WITH H_2SO_4.

Increasing the concentration of Cd SO_4 from (1.0N) to (2.0N), the crystal size was about the same, but the cover was improved and a denser deposit was obtained. The color was about the same but the adhesion was improved. Increasing the acidity to 0.1 cc the crystal size decreased but above 0.1 cc sponginess appeared.

In the case of Cd SO_4 1.5N the crystal size was slightly smaller than with (1.0N). The cover was poor but the color and adhesion were fair. A slight treeing was observed, the edges were rough and there was a tendency to produce a spongy deposit.

DISCUSSION.

It is rather difficult to say at this time which concentration would be of the most value. The effect of addition agents seems to vary considerably with the concentrstion as will be shown later. However, a higher concentration of Cd SO_4 than (1.0N) is necessary in order to eliminate the tendency to give treeing.

MISCELLANEOUS ADDITIONS TO $CdSO_4$ 1.0N.

CHROMIC ACID (2 gms.)

With this bath the deposit became covered with a loose, black, spongy mass. This may have been due to excessive chromic acid so a bath was tried containing chromic acid (0.005 gms.). In this case the deposit was very rough and spongy and similar to the above.

BORIC ACID.

With 1 gm. Boric acid the crystal size decreased slightly but the cover was poor and the deposit contained some voids. The color was about the same as without the acid and the adhesion was fair.

Increasing the Boric acid content to 2 gms. the crystal size increased slightly but sponginess appeared. On adding H_2SO_4 to this bath the sponginess disappeared, and with 0.1 cc a fairly fine crystalline deposit was obtained with no sponginess.

Increasing the boric acid in the same bath to 3 gms. the crystal size was further decreased. The voids were smaller while the color remained the same. Increasing the H_2SO_4 to 0.2 cc decreased the crystal size but the deposit still contained considerable voids. With a further increase in acidity to 1.0 cc, the voids seemed to increase.

DISCUSSION.

Apparently the chromic acid produced the conditions noted in Bancroft's first "axiom". Chromic acid has a detrimental effect on the deposit.

Boric acid did not seem to be of any particular value in the simple bath with acidity. Boric acid is used in plating solutions as a buffer to control the actual acidity. It may prove to be of value later.

ADDITIONS OF NON-METALLIC SALTS TO BATH OF $CdSO_4$ 1.0N, AND $Al_2(SO_4)_3$ (0.25N).

$(NH_4)_2SO_4$ (0.25N). There was an increase in the crystal size due to the $(NH_4)_2SO_4$ but the deposit was very fine. The color was good but a little darker. The adhesion and cover were good but there was a slight treeing and some voids. Increasing the current density decreased the crystal size, improved the cover, but gave an excessive treeing.

Increasing the $(NH_4)_2SO_4$ concentration to (0.50N), there was no material change except that treeing was decreased.

Na_2SO_4 (0.25N and 0.50N) gave about the same results as for $(NH_4)_2SO_4$.

With NH_4Cl (0.50N) the crystal size seemed larger than with either of the above. The color was slightly

darker, the cover was fair but the adhesion was poor.

DISCUSSION.

As noted before, the addition of $(NH_4)_2\ SO_4$ or similar salts tend to increase crystal size but decrease treeing. Whether or not an adjustment of concentrations will be found so that this addition will be of any value remains to be seen.

MISCELLANEOUS ADDITIONS TO 2.0N Cd SO_4.

$Cr_2\ (SO_4)_3$ (0.05N). The crystal size decreased but there were voids in the surface. The color and adhesion were good. There was no treeing but the edges were rough. Adding 0.1 Gr H_2SO_4 decreased crystal size slightly with a less tendency to form voids. The cover and color were good. Increasing the current density increased the crystal size and more voids were observed.

Cr Cl_3 (0.1N). The crystal size decreased but the color was darker. Adhesion and cover were good but there were considerable voids and a slight treeing on the corners.

The addition of H_2SO_4 decreased the crystal size slightly with but little change in the surface to decrease voids. The tendency to sponge was quite pronounced. The addition of 2.0 gms. Boric acid had very little effect on the deposit.

$(NH_4)_2\ SO_4$ (0.50N). There was no appreciable change in the crystal size. The color was the same. The cover was good but the adhesion was poor. The surface was uneven but dense. The addition of H_2SO_4 decreased the crystal size somewhat. In all cases there was a decided tendency to sponge. Increasing the concentration of $(NH_4)_2\ SO_4$ to (1.0N) did not affect the above condition to a very great degree, except that the adhesion was improved. In all the deposits with $(NH_4)_2\ SO_4$ the bath had a tendency to produce sponginess.

