ELECTRODEPOSITION OF CHROMIUM FROM CHROMIC ACID BATHS

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June 10, 1927

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ABSTRACT

A detailed study is made of the chromic acid plating solution and of the conditions for its operation and control. The three principal types of chromic acid bath which have been developed during the past 70 years are shown to be identical not only in initial behavior, but also in ultimate composition. The recent commercial success of chromium plating is therefore attributed not to any changes which have been effected in the composition of the bath, but to its more careful operation and control. It was found that minor improvements could be effected in the throwing power of chromic acid baths, but that there appears to be little possibility of materially improving this property which has hindered the more general adoption of chromium plating.

CONTENTS

I. INTRODUCTION

For 70 years the electrodeposition of chromium from chromic-acid baths has been an accomplished fact; but it has been only within the past few years that the mechanism of the process has been sufficiently understood to permit its commercial operation. The first successful applications of chromium plating served to emphasize its unusual properties and advantages, and a tremendous interest and activity in this new field has developed. Numerous patents have been granted, but relatively few articles containing specific scientific information have been published, especially in America.

413

The purpose of this paper is to summarize and correlate available existing information and the results of studies made by the authors at the Bureau of Standards during the past few years. No attempt will be made to discuss the numerous patents on chromium plating, and only such incidental references will be made to them as are essential to a general consideration of the subject.

This publication may be considered as a sequel to a previous one [1] by the Bureau of Standards which described in detail the process used for the chromium plating of printing plates at the United States Bureau of Engraving and Printing. It will be noted that the more comprehensive study of the subject has exposed certain errors in the first publication—errors of theory, however, and not of fact.

II. HISTORICAL

An impartial critical study of all of the work which has been done on the electrodeposition of chromium from chromic acid baths would, at the present time, be an extremely difficult task and one which we feel would serve no useful purpose. Instead we have decided to trace the evolution of chromium deposition by discussing a few publications which will serve to illustrate the trend of development.

Bunsen was probably the first to accomplish the electrodeposition of chromium,[2] but Geuther seems to have been the first to obtain it from solutions of chromic acid.[3] In addition to chromic acid, Geuther's solutions must have also contained small amounts of sulphate, because no special effort was made to eliminate this impurity. He states:

The chromic acid used in the experiments was precipitated from potassium dichromate with sulphuric acid in the usual way.

The reactions which occurred when these solutions were electrolyzed are described by Geuther, as follows:

Chromic acid in aqueous solution is an electrolyte and is decomposed in such a way that oxygen evolution occurs at the anode, but at the cathode, along with hydrogen evolution, a complete reduction to metallic chromium takes place, accompanied by a partial reduction of the solution.

Concerning the nature of the deposit obtained Geuther states:

This deposited on the platinum wire which served as cathode in the form of a coherent, grayish white coating with a metallic luster.

Buff [4] attempted to repeat Geuther's work, but did not succeed in obtaining a deposit, and, in consequence, questioned the accuracy

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[1] H. E. Haring, Principles and operating conditions of chromium plating, Chem. and Met. Eng. **32**, pp. 692 and 756; 1925; and also Bureau of Standards Letter Circular 177; Sept. 8, 1925.

[2] Poggendorff's Ann., **91**, p. 119; 1854.

[3] Liebig's Ann., **99**, p. 314; 1856.

[4] Liebig's Ann., **101**, p. 1; 1857.

of Geuther's results. In 1883 Bartoli and Papasogli [5] reported the deposition of chromium from chromic acid, thereby confirming Geuther's claims.

Placet and Bonnet [6] discuss the compounds of chromium which are suitable for use in chromium depositing baths and state that "the most important of these compounds is chromic acid, either the *commercial* [7] acid or chromic acid obtained from the chromate or bichromate of an alkali metal."

