THE ELECTROLYTIC DEPOSITION OF COLLOIDAL BERYLLIA ON METAL SURFACES

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by
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INTRODUCTION

When a metal surface is treated cathodically in a properly prepared solution of a salt of beryllium or aluminum, an oxide or hydrated oxide film of the metal in solution will be deposited on the base metal surface. This coating is similar in properties to protective oxide films in general, with one important exception. The base metal plays little part in the resulting film. In other words, metals having oxides which are not protective or are in some other way objectionable, may be coated with this film. Since the film is transparent, the base metal retains its original appearance but has the protection afforded by the superimposed oxide layer.

Work on the protection of metals by electrolysis in solutions of beryllium sulphate was first reported by Thomas and Price (1) in 1939. The results of their work indicated that excellent protection could be secured from such films when cathodically deposited. They employed a simple bath consisting of beryllium sulphate and sufficient ammonium hydroxide to adjust the pH to

the required value. Upon duplicating their work, it was found very difficult to secure a coating which did not have a coloration which was due to the interference patterns of the film and also a blushing of the copper surface beneath. If the process was to have commercial value, these effects must obviously be removed.

This investigation was designed to improve the process and to make it commercially feasible. The theoretical concepts were developed to a certain extent also, since it was felt that they help to put the process on a more substantial basis. This led to the examination of the work done by Britton (2) on the change in hydrogen-ion concentration of beryllium sulphate solutions as a base is added (see figure 1), and also the work by Weiser (3) on hydrous beryllium oxide.

CONDITIONS OF INVESTIGATION

It was decided at the outset of the investigation to thoroughly standardize plating procedures, methods of measurement, apparatus, and other experimental conditions. This was done so that the results of varying one factor at a time could be observed.

1. Plates: The plates which were coated were exactly 0.10 square feet in total area. The dimensions were approximately 3-1/2 by 2-1/16 by 1/32 inches thick with a 1/4-inch diameter hole for wiring while cleaning and plating.

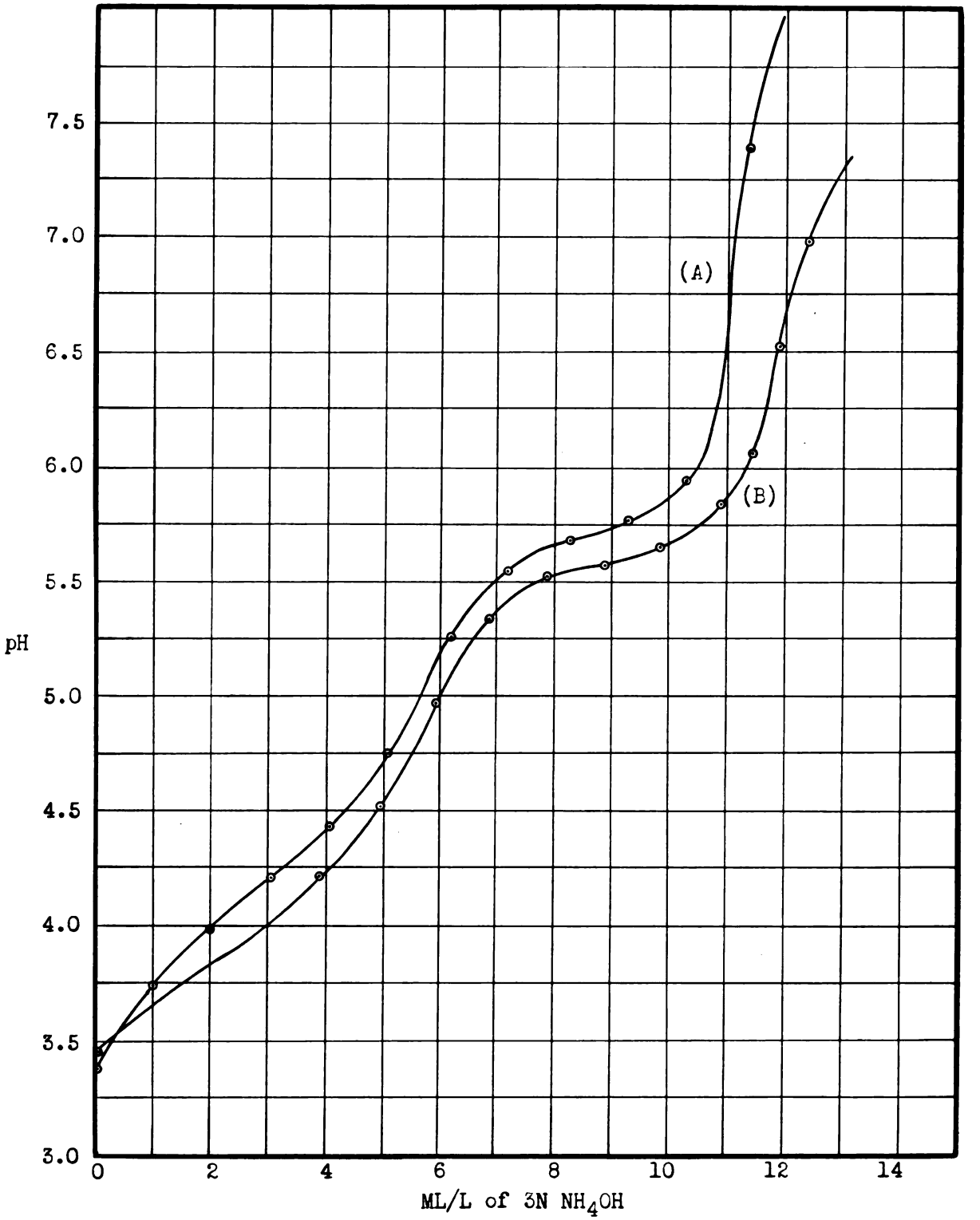

Fig. 1. Potentiometric titration of plating solutions. Solution(A) 3.4 g./l. of $BeSO_4 \cdot 4H_2O$. Solution (B) 3.4 g./l. of $BeSO_4 \cdot 4H_2O$, 5.0 g./l. of H_3BO_3.

Unless stated to the contrary, they were always of copper.

2. Buffing: All plates were rough buffed and then polished on a separate wheel with either lime or #00 rouge. This was done in order to bring out the slightest effect of interference colors.

3. Cleaning: After buffing, any excess compound was wiped off with a soft woolen cloth. The plate was then cathodically electro-cleaned for 2 minutes in a bath maintained between 60°C. and 70°C. The electro-cleaner bath was operated at 15 volts with steel anodes and 2 ounces per gallon of the Matawan #2 cleaner. (Manufactured by Hanson, van Winkle and Munning Co.)

4. Plating: The plates were then washed in distilled water and placed in the plating bath with the current on. This was necessary since the copper is attacked by beryllium sulphate solutions. The voltage and current varied with time and therefore had to be recorded at frequent intervals, as shown on the various curve sheets.

5. Drying: In the very beginning it was found that plates could not be dried in hot water after they were coated, since this action would affect the film. The procedure followed was to wash the plates in distilled water, then alcohol, and finally ether.

6. Heat Treatment: This was varied as the process was improved. Almost all the plates were treated for 2 minutes at 250°C. or 1 minute at 300°C. immediately after drying.

7. Testing: Both silver and copper plates were exposed to 2 minutes of the fumes from concentrated ammonium polysulphide. Hydrogen sulphide gas was also tried, but a consistent spread of results could not be secured. Copper plates were also exposed to high temperatures to test their resistance to oxidation in air. This was done in a furnace at 300°C. for 30 minutes. Only the very best films stood these tests 100 per cent and it was therefore possible to obtain a good quantitative spread of results as the various factors were investigated. The amount of tarnish was reported as the per cent of surface corroded.

8. Measurements: The pH was controlled by means of a saturated calomel half-cell which was made especially for this work. Ten ml. of solution were required to make a measurement, 5 of which were employed to wash the apparatus. The calomel half-cell was used in conjunction with the quinhydrone half-cell and standardized with 0.05 M potassium acid phthalate for a value of pH 3.98 at 25°C., plus or minus pH 0.01. A standard Weston milliammeter and a voltmeter were employed to measure milliamps and volts.

9. Apparatus: In figure 2 is shown a wiring diagram of the plating apparatus. Only one tank was in use at a time, but this arrangement facilitated the investigation of one variable while the other factors were held constant; i.e., temperature and other surrounding conditions were the same, as the pH, current density, or concentration were varied in the 4 tanks.

EXPERIMENTAL WORK

Anode Material: One of the first considerations was the determination of an anode material which would not interfere with the operation of the bath and also was commercially inexpensive. Thomas and Price (1) employed platinum which was no doubt entirely satisfactory from every standpoint except cost. Lead was the most obvious to start with, since the bath contained the sulphate ion. However, it was soon eliminated because it is so readily attacked by water. By electrolyzing lead in a 20 per cent sulphuric acid bath, an oxide film was prepared which rendered lead inert to water solutions of beryllium sulphate. Although many plates were prepared employing this type of anode, it was felt that a better material could be found.