$Al_2\ (SO_4)_3$ (.25N). The crystal size was fairly fine but there was a tendency to leave voids. The color and cover were good as was the adhesion. No treeing was observed but the edges were rough. Increasing the current density, decreased the crystal size and improved the cover so that a more uniform deposit was obtained. There was no tendency to sponge. Increasing the acidity tended to increase the crystal size but improved the cover. The adhesion was good.

$Al_2\ (SO_4)_3$ (1.0N). The deposit was finer in texture and the color was very good. The cover was better than with the lower concentration of aluminum. Cohesion was good but there was a slight treeing and the edges were rough. Increased current density decreased the crystal size to a very fine uniform deposit but the tendency to treeing was excessive. Increasing the acidity decreased the crystal size but the deposit was not as good as without the acid.

With an acidity above 2.0 cc sponginess appeared. The concentration of aluminum was probably excessive.

$Al_2 (SO_4)_3$ (0.25N) and $(NH_4)_2 SO_4$ (0.50N). The crystal size was increased slightly due to $(NH_4)_2 SO_4$. The color and cover were good but there were some voids on the surface. There was no treeing but the edges were slightly rough. Increased current density decreased the crystal size but sponginess was observed.

$Al_2 (SO_4)_3$ (0.25N), $(NH_4)_2 SO_4$ (1.0N). The crystal size was slightly larger. Otherwise, the effects were the same as noted above.

$Al_2 (SO_4)_3$ (0.50N), $(NH_4)_2SO_4$ (0.50N). The crystal size was slightly smaller than in the case of $Al_2 (SO_4)_3$ (0.25N) $(NH_4)_2 SO_4$ (0.50N). The other effects were about the same as noted above. No treeing was noted.

SUMMARY.

The most uniform deposit as well as having the best color was obrained by using only the $Al_2 (SO_4)_3$ as an addition agent. The addition of $(NH_4)_2 SO_4$ had the detrimental effect noted previously.

It appears that with Cd SO_4 2.0N the best assition is $Al_2 (SO_4)_3$ (0.50N).

VARIOUS ADDITIONS TO $CdSO_4$ (1.5N).

$(NH_4)_2 SO_4$ (0.50N). The crystal size increased slightly. The color and cover were poor but the adhesion was improved. There was no tendency to tree except with the higher current densities.

$Al_2 (SO_4)_3$ (0.25N). The crystal size was fine. The cover was good and the color very good with a high luster. The adhesion was good. There was no noticable treeing except with the higher current densities but the edges were slightly rough. Increasing the current density decreased the size of the crystals and also decreased the formation of voids and gave a more even deposit.

$Al_2 (SO_4)_3$ (0.50N). The deposit appeared denser but the surface was rougher in that more voids were observed.

$Al_2 (SO_4)_3$ (0.25N), $(NH_4)_2 SO_4$ (0.50N). The crystal size was increased. The cover and color were not as good and there was a slight tendency to give a spongy deposit.

$Al_2 (SO_4)_3$ (0.25N), $Cr Cl_3$ (0.1N). The crystal size was decreased and a denser deposit was obtained. The color was slightly darker. The cover was fair but the adhesion was poor. Agitation with air decreased treeing.

$Al_2 (SO_4)_3$ (0.25N), $Fe Cl_3$ (5 gms.). The crystal size increased considerable and the color was darker. The adhesion was poor but the cover was fair. There was no treeing but rough edges were observed.

$Al_2(SO_4)_3$ (0.25N), Na $C_2H_3O_2$ 3 gm. The crystal size was fairly large with a tendency to exist as individual crystals. The color was darker and the cover was poor while the adhesion was fair.

SUMMARY.

The best deposit observed up to the present time was obtained from a bath containing Cd SO_4 (1.5N), and $Al_2(SO_4)_3$ (0.25N).

EFFECT OF VARIOUS ACIDS.

The bath used for this observation was as follows: Cd SO_4 (1.5N), $(NH_4)_2SO_4$ (0.50N), $Al_2(SO_4)_3$ (0.25N). The acids were added in very small quantities and the effects noted in each case.

H_2SO_4. The crystal size was increased but was more uniform and there were less voids.

$HC_2H_3O_2$. The crystal size increased considerable with increased concentration of acid. The cover was good but the color was darker. There was a tendency to produce sponginess.