Carveth and Curry [8] made a thorough survey of the work which had been done on the electrodeposition of chromium from chromic acid baths prior to 1905. This study, which included a repetition of Geuther's experiments as well as original work of their own, led them to conclude that those investigators who claimed that they had deposited chromium from chromic acid solutions were entirely justified, and that those who claimed that it could not be done were using too low a current density. They also concluded that in no investigation had chromic acid absolutely free from sulphate been used [9] and furthermore, they proved that the presence in the bath of this impurity or others of a similar nature (in amounts up to 1 per cent) materially facilitated the deposition of chromium. One of the most significant of their statements is as follows:

Our results prove conclusively that Placet and Bonnet were right in stating that metallic chromium can be obtained by the electrolysis of commercial chromic acid.

The data given by Carveth and Curry clearly show that chromium was deposited by them from solutions containing comparatively large concentrations of CrO_3 (for example, 14.28 per cent) and small amounts of a sulphate, usually in the form of H_2SO_4, in concentrations up to 1 per cent. The scope of their work is indicated by the following statement, which is also evidence of the fact that the chromic acid used by Geuther contained sulphate as an impurity in quantities greater than 0.01 per cent.

Under no circumstances have we by working within a temperature range of 20 to 90° C., current density of 10 to 250 amp./dm², concentration from 1 per cent to 50 per cent, been able with a pure [10] acid to get results at all comparable with those of Geuther.

Comparable results were obtained, however, when small amounts of sulphate were present in the bath.

[5] Gazz. Chim. Ital., **13**, p. 47; 1883.

[6] United States Patent 526114 Sept. 18, 1894.

[7] Italicized by the present authors.

[8] J. Phys. Chem., **9**, p. 353, 1905; and also Trans. Am. Electrochem. Soc., **7**, p. 115; 1905.

[9] It has been the experience of the authors of this paper that it is impossible even at the present date to obtain chromic acid entirely free from sulphate (either in the form of H_2SO_4 or Na_2SO_4).

[10] Carveth and Curry refer to their CrO_3 which contained 0.01 per cent H_2SO_4 as "pure."

The experiments of Carveth and Curry were not confined to solutions of CrO_3 and H_2SO_4. Deposits were also obtained from solutions in which instead of the sulphuric acid was substituted a small amount of another compound, such as nitric acid, hydrochloric acid, potassium chloride, potassium sulphate and sulphuric acid.

Carveth and Curry indicated that the electrodeposition of chromium from chromic acid baths was commercially feasible especially for "fine platings." In this connection they also state that—

Platings made without stirring the solution and without finishing by buffing, etc., resemble the very finest work done with silver. In fact, for plating purposes the metal should have a great future before it.

In 1920, Sargent published [11] the results of an investigation made by him some years previously. This research and also that of Carveth and Curry were conducted at Cornell University. Sargent noted that previous investigators had apparently found that the efficiency of chromium deposition from chromic acid baths containing small amounts of sulphuric acid tended to increase with electrolysis. He believed that this increase in efficiency was due to the gradual replacement of the sulphuric acid by chromic sulphate, as the result of electrolytic reduction. He therefore logically concluded that it was preferable to make the substitution initially rather than to wait for electrolysis to accomplish the same result. His views on this point were expressed as follows:

The variation of the yields of chromium with electrolysis observed by Carveth and Curry and by Skillman must have been caused by a corresponding change in the composition of the plating solution. In all cases where chromium is deposited from chromic acid solutions a very considerable amount of chromic acid is reduced to the chromic state. Thus, the electrolysis of chromic acid solutions containing free sulphuric acid, under conditions giving chromium deposits, should result in the formation of chromic sulphate until all the sulphuric acid had been neutralized. Tests showed that the addition of small amounts of chromic sulphate to C. P. chromic acid solutions increased the yield of chromium very greatly, and that the yields of chromium obtained from these solutions did not increase with electrolysis. These facts show that the change in the yields of chromium with electrolysis from chromic acid solutions containing free sulphuric acid is due to the effect of the chromic sulphate formed in the plating solution.

Regardless of whether Sargent proved that a solution containing chromium sulphate is superior to one containing sulphuric acid, he at least showed that satisfactory deposits, even up to 1.25 cm in thickness, can be obtained from a bath containing only chromic acid and chromium sulphate. Sargent made no recommendations as to the exact concentrations of CrO_3 and $Cr_2(SO_4)_3$ which should be used. He clearly indicated, however, that satisfactory results were obtained with solutions containing from 20 to 30 per cent of CrO_3 and from 0.3 to 0.5 per cent of $Cr_2(SO_4)_3$. The thickest deposit was

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[11] Trans. Am. Electrochem. Soc., **37**, p. 479; 1920.

made by him from a solution containing 25 per cent of CrO_3 and 0.3 per cent of $Cr_2(SO_4)_3$.