An alloy of tin and lead was next investigated and excellent results were obtained. It was the commercially

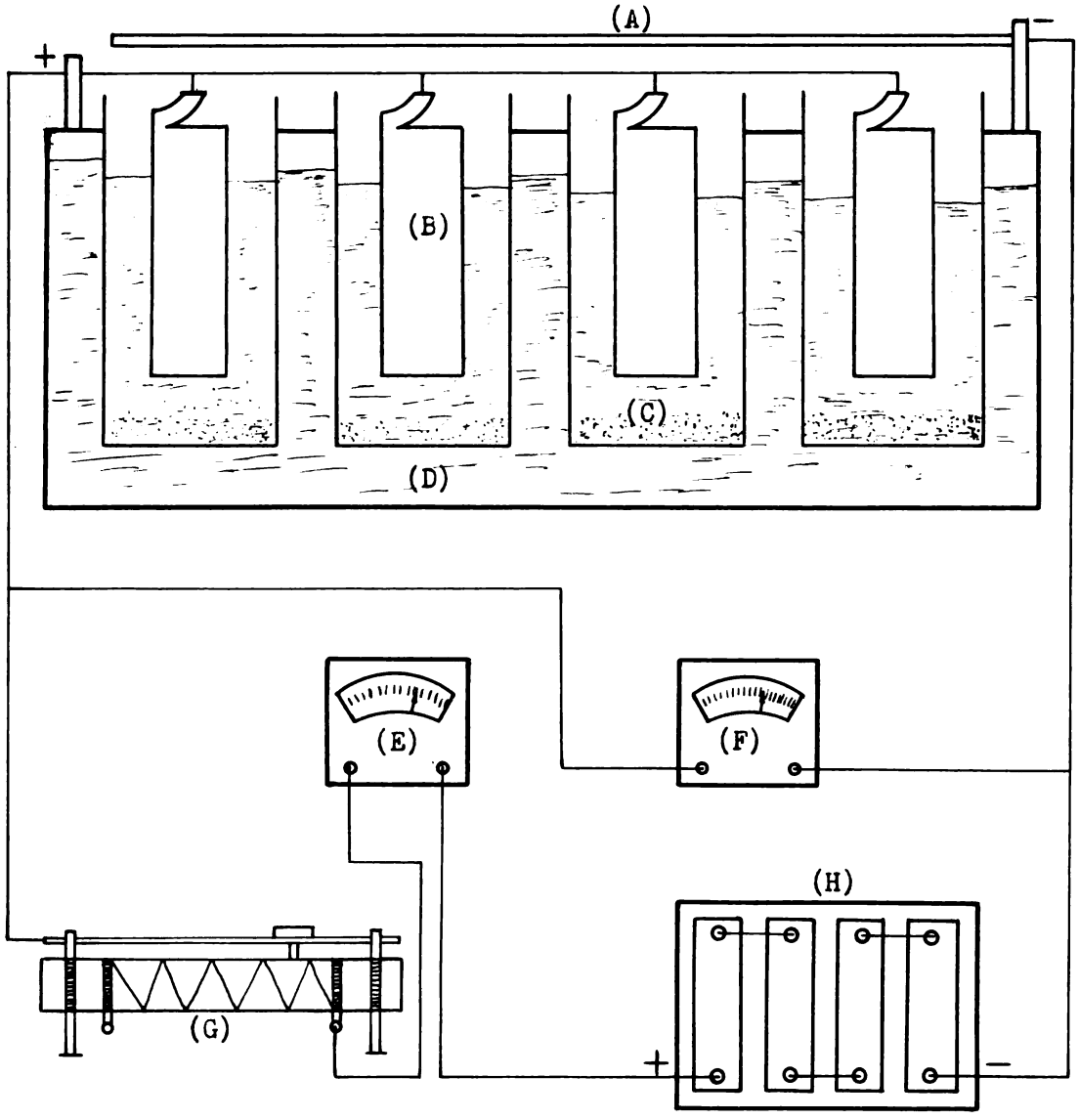

Fig. 2. Wiring Diagram

(A) Cathode bar
(B) Lead-tin alloy anodes
(C) Colloidal plating solutions
(D) Temperature control tank
(E) Milliammeter
(F) Voltmeter
(G) Slide-wire resistor
(H) Edison cell

available 7 per cent tin - 93 per cent lead alloy as generally employed in the chrome-plating industry. The anodes were allowed to stand in water for 24 hours and were then electro-cleaned before use. Solutions in which these anodes were used for over a month, did not show the presence of either element even when analyzed by spectrographic methods.

Duplication of Past Work: Next, it was desired to reproduce the results which were already reported on this type of coating. A concentrated solution of beryllium sulphate (10 per cent by wt. $BeSO_4.4H_2O$) was prepared by dissolving the crystalline salt in distilled water and then filtering several times. The solution was allowed to stand over night and then decanted, this being done in order to remove as much as possible, any suspended matter which might absorb a charge or be absorbed. It was noticed that there was an appreciable amount of the anhydrous beryllium sulphate which settled out. This would definitely interfere in the electrodeposition of a colloid. Spectrographic analysis of the concentrated solution showed that there was a small amount of aluminum present. This was not detrimental since it was shown that salts of aluminum (1) react much in the same way as salts of beryllium.

The stock solution, thus prepared, was then diluted to a concentration of 3.4 g./l. as suggested by Thomas

and Price (1) and ammonium hydroxide added until the pH was between 5.75 and 5.85. The precipitate which formed was given 1 hour to settle. Approximately 100 copper plates were electroplated in solutions as indicated above, the results proving that excellent protection could be secured, but that the appearance was not entirely satisfactory.

The entire range of pH from 3.4 to 7.0, as shown in figure 1, was investigated with results showing that only between a pH of 5.5 and 5.9 could there be a protective coating secured. This coating in all cases had some degree of coloration which was attributed to the thinness and unevenness of the film as described in detail later in this work.

As the ammonium hydroxide is added to the beryllium sulphate solution, in making up the bath, a gelatinous precipitate results which settles out in about 30 minutes. As shown later, colloidal particles of beryllium hydroxide remain in suspension. With this in mind, it was believed advantageous to investigate the effect of higher temperatures, hoping to increase the speed of travel of the colloid which is ordinarily relatively slow. Temperatures up to 55°C. were tried with but a slight improvement in appearance and a decrease in the protective powers of the film. After 2 one-hour periods at 55°C., the solution no longer contained a colloid. This was evidenced by a change

in pH from 5.75 to below 5.00 and also the fact that no protective film could be secured. It is probable that the colloid lost its absorptive powers and precipitated. Weiser (3) states that "Like most gelatinous oxides, the absorbability and solubility of hydrous beryllia decrease slowly on standing at room temperature and rapidly at higher temperatures, particularly if heated in a current of steam or in the presence of a solution of ammonia or of alkali hydroxide or carbonate."

Agitation of the solution at room temperature did not improve the appearance of the film, but slight movement of the plate itself did help remove any bubbles of gas or the larger particles which were carried over.

Original Research: It was decided that sufficient work had been done with the solution as established by Thomas and Price (1), and that if a suitable coating were to be obtained, it would be necessary to make some fundamental improvement in the process itself.

One of the difficulties encountered was the maintenance of the pH with any degree of accuracy over an operative period of several days. It was always necessary to add ammonium hydroxide and this addition was critical since it would require smaller and smaller quantities to arrive at the correct pH value. In the event this value was overstepped, the solution had to be discarded, since the colloid was destroyed. This impediment was the subject of the

first part of the investigation to effect a change in the process.

The most natural correction for the instability of the acidity of a solution would be the addition of a buffer. Several were tried, including ammonium acetate, ammonium formate, ammonium sulphate, and boric acid. The effect of the first two was not noticeable in concentrations below 5.0 g./l., and above that, it became increasingly more difficult to get any film deposited at all. In the case of the ammonium sulphate, results were the same except more pronounced, probably because of the common ion effect. Boric acid proved to be quite different. In concentrations as low as 1 g./l., an improvement in the appearance of the coating was apparent, but the buffer action was not very effective (see figure 1).

Addition of Boric Acid: In figure 3 are shown the results of the addition of varying amounts of boric acid. It will be noted that as the quantity is increased, there is a corresponding decrease in the total rise in potential for a given period of time. The plates from which these data were taken all showed better than 95 per cent protection against ammonium polysulphide. As the content of boric acid increased in the bath, there was a notable decrease in film coloration. At 5 g./l., plates could be obtained which showed no indication of interference bands. At 10 g./l., the potential rise was almost the same as at