$HClO_4$. The crystal size increased considerably with increased concentration of acid. There was a decided tendency to produce sponginess.

H_3PO_4. Crystal size was increased considerably with increased concentration of acid. The adhesion was poor,

a decided tendency to produce sponginess.was observed.

H_3PO_4. Crystal size was increased considerably with increased concentration of acid. The adhesion was poor and there was a decided tendency to produce sponginess.

$H_2C_2O_4$ (1 gm.). The crystal size was increased slightly. The cover was fair but there were considerable voids. There was no treeing but the adhesion was poor while the color was darker.

Citric Acid (1 gm.). The effects noted were the same as under $H_2C_2O_4$.

SUMMARY.

In all cases the addition of the acids had a very detrimental effect on the deposit. It would appear that the electrolytic deposition should be carried out in a neutral or very slightly acid solution.

EFFECT OF ORGANIC ADDITION AGENTS.

The bath used consisted of Cd SO_4 (1.5N), and $Al_2(SO_4)_3$ 0.25N to which was added the following organic compounds.

H CHO (0.1 cc). There was a decrease in the crystal size but the color was slightly darker. The adhesion

and cover were fair. There was no treeing but the edges were rough and there was a decided tendency to form a streaked deposit. Increasing the concentration of HCHO to 0.5 cc increased the size of the crystals but did not appear to effect the other factors.

CH_3 CHO (0.1 cc). The deposit was rather coarsely crystalline. The color was darker and the adhesion poor. Agitation decreased treeing as well as the crystal size, but sponginess was more noticable.

CH_3 CHO (0.5cc). The deposit was coarsely crystalline even with agitation. The color was lighter than the above. Adhesion and cover were poor.

C_2H_5 OH (1.00 cc). There was a decrease in crystal size but no other change was noticed. Increasing the concentration of C_2H_5 OH to 5 cc increased the crystal size but this was decreased by adding H_2SO_4 0.5 cc. There was a noticable tendency to striate the deposit. Further additions of acid had little effect expect to increase cathode gassing.

Clove Oil (2 drops). The crystal size was decreased considerably so that a very fine deposit was obtained, except for some voids. The color was excellent. The cover was good but the adhesion was fair. There was no treeing but the edges were rough.

Clove Oil in alcohol ($\frac{1}{2}$ drop oil to 1.0 cc alcohol).(1 cc There was no change observed. (2 cc). The crystal size decreased very slightly. There was a noticable tendency to

give a striated deposit.

On adding H_2SO_4 0.5 cc, the crystal size decreased slightly and there was no tendency to form a striated deposit.

Gelatin (0.1 gm.). A very fine deposit was obtained. The cover and adhesion were good. The color was about the same as that obtained from a cyanide bath. At low current densities there was no treeing and the edges were only slightly rough which was eliminated by agitation. At higher current densities the edges were rougher but the deposit was better.

Gelatin (0.02 gm.). The deposit was slightly rougher and the color and adhesion were not as good as above.

Cd SO_4 (1.5N) $Al_2(SO_4)_3$ (0.50N). The crystal size was fine and decreased with increased current density, but the edges became correspondingly rougher. The color was darker but the adhesion and cover were good. The deposit was finer but darker than with 0.02 gm. Gelatin was rougher than with 0.1 gm.

Cd SO_4 (2.0N), $Al_2(SO_4)_3$ (0.50N), Gelatin 0.05 gm. The deposit was about the same as noted just above.

Dextrose (0.02 gm.). This addition had very little effect, except to make the color slightly darker.

Dextrose (1.0 gm.). The crystal size was increased considerably even at relatively high current densities.

Peptone (0.1 gm.). The crystal size was very fine, but there were considerable voids. The color was darker

and the adhesion and cover were fair. There was no treeing but the edges were slightly rough.

Blood Fibrin (0.1 gm.). The deposit was very coarsely crystalline and about the same as the simple salt solution with no additions.

Egg Albumin (0.1 gm.). The crystal size was very fine but the plate was pitted. The color was very dark but the cover and adhesion were good. The edges were slightly rough and the plate had a slight tendency to striate.

Egg Albumin (0.02 gm.). The crystal size increased some, but the color was much lighter, but as yet slightly dark. The adhesion and cover were good. The deposit was rough and had a pronounced tendency to striate.

Licorice Root (0.2 gm.). The root was cut into fine shreads and allowed to soak in the solution over night. The crystal size was very fine. The color was excellent. The cover was good and the adhesion was very good.