That Sargent realized chromium plating is a process which requires careful control for best results is indicated by the following quotation:

The deposition of chromium is affected very markedly by the per cent of chromic acid and chromic sulphate present and by the temperature of the solution and the cathode current density used, so that good results are obtained only by a careful control of these factors.

He noted, as had Carveth and Curry, that an increase in current density is equivalent in its effect on the deposit to a decrease in bath temperature, a relation which is common to plating baths. He called attention to the fact that the best deposits are obtained from warm solutions, but that the efficiency of deposition is then much lower than at ordinary temperature.

In September, 1923, Schwartz added to the growing interest in chromium plating by the publication of a paper entitled, "Chromium Plating Steel Using Chromium Anodes." [12] After a thorough investigation of previous work on chromium deposition he concluded that "Sargent's solution" was a practicable plating solution. By using this solution and duplicating Sargent's operating conditions he found that "A bright crystalline deposit was obtained which proved satisfactory in all respects."

On June 30, 1925, the successful application of electrodeposited chromium to printing plates at the United States Bureau of Engraving and Printing was announced and the method used was fully described. [13] A detailed description of the process was published [14] in August, 1925. In this article the author expressed the opinion that more satisfactory results than had, in general, been obtained with Sargent's solution would be possible if "chromium chromate" was included as an initial constituent of the bath. Chromium chromate is a compound of trivalent and hexavalent chromium, the first reduction product of chromic acid, the presence of which in colloidal form had been noticed by Sargent and previous investigators in solutions which had been electrolyzed for a time and from which satisfactory chromium deposits were being obtained. It seemed logical to add this apparently desirable ingredient of the bath initially rather than to wait until the same result had been accomplished by electrolysis.

The author stated that the chromium chromate would exert a buffer action and insure a more constant acidity—a factor which apparently had not been previously considered and controlled. Numerous methods for forming chromium chromate in the bath

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[12] Trans. Am. Electrochem. Soc., **44**, p. 451; 1923.
[13] At the annual meeting of the American Electroplaters' Society.
[14] H. E. Haring, Chem. and Met. Eng., **32**, pp. 692 and 756; 1925; and also Bureau of Standards Letter Circular No. 177; Sept. 8, 1925.

prior to electrolysis were suggested, and it was stated that the Bureau of Engraving and Printing employed the addition of chromic carbonate $Cr_2O(CO_3)_2$, (7 g/L or 1 oz./gal.).

The necessity for the careful adjustment and control of the operating conditions (bath temperature and cathode current density) in chromium deposition was strongly emphasized, and conditions under which the three types of deposit (namely, "frosty," "bright," and "milky") could be obtained were closely defined. As a result the chromium plating process at the Bureau of Engraving and Printing has been a complete success.

From the brief review of the history of chromium plating in the preceding pages it is evident that, since 1905, when Carveth and Curry proved conclusively that chromium could be deposited from solutions of chromic acid containing small amounts of sulphuric acid or a sulphate, there has been a trend from (1) their "acid" type of bath, containing initially free sulphuric acid and chromium in the valence of VI only, to (2) the "neutral" type of bath, usually referred to as "Sargent's solution," in which the sulphuric acid is replaced by chromic sulphate, to (3) the "basic" type of bath, which is simply Sargent's solution plus a small amount of "chromium chromate."