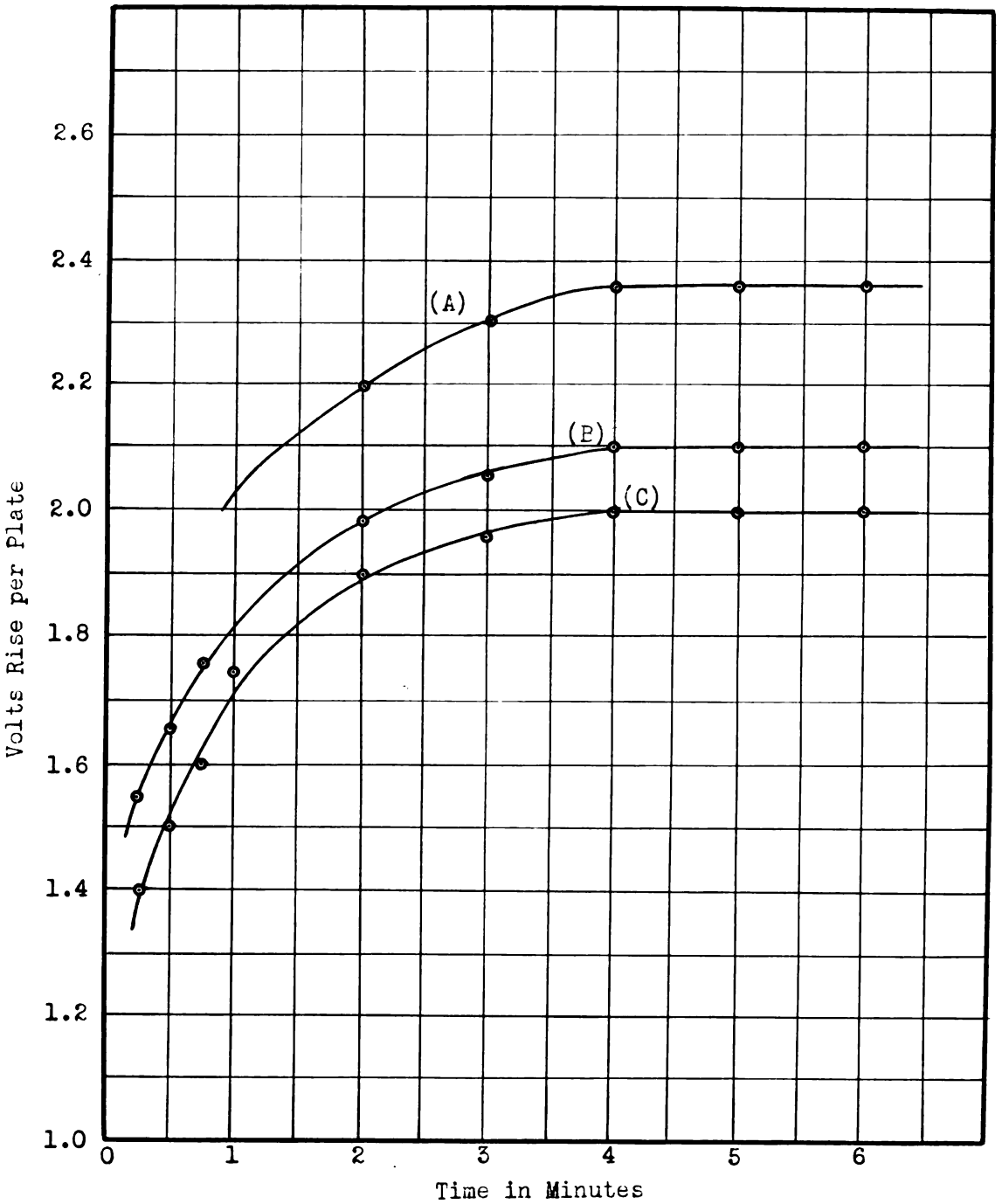

Fig. 3. Effect of boric acid on potential rise. Solutions of 3.4 g./l. $BeSO_4 \cdot 4H_2O$ at pH 5.63-5.76 and C.D. 100-140 ma./sq.ft. (A) 0.0 g./l. H_3BO_3. (B) 1.0 g./l. H_3BO_3. (C) 5.0 g./l. H_3BO_3

5 g./l., but the deposit was cloudy in appearance. This work was duplicated several times and 5.0 g./l. of boric acid was taken as optimum concentration. Later, it was shown that 3.0 g./l. could be employed with just as much effect if the solution was allowed to stand 48 hours before use. This allowed time for the larger particles to precipitate and collect on the bottom.

From figure 1, it is apparent that the buffer action of the acid consumes only a small quantity of the ammonium hydroxide added to obtain a pH of 5.70. The shape of the curve has not changed appreciably, so that quantity could have been taken up in just neutralizing the acid. The action of the boric acid was not that of a buffer.

An attempt was made to deposit boric acid itself, but without any success. It was not precipitated at all by the ammonium hydroxide. In figure 4, the change in pH with concentration of boric acid is shown. Figure 5 is the same for beryllium sulphate.

Another phenomenon which was observed as an action of the boric acid was the change in pH on standing. This is best shown in figure 6. The slight drop in the case of solutions not containing any boric acid is due to the decrease in the absorbing power of the colloidal beryllium hydroxide according to Weiser (3) as stated previously in this work. Solutions containing 5 g./l. of boric acid experience a steep drop in pH during the first 48 hours from

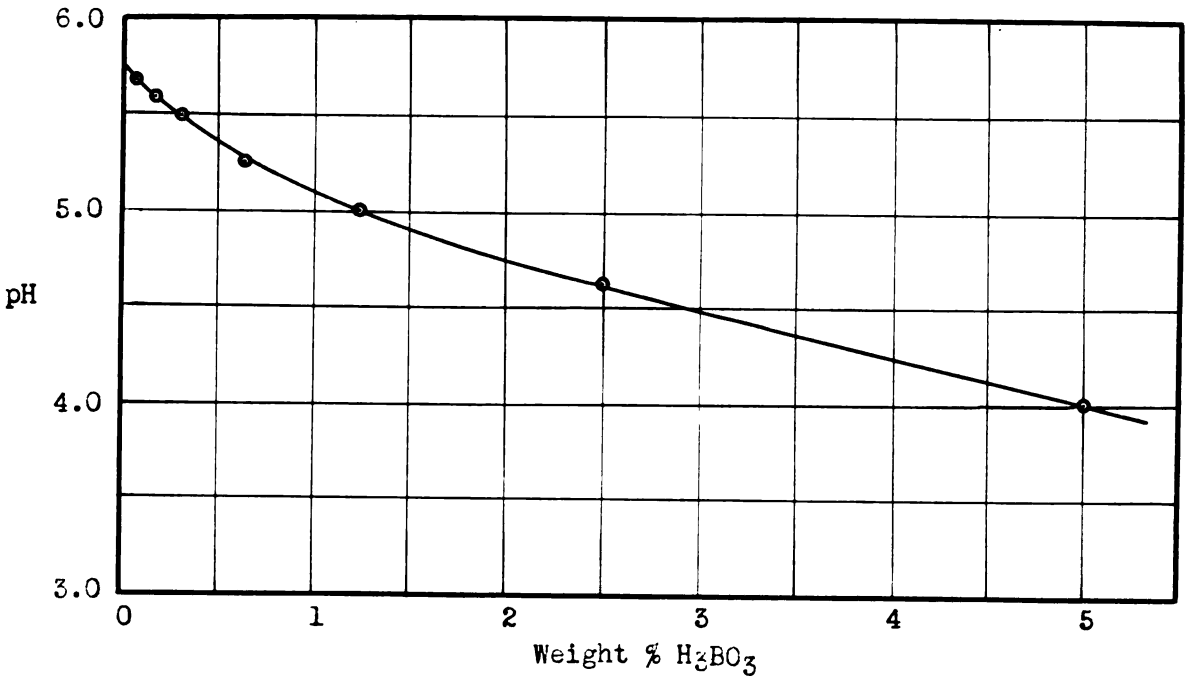

Fig. 4. Concentration of boric acid vs. pH.