Gum Tragacanth (0.05 gm.) There was very little change in crystal size but the tendency to sponge was very pronounced. The cover was fair but the adhesion was poor. The color was slightly darker.

Gum Arbic. The crystal size was fairly fine but there was a decided tendency to give sponginess. The cover and adhesion were poor. Adding $Na\ H_2\ PO_4$ (10. gms.) increased the crystal size very much. The cover and adhesion were poor. The color was darker.

Glue (0.05 gm.). The crystal size was very fine, but there was a decided tendency to give sponginess. The

cover and adhesion were poor and the color was darker.

Uric Acid (0.05 gm.). The crystal size was considerably increased. The cover was poor, the color darker; and the adhesion, fair.

B. Naphthol (0.05 gm.). As this solution was used it became slightly colored probably due to a reaction of the B. Naphthol. The deposit was very fine. The color, cover and adhesion were good. There was no treeing and the edges were smooth, except at the higher current densities. Excessive rough edges were elinimated by using mechanical agitation.

SUMMARY.

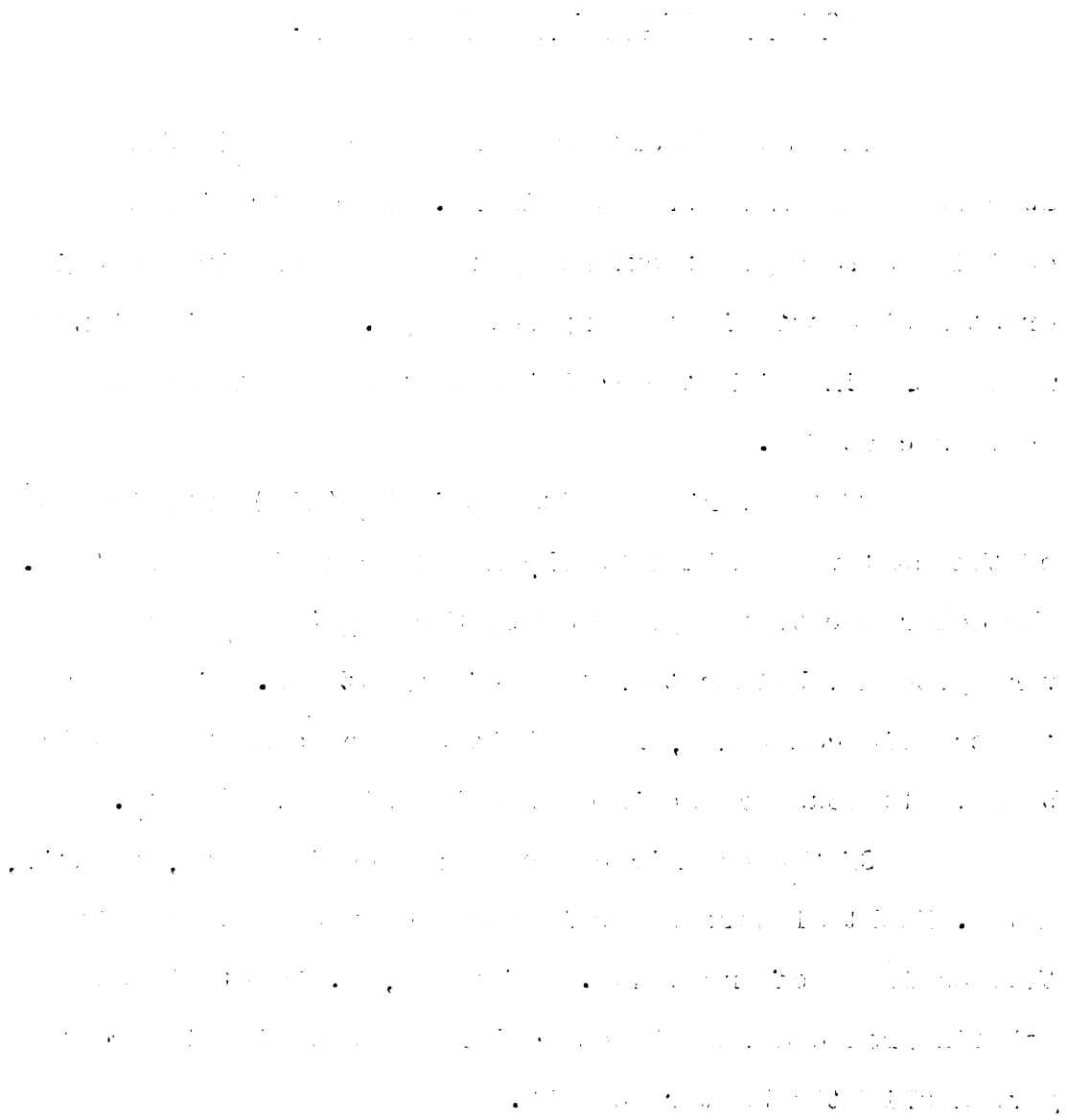
Reducing agents such as aldehydes did not produce a sufficiently good deposit. Of the addition agents used the most likely ones to be of any use were, gelatin, and B. Naphthol and Licorice Root. The other addition agents were more or less detrimental to the deposit. Agitation reduced or eliminated any tendency to form rough edges.