This historical development corresponds in chronological order to the changes which normally tend to occur in the operation of a chromic acid bath. If it is initially "acid" (type 1), it tends to become "neutral" (type 2), and finally "basic" (type 3). The historical transition was based upon the then apparently logical assumption that best results would be obtained by starting out with a solution having the composition that it would eventually tend to assume. Actually, however, as will be shown in this paper, the progress made in chromium plating has not been *because of* these modifications in the composition of the solution, but *in spite of* them. The industrial success of chromium plating is due entirely to the careful application to this process of the same principles which govern the deposition of other metals. Apparent differences are matters of degree and not of kind. The "bright," mirror like deposit of chromium is not an abnormality; on the contrary it is exactly analogous to bright deposits of nickel and other metals which as frequently produced require no buffing subsequent to deposition. The conditions for depositing "bright" chromium are approximately those that might be predicted from general considerations.

III. COMPARISON OF THE " ACID," " NEUTRAL," AND " BASIC " BATHS

Solutions of the following compositions may be considered representative of the three types of bath:

Type 1. "Acid" bath_____ { Chromic acid.[15]
{ Sulphuric acid.

Type 2. "Neutral" bath_____ { Chromic acid.
{ Chromic sulphate.

Type 3. "Basic" bath_____ { Chromic acid.
{ Chromic sulphate.
{ "Chromium chromate."

The effect of a change in the sulphate content of these three types of bath on the character and efficiency of the deposit was first determined. The CrO_3 content was in all cases fixed at 2.5 M (250 g/L) and the quantity of chromic carbonate added to produce the "basic" bath was 7 g/L. Solutions of these compositions containing increasing amounts of sulphate in the form specified were electrolyzed,[16] using steel cathodes, at a temperature of 45° C. and a cathode current density of 10 amp./dm² for one hour. Efficiencies were determined by means of a copper coulometer in series with the plating bath.

Whenever the sulphate content of a bath is mentioned in this paper, total sulphate content, as determined by actual analysis of the bath constituents, is meant. The "C. P." chromic acid used in this investigation contained an amount of sulphate (0.015 per cent of SO_4) which was, for our purposes, negligible. But the so-called "C. P." chromic carbonate used in both this and the previous investigation on chromium plating [17] contained sulphate equivalent to 16 per cent $Cr_2(SO_4)_3$. The chromic sulphate, also "C. P." and readily soluble in cold water contained only 72 per cent $Cr_2(SO_4)_3$. It therefore contained 28 per cent H_2O, corresponding approximately to $Cr_2(SO_4)_3.10H_2O$; that is, intermediate between the salts recorded as containing 5 and 15 molecules of water, respectively.

The results obtained with the "acid" type bath are plotted as curve *1*, Figure 1. Bright deposits were obtained between the sulphate normalities indicated by the arrows. Results with the "neutral" and "basic" type baths, both as regards appearance and efficiency, were identical with those obtained from the "acid" type. (By identical is meant that the agreement between data was as good as the reproducibility of the data.) In a similar series of

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[15] Throughout this paper CrO_3 will be referred to as chromic acid, although, strictly speaking, it should be designated as "chromium trioxide" or "chromic anhydride."

[16] Each electrolysis was conducted in a rectangular glass jar (9 by 9 by 13 cm) containing solution to a depth of 10 cm. The cathode, 5 cm in width, was immersed to a depth of 5 cm and was located half-way between the lead anodes (each 2.5 by 5 cm) which were in contact with opposite sides of the jar.

[17] H. E. Haring, Chem. and Met. Eng., **32**, pp. 692 and 756; 1925.

experiments it was also found that the substitution of the sulphates of sodium, ammonium, potassium, aluminum, magnesium, or iron for chromic sulphate made no apparent difference in the results. Likewise the addition to the type 2 solution, of boric acid (3 g/L), or of sodium hydroxide (7 g/L) to form a type 3 bath, was without effect. The sulphate-cathode efficiency curve for brass was found to be practically the same as for steel.