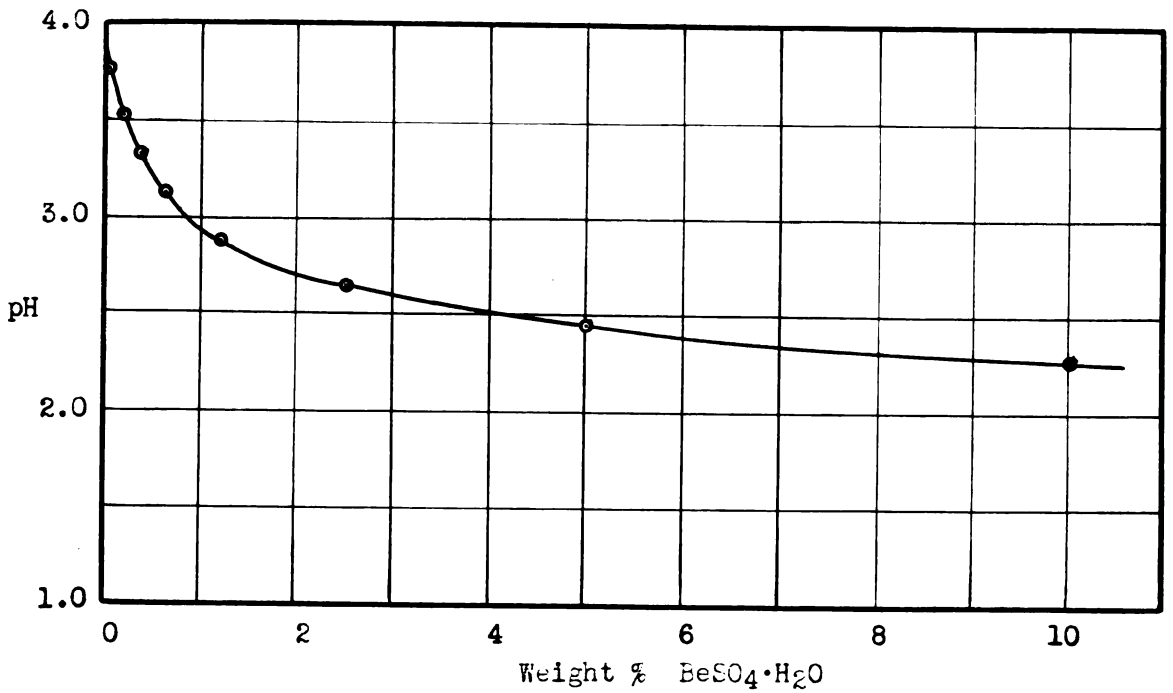

Fig. 5. Concentration of beryllium sulphate vs. pH

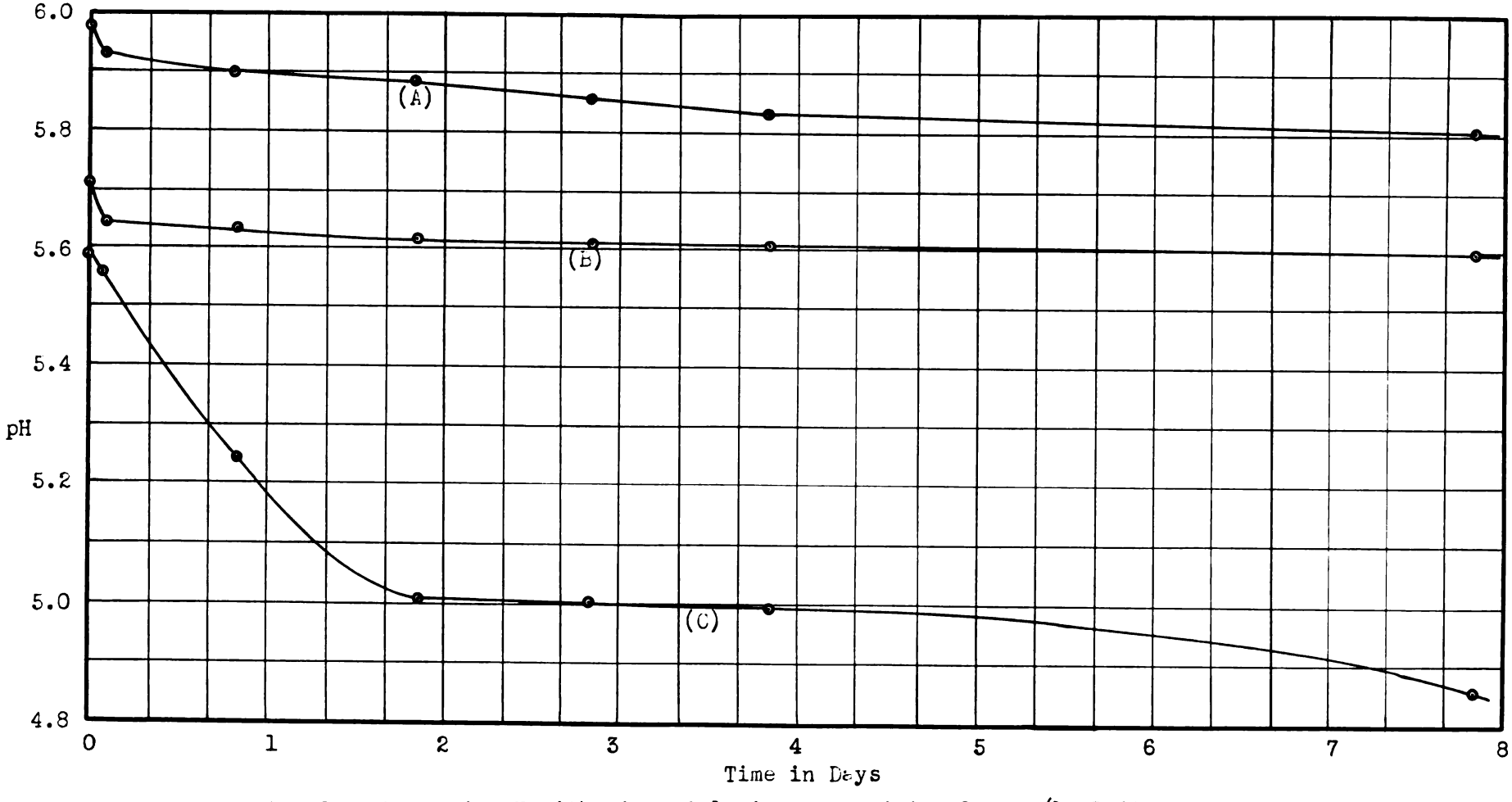

Fig. 6. Change in pH with time. Solutions containing 3.4 g./l. $BeSO_4 4H_2O$. (A) pH 5.98. (B) pH 5.72. (C) pH 5.61, 5.0 g./l. H_3BO_3.

an entirely different cause. It is believed that the boric acid causes the slow coagulation of the larger colloidal particles of beryllium hydroxide. That the boric acid is absorbed on the colloid was indicated by the presence of relatively large amounts of the compound in the precipitate which settled out.

After solution (C) from figure 6 had dropped to a pH of 4.9, a plate was coated at a current density of 80 ma./sq. ft. The appearance of the plate was excellent and its corrosion resistance 100 per cent according to previous standards mentioned. It was noticed at the time of plating that the potential rise was unusually high for this current density. Several solutions of similar concentration were prepared and plates coated as soon as they were prepared. The potential rise was recorded. Two days later the same procedure was followed on these solutions in order to observe the difference in potential rise. These data were correlated and appear in figure 7. In all cases, as was expected, the plates which gave the greater rise in potential for a given current density also gave higher corrosion resistance. This is in accordance with the work by Wagner (4) which infers that the higher the electrical resistance of an oxide film, the greater will be its tarnish resistance.

Conductivity Measurements: Next, the conductivity of the bath was investigated since it was desired to determine

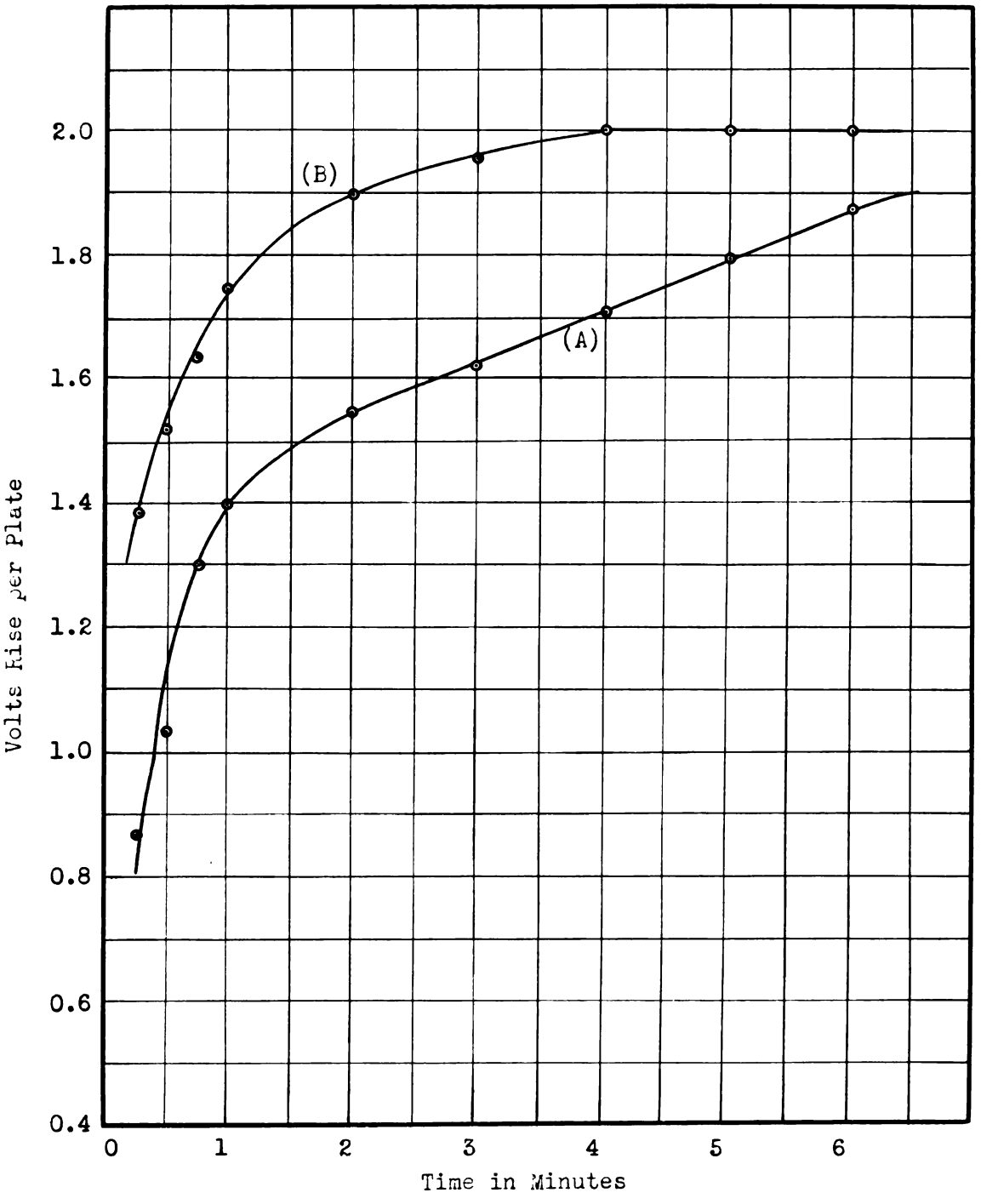

Fig. 7. Effect of ageing bath on potential rise. Solution containing 3.4 g./l. $BeSO_4 \cdot 4H_2O$, 5.0 g./l. H_2BO_2, pH 5.61, C.D. 100 ma. / sq.ft. Curve (A) at time bath was made up and curve (B) 48 hours later.

the effect of the boric acid. The amount of boric acid was varied in a solution containing 2.5 g./l. of beryllium sulphate. The results of the measurements are illustrated in figure 8. All conductivity determinations were made at 25°C. It readily can be seen that very little change takes place. The conductance of various strength beryllium sulphate solutions was also observed and a typical curve for salts of that type resulted as shown in figure 9.

The data reported in the previous paragraph served their purpose, but really were not very enlightening since actual operating conditions are at acidities between a pH of 5.0 and 6.0. In order to determine the conductivity over this range, it was measured as the ammonium hydroxide was added. The pH was determined simultaneously and the results plotted in figure 10.

The increase in conductivity which appeared in figure 8 can be seen to diminish as the pH rises, or in other words, the amount of ammonium hydroxide becomes greater. One other important point to be observed is that the conductivity does not change appreciably beyond a pH of 6.0 which shows it is not a function of pH. This is no doubt due to the fact that very little base was added to incur this change and that the base is actually carrying the greater part of the current. This explains why the current does not go to zero as the potential rises during plating. The colloid obviously could not be carrying 100 ma./sq. ft.