GENERAL SUMMARY AND DISCUSSION.

The use of salts of the type of $(NH_4)_2\ SO_4$ appeared to be more of a detriment. Altho treeing was deminished to a great extent by their use the increase in crystal size outweighted any advantage. No combinations were found in which the addition of these salts would prove successful.

Of the various salts used $Al_2\ (SO_4)_3$ was deemed of the most value altho $Ce\ Cl_3$ might be used to advantage. The color due to the presence of the $Al_2\ (SO_4)_3$ was very good and better than that of any others. Other than the organic compounds, no additions were found that would be advantageous to use in connection with $Al_2\ (SO_4)_3$.

Of the organic compounds; Licorice Root, gelatin, and B. Naphthal were the only ones to produce a deposit that could be of any value. Of these, B. Naphthol and gelatin produced the highest color but the licorice root gave a slightly better deposit.



RECOMMENDATIONS FOR A BATH.

The electrolytic deposition of cadmium can be accomplished to give satisfactory deposits. In any plating bath it is important that the solution be as simple as possible. In the case of cadmium, the bath should have the following composition: Cd SO_4 1.5N, $Al_2 (SO_4)_3$ 0.25N, with an organic addition agent. Of the organic addition agents any one of the following should be used: Gelatin 0.1 gm., licorice root 0.2 gm., or B. Naphthol 0.05 gm.

A cathode current density of 1.5 - 2.2 amperes per square decimeter should be used. The anode area should be from 1.5 - 2.0 times as great as the cathode area. The temperature should be approximately that of ordinary room temperature. The solution should be agitated mechanically for successful operation.

KEY TO PHOTOMICROGRAPHS.

FIGURE	BATH.
1	$CdSO_4$ 1.0N.
2	$CdSO_4$ 1.5N.
3	$CdSO_4$ 2.0N.
4	$CdSO_4$ 1.5N, $(NH_4)_2SO_4$ 0.50N.
5	$CdSO_4$ 1.5N, $Al_2(SO_4)_3$ 0.25N.
6	$CdSO_4$ 1.5N, $(NH_4)_2SO_4$ 0.50N, $Al_2(SO_4)_3$ 0.25N.
7	$CdSO_4$ 1.5N, $Al_2(SO_4)_3$ 0.25N, Gelatin 0.1 gm.
8	$CdSO_4$ 1.5N, $Al_2(SO_4)_3$ 0.25N, B. Naphthol 0.05 gm.
9	$CdSO_4$ 1.5N, $Al_2(SO_4)_3$ 0.25N, Licorice Root 0.2 gm.
10	$CdSO_4$ 1.5N, $Al_2(SO_4)_3$ 0.25N, Egg Albumin 0.1 gm.
11	$CdSO_4$ 1.5N, $Al_2(SO_4)_3$ 0.25N, Clove Oil 2 drops.

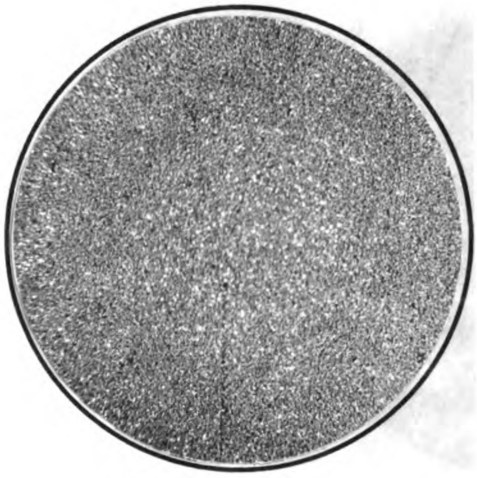


Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Figure 10.

Figure 11.

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