Curve 1 shows that the optimum efficiency is obtained in a bath 2.5 M in CrO_3 under the conditions used, when the sulphate content
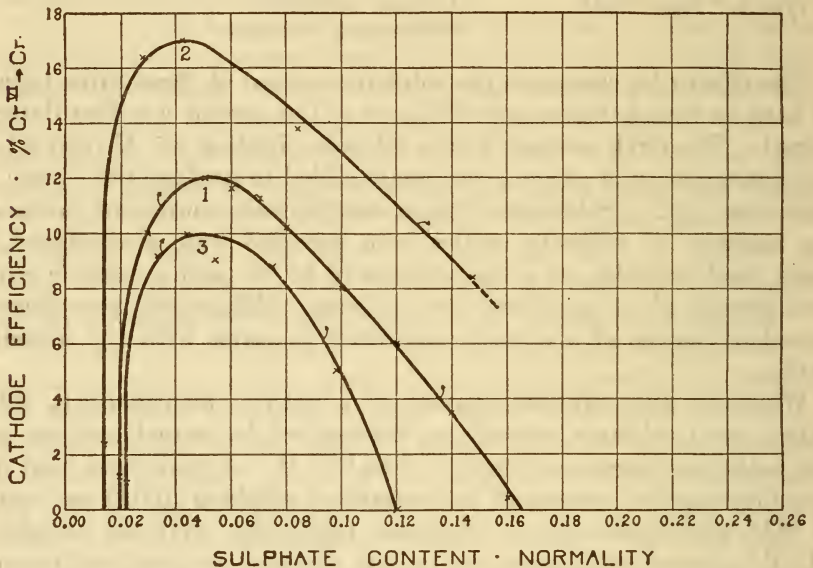

FIG. 1.—*Sulphate-cathode efficiency curves for steel cathodes in baths 2.5 M in CrO₃*

Curve	Temperature (±1° C.)	Current density (amp/dm²)
1	45	10
2	33	10
3	38	5

"Bright" deposits are formed between the arrows.

is 0.05 N. Deposits of equally good appearance can, however, be obtained in the range from 0.03 to 0.13 N sulphate content.

In order to determine, at least within certain limits, whether the sulphate content found to be optimum for the conditions used would be the optimum for any given set of operating conditions, curves similar to curve 1 were plotted from data obtained at a temperature of 33° C. and a cathode current density of 10 amp./dm² (curve *2*) and at a temperature of 38° C. and a cathode current density of 5 amp./dm² (curve *3*). The results indicate that with

respect to efficiency the optimum sulphate content for a bath 2.5 M in CrO_3 is in all cases approximately 0.05 N, but that with respect to the bright deposit the optimum sulphate content varies with the conditions used. For example, under the conditions represented by curve 2, baths 0.05 N in sulphate produce burnt or frosty deposits and bright deposits are obtained by increasing the sulphate content.

A comparison of the "electrochemical properties" of the "acid," "neutral," and "basic" types of bath was next made. The "electrochemical properties" of an electroplating solution (as applied to the cathode) may be defined as those properties which determine the result of electrolysis in so far as the cathode is concerned. They are (1) cathode polarization, (2) solution resistivity, (3) cathode efficiency, and (4) throwing power, which is a resultant of the first three factors.

TABLE 1

Type of bath	Constituents	Actual initial composition			"C. P." chemicals used	
		M	N	g/L	Purity	g/L
					Per cent	
"Acid"	Chromic acid	2.50		250	99	253
	Sulphuric acid		0.05	2.5	95	2.6
"Neutral"	Chromic acid	2.50		250	99	253
	Chromic sulphate		.05	3.3	72	4.5
"Basic"	Chromic acid	2.50		250	99	253
	Chromic sulphate [1]		.05	3.3	72	3.0
	Chromic carbonate		.15	5.9	84	7

[1] As mentioned previously, the chromic carbonate used in this investigation contained 16 per cent $Cr_2(SO_4)_3$. This correction has been applied in the computation of the actual sulphate content.

For this study the solutions indicated in Table 1 were used. In addition to the actual initial compositions of these baths (as predetermined by analysis of the constituents), the purities and quantities of the so-called "C. P." chemicals used in preparing them are also given. All of the baths contained 250 g/L of CrO_3 and were 0.05 N in sulphate, the optimum sulphate content for the conditions used. It will also be observed that the "acid" bath is the type of solution used by Carveth and Curry, that the "neutral" bath is well within the range of compositions indorsed by Sargent, and that the "basic" bath is identical in every respect with that previously suggested by this bureau. It is of interest that the sulphate impurity in the carbonate used in the "basic" bath and in the original bath at the Bureau of Engraving and Printing was just sufficient to give the optimum sulphate content for the conditions used.