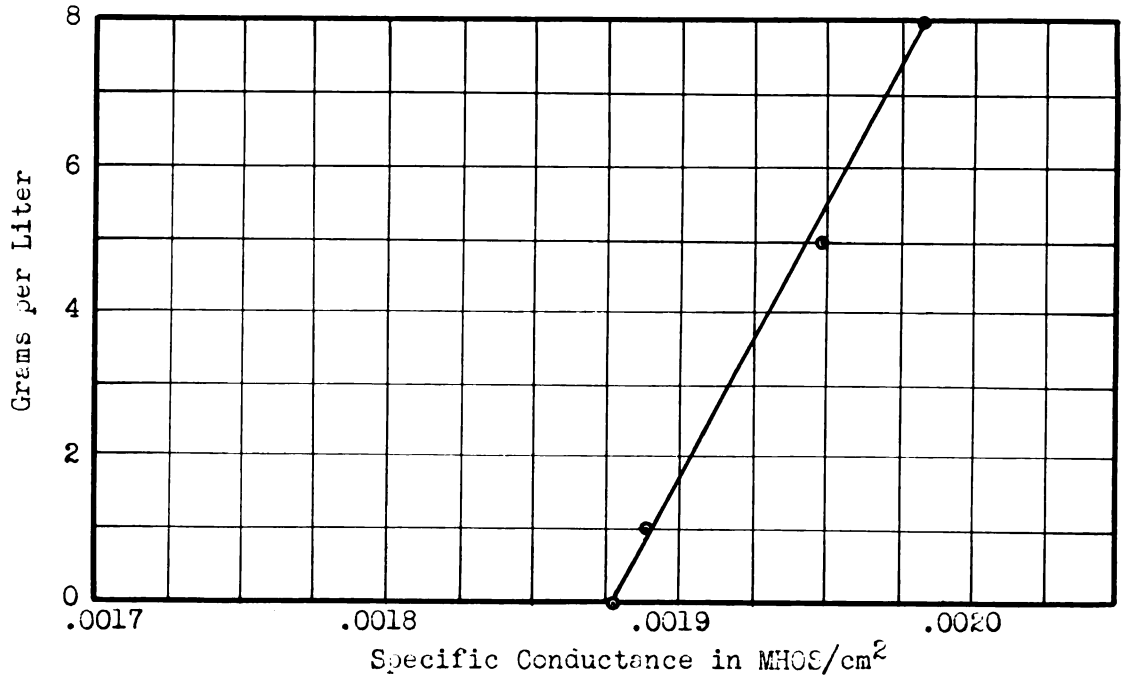

Fig. 8. Change in conductance with concentration for boric acid in 0.25% beryllium sulphate solution.

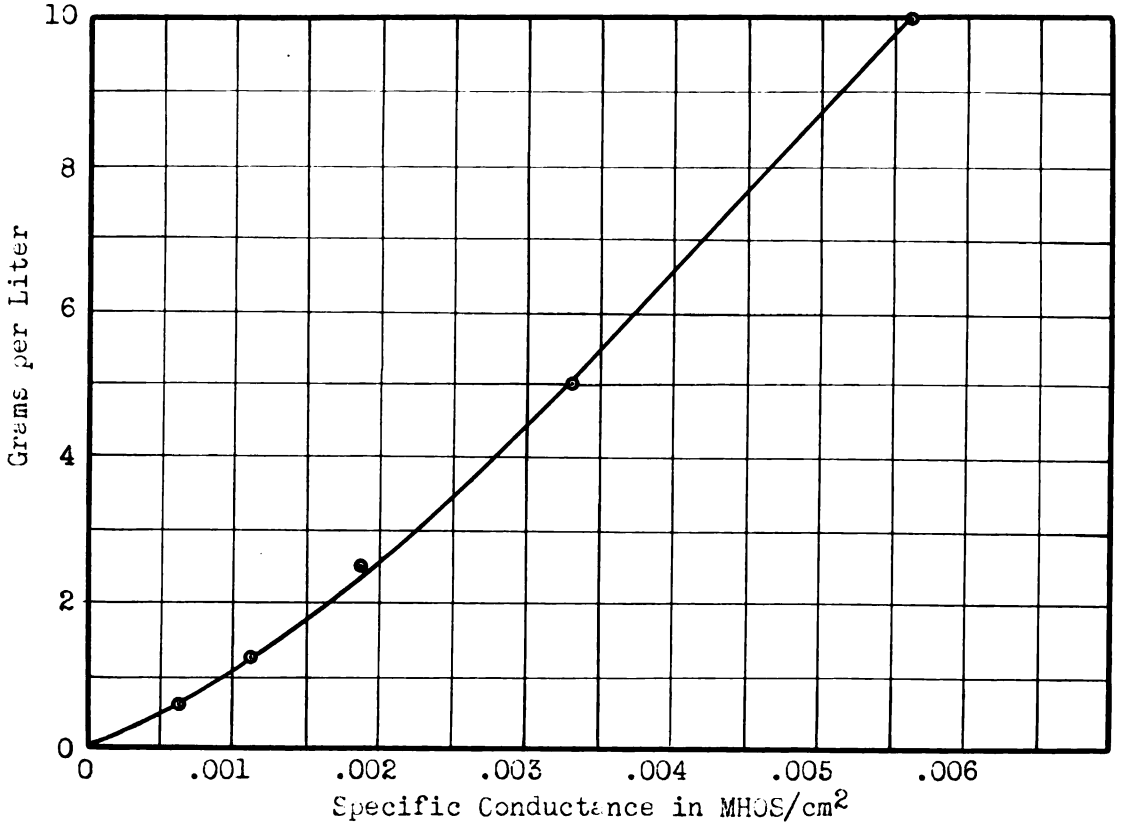

Fig. 9. Change in conductance with concentration for beryllium sulphate solution.

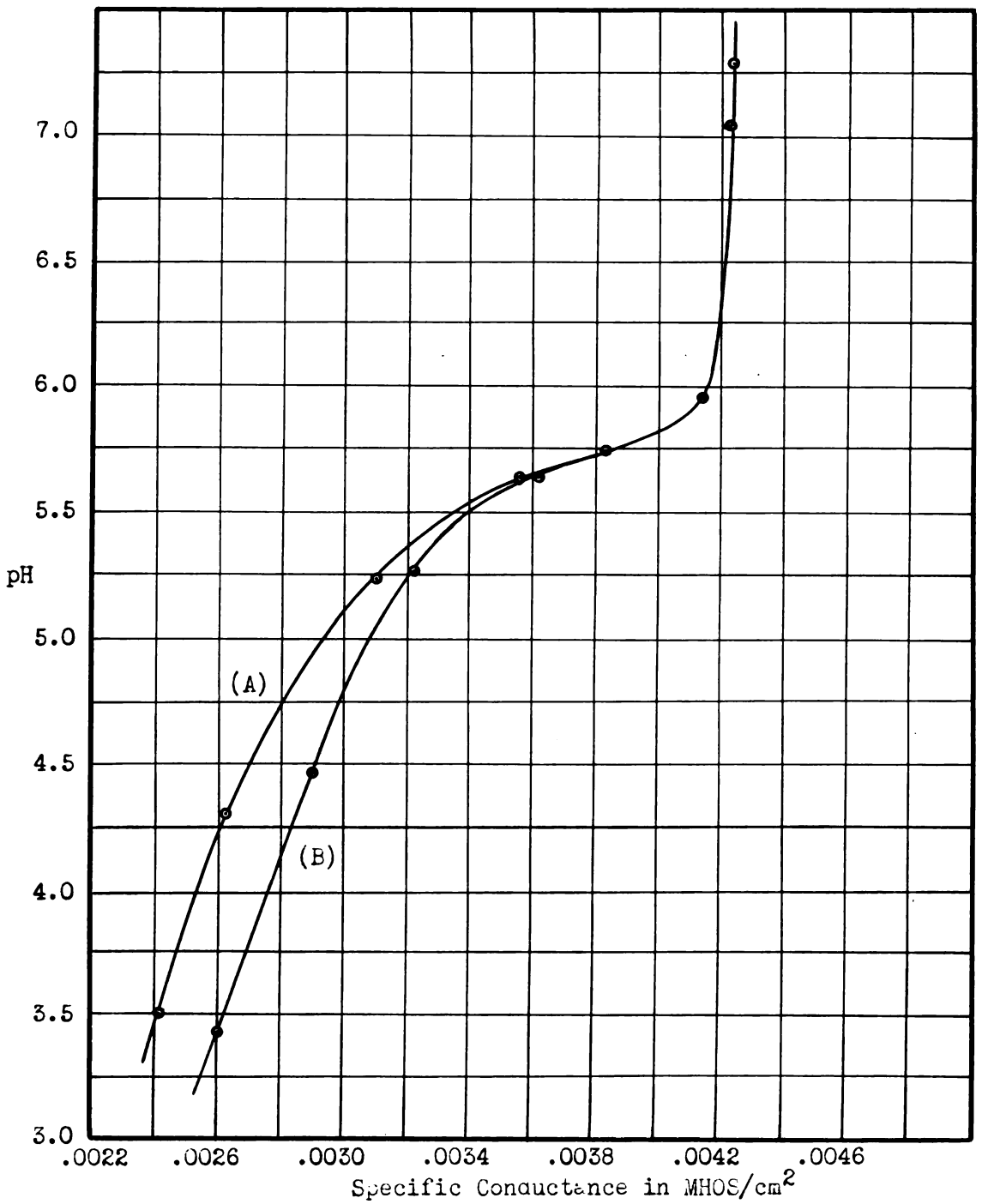

Fig. 10. Change in conductance with pH. (A) 3.4 g./l. $BeSO_4 \cdot 4H_2O$. (B) 3.4 g./l. $BeSO_4 \cdot 4H_2O$, 5.0 g./l. H_3BO_3.

at peak voltage. Other data which were recorded for pH's beyond 7.0 showed that the conductivity again increased as the ammonium hydroxide was added.

Action of Citric and Tartaric Acids: Since the boric acid was rather unusual in its action, it was thought that perhaps compounds such as citric acid and tartaric acid might also be worth investigating. Quantities of 5 g./l. of either compound completely complexed the beryllium sulphate and no precipitation resulted even when great amounts of the base were added. The effect of adding 1.0 g./l. of citric acid was determined by potentiometric titration of a solution containing 3.4 g./l. of beryllium sulphate. A slight break in the curve is detectable (figure 11) and very slight precipitation occurred. Upon electrolyzing the solution, no rise in potential was obtained nor was there any evidence of deposit. It is highly possible that there was some free beryllium sulphate in the solution which went to the hydroxide as the base was added, but action of the complex salt was not conducive to the formation of a colloid.

Investigation of pH Range: The pH range of a bath containing only beryllium sulphate and ammonium hydroxide was reported (1) to be approximately 5.6 to 6.1. In the process of investigating this solution, no protective coating could be secured above a pH of 5.90. Plates coated at a pH of 5.95 failed 100 per cent in the sulphide tests.

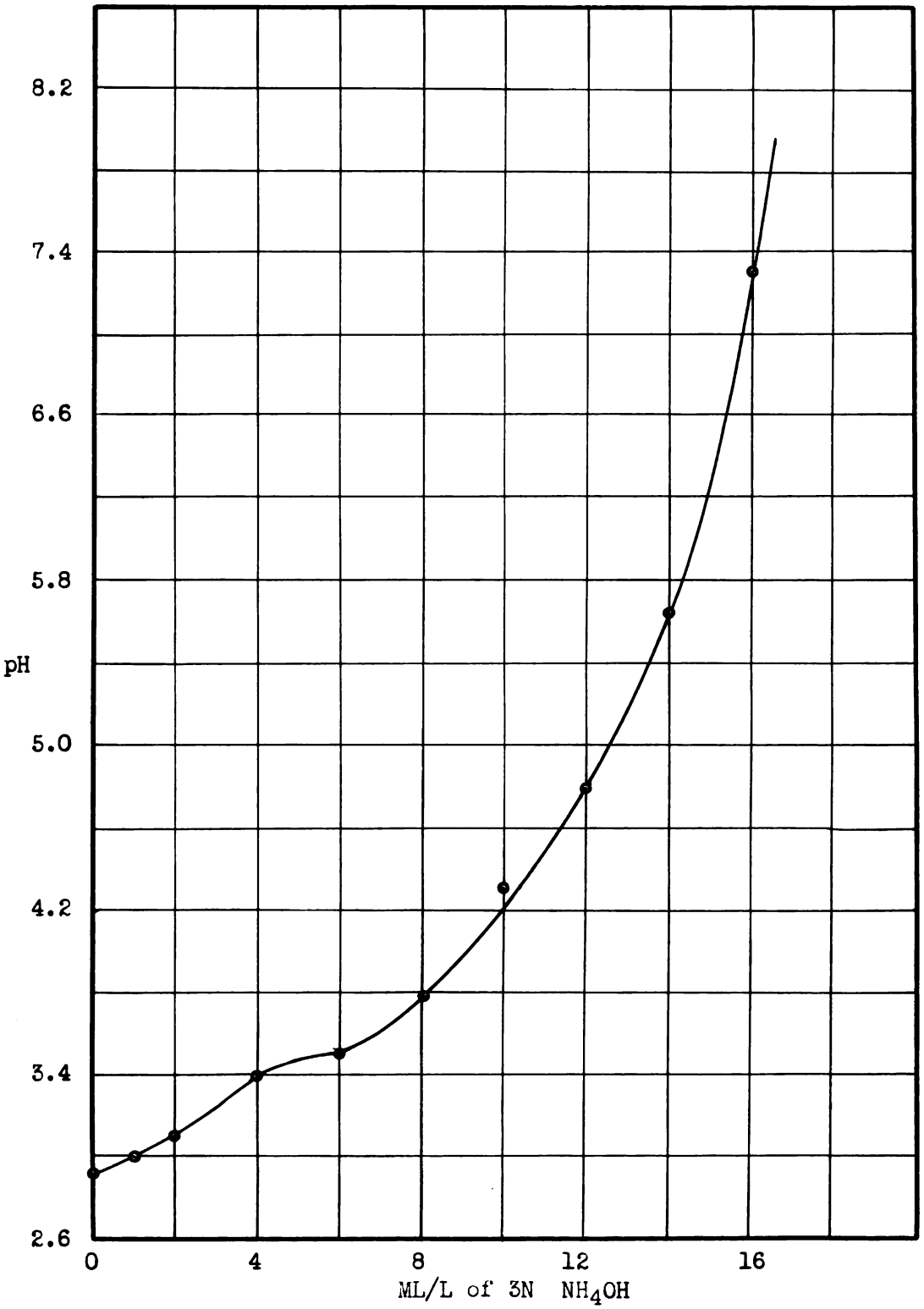

Fig. 11. Potentiometric titration curve for a solution containing 3.4 g./l. of $BeSO_4 \cdot 4H_2O$ and 1.0 g./l. of citric acid.

At the other extremity of the range there was not such a definite break. At a pH of 5.50, excellent plates were secured, but at 5.40, the protective value of the coating fell off to about 50 per cent. This was true only of the baths not containing any boric acid. However, when this agent was added to the bath in quantities of from 3 to 5 g./l., the initial adjustment of pH had to be between 5.5 and 5.9, but as the solution was operated, the pH could drop as low as 4.9 without any decrease in the protective powers of the film deposited. The upper limit remained at a pH of 5.90.

Effect of Concentration: In determining the effect of various concentrations of beryllium sulphate solutions, the potential rise per plate was again recorded (figure 12). The rate of rise per plate varied with the change in concentration, but the peak voltage was practically the same in almost all cases. Protective coatings, however, could be secured only over a limited range, as illustrated in table I. The plates from which these data were taken were plated at a current density of 100 ma./sq. ft. for 6 minutes.

Table I

Conc. $BeSO_4.4H_2O$	Amt. of Tarnish
0.5 g./l.	95%
2.0 "	5%
3.0 "	0%
4.0 "	0%
5.0 "	2%

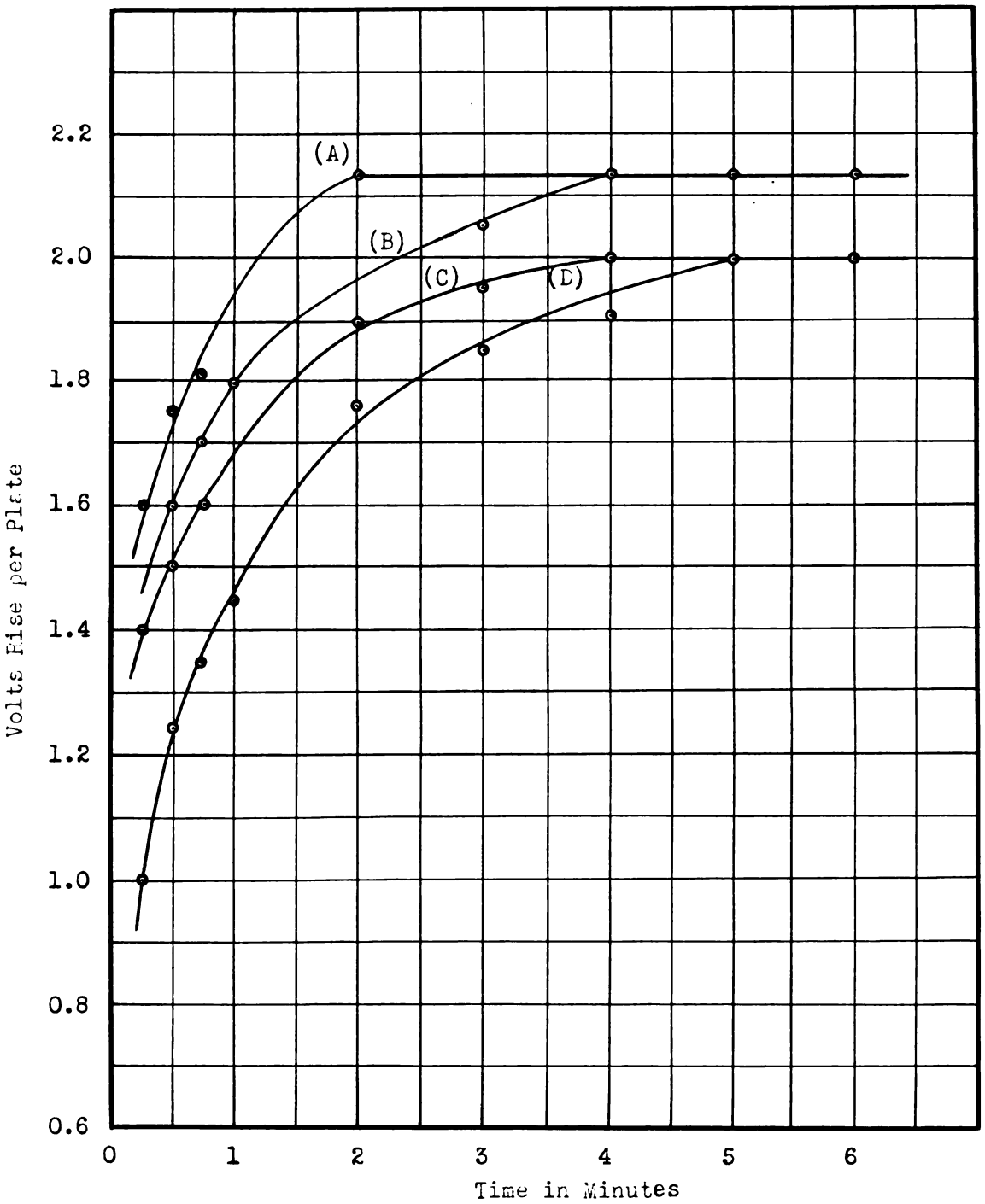

Fig. 12. Rise in potential vs. concentration of beryllium sulphate solutions containing 5.0 g./l. H_3BO_3 at pH 5.62 and a current density of 100 ma./sq.ft. (A) 5.0 g./l. (B) 3.4 g./l. (C) 2.0 g./l. (D) 0.5 g./l.

Several observations may be made from these results. First, the peak voltage reached is not necessarily indicative of the protective value of the coating. Second, the concentration of beryllium salt is not critical and a satisfactory range would be 3 to 4 g./l. It should be noted that this is in agreement with the value of 3.4 g./l. as given by the published work of Thomas and Price (1).

Effect of Current Density: Current density also proved to be a factor which influenced the nature of deposit. From figure 13 it can be seen that the peak voltage becomes greater as the current density rises. Again it was made apparent from tarnish tests (tables II and III) that the peak voltage does not necessarily indicate the nature of the film which has been deposited.

Table II

Bath conditions -- 2.0 g./l. $BeSO_4.4H_2O$ and 5.0 g./l. H_3BO_3 at a pH of 5.07

Current Density	Amt. of Tarnish
20 ma./sq. ft.	0%
55 "	0%
100 "	5%
150 "	50%
190 "	95%
240 "	100%

Table III

Bath conditions -- 3.4 g./l. $BeSO_4.4H_2O$ and 5.0 g./l. H_3BO_3 at a pH of 4.90

Current Density	Amt. of Tarnish
20 ma./sq. ft.	0%
50 "	0%
100 "	15%
195 "	25%

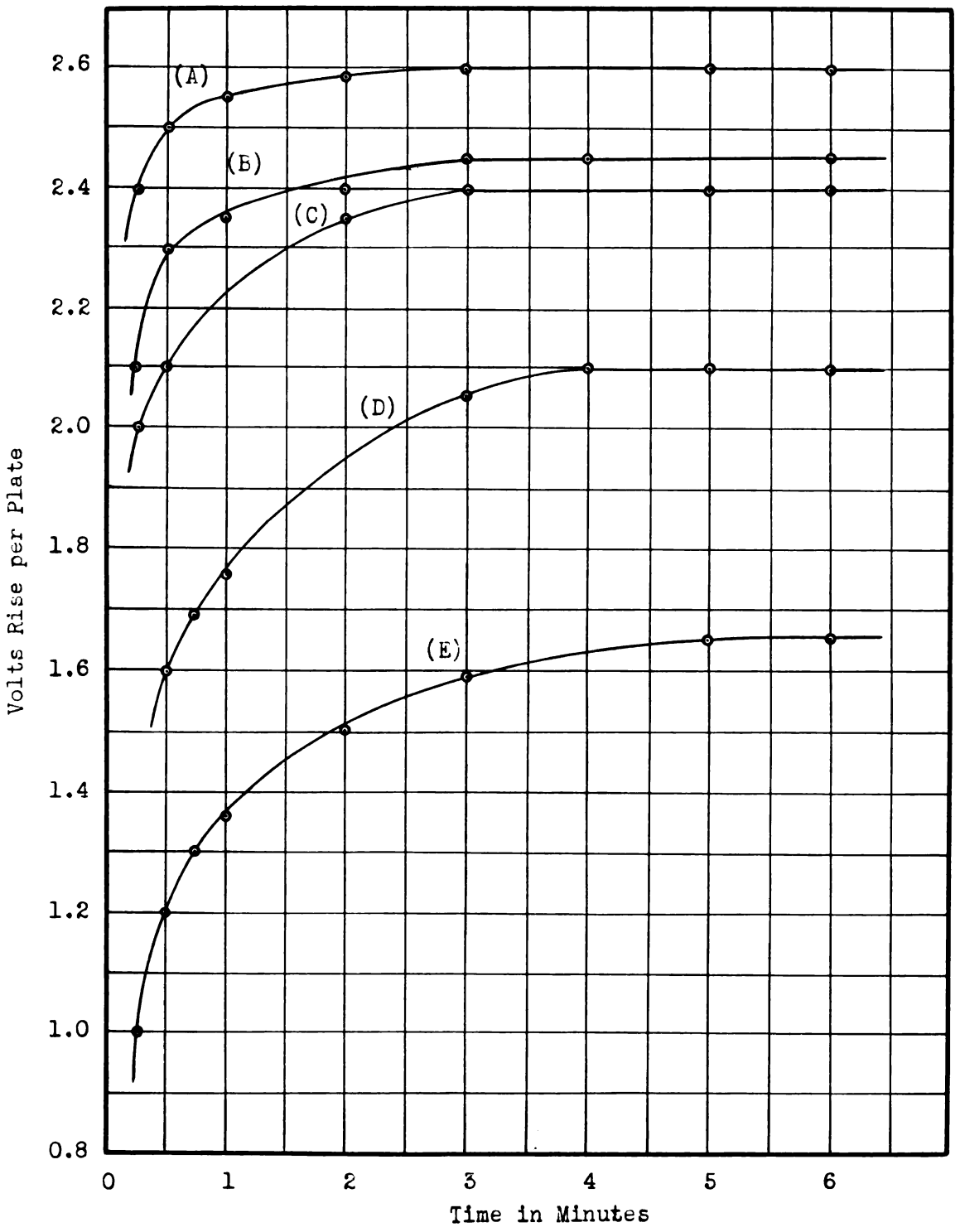

Fig. 13. Effect of current density on rise in potential for solution containing 2.0 g./l. $BeSO_4 \cdot 4H_2O$, 5.0 g./l. H_3BO_3 at pH 5.07. (A) 240 ma./sq.ft., (B) 190 ma./sq.ft., (C) 150 ma./sq.ft., (D) 100 ma./sq.ft., (E) 55 ma./sq.ft.

The current density range is greater at the optimum concentration of 3.4 g./l. beryllium sulphate than at 2.0 g./l. as shown in tables II and III. Actually, plates were coated much lower than 20 ma./sq. ft., but the time of plating was longer and the relative value of the readings was lost. The optimum range would seem to be 50 to 100 ma./sq. ft., considering both the protective value and time of deposition.

Time of Deposition: The time of deposition is another factor in the consideration of protection and appearance. Obviously a heavier deposit will give greater protection, but unless the particles have been restricted somewhat to the smaller, secondary sizes, the interference colors will then be present. In any event, the thickness is not a linear function of the time of electrolytic treatment. As would be supposed, there is little change after the maximum potential has been reached and this usually takes from 3 to 5 minutes, depending upon bath composition and current density.

From a beryllium sulphate solution containing boric acid, plates can be secured having maximum thickness but no coloration of film. If the bath contains only beryllium sulphate, the interference colors start to appear within 2 minutes of plating and less than the maximum thickness.

Heat Treatment: While determining the proper method for drying coated plates, it was discovered that boiling

water would remove the film. This effect gradually disappeared as the film aged. Plates tested after standing at room temperature for a period of two weeks were not affected by the boiling water. The test consisted of submerging the lower half of the plate in boiling water for one minute and then subjecting the whole plate to the sulphide fumes to determine if the film had been removed. It was found later that films which had been given the oxidation test at 300°C. for half an hour also were not affected by the water.

Correlating all the data presented in the preceding paragraph, the necessity for a heat treatment was readily seen. One of the limiting factors which immediately became apparent was the effect of the heat treatment upon the base metal. Most metals would be annealed after one half hour at 300°C.

An investigation was made to determine the proper heat treatment to give the film stability against the boiling water. As little as 1 minute at 300°C. was found sufficient to render the coating inert to this test. At 250°C., approximately 2 minutes were required.

In attempting to strip the film from some copper samples which had been coated and tested for resistance against oxidation at 300°C., it was found that the film was apparently inert to the acid bath. The material had been finished in the regular manner and heated

for one half hour. The acid strip bath consisted of half-and-half concentrated nitric and sulphuric acids.

A detailed investigation disclosed that this unusual resistance was not developed until the film was heat-treated for 8 to 10 minutes at 300°C. Heat treatment for less than that time would not give copper any resistance whatsoever against the acid dip. Heat treatment for longer periods of time did not increase the resistance of the film which was approximately 2 minutes in the strip bath. Plates coated in solutions not containing any boric acid were resistant for about 1 minute and it was noticed that the heat treatment removed most of the interference patterns from these plates. This indicated a change in composition of the film, and an explanation of this change is advanced under the theory of the process.

Thickness Measurements: Thomas and Price (1) calculated a theoretical value for the thickness of this type of coating. Basing their calculations upon the deposition of either the oxide or hydroxide and a 100 per cent efficient process, they reported 30 A. If this were true, the film would be in the order of only one colloid particle deep. Desiring at least to determine the order of the thickness accurately, a method of physical measurement was sought.

The only instrument suitable to measure such small films is the interferometer. Several extra mirrors which

had been employed on a Michelson interferometer were re-silvered by the rochelle salts reduction process and washed in distilled water. A small phosphor-bronze clamp was made to hold a single mirror, just making contact with the silver film along the edges. While the mirrors were still wet, they were placed in the fixture and the lower half of the surface coated with a film of beryllia, the first for 4 minutes and the second for 6 minutes. They were dried in alcohol and ether and then maintained at 22°C. until the measurements were taken. An attempt was made to adjust the current density to approximately 100 ma./sq. ft.

When the mirrors were located in the interferometer and properly adjusted, a displacement of one quarter of a wave length of sodium light was detected on both mirrors. These measurements indicated two facts; first, that the thickness was in the neighborhood of 700-800 A., second, that the thickness did not increase with time. The latter factor was quite obvious from the very nature of the process.

Other Metals and Solutions: At first, only copper was employed as a base metal. Later, when the process was sufficiently advanced, silver plates were coated also. The same protection was secured, but in some cases, a slight interference coloration appeared if the plates were coated longer than the 5-minute period. This was always entirely removed by the heat treatment.

Nickel-plated, brass, and steel articles were also coated with films of beryllia. There was evidence of the protective powers of the coatings but no quantitative investigation was made.

A bath employing aluminum sulphate instead of beryllium sulphate was prepared and several copper plates coated. The same protection was secured as in the case of the beryllium salt. No detailed investigation was made.

The impurities which will affect this type of bath most are copper, silver, and iron. This is because they are attacked by the solution and go into solution. Their oxides are not protective and make the resulting film porus. Spectrographic analysis disclosed that simply immersing a copper plate or wire in the bath was sufficient to contaminate it.

CHARACTERISTICS OF FILM

A thickness of 700 to 800 A. is approximately 0.000003 inch. That is rather thin for a protective coating, but tests have proved that the film can be very effective even in such thicknesses.

If one of the copper plates used for the experimental work were coated with beryllia and then heat-treated for one minute at 300°C., it would not be affected by H_2S fumed for 3 to 4 hours.

Copper may be protected from oxidation at elevated or room temperatures in this manner also. Test plates heated at 300°C. to 350°C. for 3 hours showed no oxidation to the copper or any discoloration to the film.

There are 3 types of coatings obtainable by varying the heat treatment; first, no heat treatment at all, second, 1 minute at 300°C. or its equivalent of 2 minutes at 250°C., and third, 10 minutes at 300°C. These films may be characterized by the following tests: The first will withstand the action of H_2S fumes but will not be stable to the boiling water test; the second will give better resistance to H_2S fumes and will withstand the action of boiling water but will not give any protection against the concentrated acid mixture; and the third will be the best film, not affected by the boiling water test and not attacked for about 2 minutes in the concentrated acid mixture.

An oxide film three millionths of an inch thick would have one inherent weakness when applied on the surface of a different metal. That weakness is its low resistance to mechanical abrasion or scratching. This film will withstand a great deal of handling and rubbing with cloths, but the continuity of the film is destroyed when an abrasive scratches the surface. In general, it may be stated that the adhesion of a heat-treated sample is excellent in spite of this condition.

Since the deposited particles of colloidal beryllia have a high electrical resistance they are not deposited to any great depth, but this has one advantage and that is the increase in throwing power. The film builds up uniformly even in recessed areas. This fact was evidenced when the plates were put in the concentrated acid mixture. The copper was attacked evenly over the whole surface. Part of this was no doubt due to the uniformity of the colloid particles which had been deposited.

THEORY

It is important to consider what happens to a solution of beryllium sulphate as ammonium hydroxide is added. In figure 1 will be seen the change in pH of such a solution as the base is added. This same effect was reported by Britton (2) and Thomas and Price (1). Britton's work was a little different in that the base was sodium hydroxide, but the resulting curve was much the same as that found in figure 1.

The effective range for the initial pH adjustment is 5.5 to 5.9 (figure 1). This may be called the flat portion of the curve. Britton maintains that the composition within this range would be $BeSO_4.Be(OH)_2$. This is no doubt true, but is not a clear enough picture because no mention is made of the colloid particles. A more complete analysis is suggested below.

As ammonium hydroxide is added to a solution containing between 3 and 4 grams of beryllium sulphate, precipitation does not start until a pH of 4.8 is reached. As more base is added the pH rises more quickly and precipitation continues. This increase in rise is due to the absorption of $BeSO_4$ on the precipitate to form what is equivalent to the compound $BeSO_4.Be(OH)_2$ as advanced by Britton. That hydrous beryllium oxide is highly absorptive, is indicated by Weiser (3). As still more ammonium hydroxide is added to go beyond, say a pH of 5.5, the $BeSO_4$ is removed from the precipitate by neutralization and the flat portion of the curve results. The equivalence point is reached at a pH of 6.0.

Now the reason that it is impossible to deposit a protective coating as soon as a precipitate is formed may be because there has not been any peptizing action to form a colloid. The precipitate itself will migrate towards the cathode but will not form an adherent deposit. This was shown in cataphoresis experiments. The charge is positive from a pH of 4.8 up to at least 9.5, but measurements were not made any higher. Once the colloid has been formed (pH 5.5 to 5.9) it will remain stable even if the pH drops back to 4.8. The protective power of the film deposited begins to fall off after a pH of 4.9 has been reached.

The previous paragraphs alone still do not prove that there is a colloid in the solution. The one pertinent fact

which does, however, is that the Tyndall phenomenon may be observed only when the solution can be used to secure a protective coating. By continuous plating, a bath may be deplenished of its colloid and then no Tyndall phenomenon can be observed.

The effects of boric acid may be several in number, but it does serve at least one important purpose. That purpose is to cause the coagulation of the larger primary particles and leave the secondary particles for plating. Much evidence is advanced by Thomas (5) for this grouping of colloidal particles into primary and secondary classes. Weiser (6) goes so far as to present the actual sizes of the particles in each group.

The fact that these larger particles are removed is evidenced in at least three ways. First, because during a 48-hour period of standing, these particles gather in clusters large enough to be seen; second, because the deposit is thinner as shown by the disappearance of the interference colors; and third, because of the higher potential rise per plate for a given solution (figure 7).

The potential rise per plate does not necessarily indicate the protective powers of a coating. This was shown in the investigation of both the concentration of beryllium salt (figure 12) and the current density (figure 13). However, the work of Wagner (4) still holds and it may be said that for a given set of conditions, i.e., bath composition

and current density, the higher the potential rise per unit area the more will be the protective value of the film.

If the particle sizes as advanced by Weiser (6) are correct, that would explain why Thomas and Price (1) were unable to eliminate the interference colors. Particles equivalent to the primary sizes were given dimensions of 5 by 10^{-5} to 1 by 10^{-7} cm. This being true, it would be possible for films just 2 or 3 particles deep to become visible, interference colors starting at a depth of the order of 10^{-4} cm. The secondary or molecular dispersed particles were given a range of from 10^{-7} cm. down to the size of the molecules themselves. It is quite obvious that the secondary particles could build up a much more dense and protective film.

It might be thought, at first, that the larger particles could be removed by plating out. This is not the case. Thomas (7) in the following equation shows that the mobility of a colloid micelle is inversely proportional to the mass of dispersed phase per cc. of original hydrosol, but this does not concern the size of the individual colloid particles:

$$U = \frac{mk}{MIt}$$

U - mobility of particle
t - time in seconds
I - current in amperes
M - mass of dispersed phase per cc. of the original hydrosol
m - mass of dispersed phase transported from one compartment to the other
k - specific conductivity of the original hydrosol

This fact was also shown in the experimental work on the solution as established by Thomas and Price (1). The bath gave interference colors even after many plates had been coated.

The exact composition of the film which is deposited is difficult to determine. Spectroscopically, the film was shown to contain mainly beryllium but also a little boron. There can be little doubt that the colloid particle is $Be(OH)_2$. The charge is probably due to the absorbed $BeSO_4$ on the surface of the particle. Some boric acid is also carried over with the colloid, but it would be difficult to say whether it was absorbed in any quantities or not. In any event, the film deposited must consist mainly of $Be(OH)_2$ or $BeO.H_2O$ as Weiser (3) puts it.

When heated, hydrous beryllium oxide loses its absorptive powers and consequently loses part or all of the water molecule depending upon the temperature. Weiser gives data on temperatures up to 280°C. where all but 0.13 H_2O has been driven off. He also makes the statement that moisture will again be absorbed unless the oxide is heated higher. These data would indicate that the film consists mainly of $BeO.0.13\ H_2O$ after heat treatment at 300°C. For convenience it is well to call the substance beryllia, regardless of its composition.

As mentioned before, films deposited in the manner suggested by Thomas and Price (1) contained interference

colors which were removed almost entirely by heat treatment. This can now be explained as the reduction in thickness due to the removal of 0.87 molecules of water from the film. No decrease in interference colors results from the change in index of refraction because the oxide has a higher index than the hydrous oxide.

SUMMARY

1. Many metals, including copper, silver, and their alloys, may be treated cathodically in a solution of beryllium sulphate and ammonium hydroxide to give them excellent protection against oxidation in air at elevated temperatures or tarnishing from sulphur fumes.

2. Deposition is made from a bath containing 3 to 4 g./l. of beryllium sulphate nearly neutralized with ammonium hydroxide. The film is probably composed of colloidal beryllium hydroxide which has a positive charge in the solution and migrates towards the cathode when a potential is applied.

3. The addition of 3 to 5 g./l. of boric acid to the bath causes coagulation of the larger colloidal particles. This leaves the smaller, secondary particles to be plated out. A transparent and colorless film is thus formed.

4. General plating conditions include: anodes of 7 per cent tin and 95 per cent lead, a current density range of

50 to 100 ma./sq. ft., a period of plating of 4 to 6 minutes, and a pH which is initially adjusted to between 5.5 and 5.9 and may be operated as low as a value of 4.9.

5. The film is limited to a thickness of approximately 3 millionths of an inch, this being attained after the maximum potential has been reached during electrolytic treatment. The film, although limited to this small value, will withstand rubbing with non-abrasives. The main weakness is its low resistance to mechanical abrasion.

6. Heat treatment of the film will materially increase its protective powers. Two types of treatment are suggested depending upon whether it is desirable to anneal the base metal or not. The first consists of 1 minute at 300°C. or its equivalent of 2 minutes at 250°C.; the second consists of 10 minutes at 300°C.

7. The final film exhibits remarkable resistance to oxidation in air, to tarnish from sulphur fumes, and even will stand 2 minutes in a concentrated mixture of half sulphuric and half nitric acids.

8. The film deposited consists of hydrous beryllium oxide ($BeO.H_2O$) and after heat treatment, probably has the composition $BeO.0.13H_2O$.

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