Electrode polarization, solution resistivity, and cathode efficiency were determined simultaneously by means of the apparatus and method previously described by one of the authors.[18] The results

[18] H. E. Haring, Trans. Am. Electrochem. Soc., **49,** 417; 1926.

obtained for polarization and resistivity were found to agree closely with calomel electrode and a. c. conductivity measurements, respectively.

The cell used for these experiments was of such dimensions that the four electrodes divided the solution into three equal cubical portions, 5.0 cm. on a side. The interior of the hard rubber cell was protected from attack by chromic acid by means of a bituminous paint.[19] It was found that the gauzes might consist of any metal which becomes passive in chromic acid. In time all such metals reach practically the same potential. For these experiments nickel gauze which had been chromium plated was used. To insure that these electrodes would be in equilibrium with the solution in which they were to be used, they were immersed in it for 24 hours prior to the experiment. The static potential e_h of these electrodes, regardless of which of the three solutions was involved, was invariably $+1.25 \pm 0.01$ V (measured with a normal calomel electrode).

A cathode of sheet steel and an anode of sheet lead were used in each experiment. All measurements were made with the bath at $45 \pm 1°$ C. In order to facilitate temperature control, the cell was immersed in a water bath which could be heated or cooled as desired.

Measurements were made at various current densities as described in the article previously mentioned. The determination of cathode efficiency was based on the weight of chromium deposited by the current used. Theoretically one ampere hour deposits 0.323 g. of chromium from a valence of six. A potentiometer was used for the voltage measurements, although experiments indicated that a high resistance voltmeter would be satisfactory for approximate results. It was found that for all practical purposes, equilibrium was reached in a few minutes after insertion of the cathode had closed the circuit. The length of the runs was usually one-half hour.

The results of this study are illustrated by Figures 2 and 3 and Table 2. It is evident that *all of the electrochemical properties of the three solutions are identical* and that they should, therefore, give identical results when used for plating purposes.

TABLE 2.—*Resistivity of chromic acid baths at $45 \pm 1°$ C.*

Type	Resistivity (ohm–cm)	Free [a] chromic acid (molarity)
"Acid"	1.49	2.50
"Neutral"	1.49	2.50
"Basic"	[b] 1.57	2.35

[a] By "free" chromic acid is meant chromic acid (H_2CrO_4) uncombined with Cr^{III}, to form "chromium chromate" or more correctly, chromium *dichromate*.
[b] This increase of 5 per cent in resistivity is entirely accounted for by the 6 per cent decrease in free chromic acid content, which resulted from the addition of the chromic carbonate.

[19] This paint consisted of equal weights of gilsonite and Mexican asphalt dissolved in a mixture of equal volumes of benzol and petrolic naphtha.
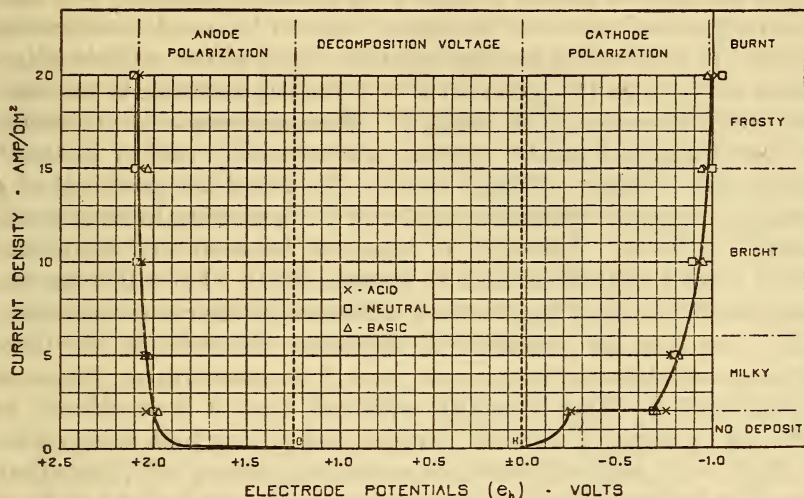
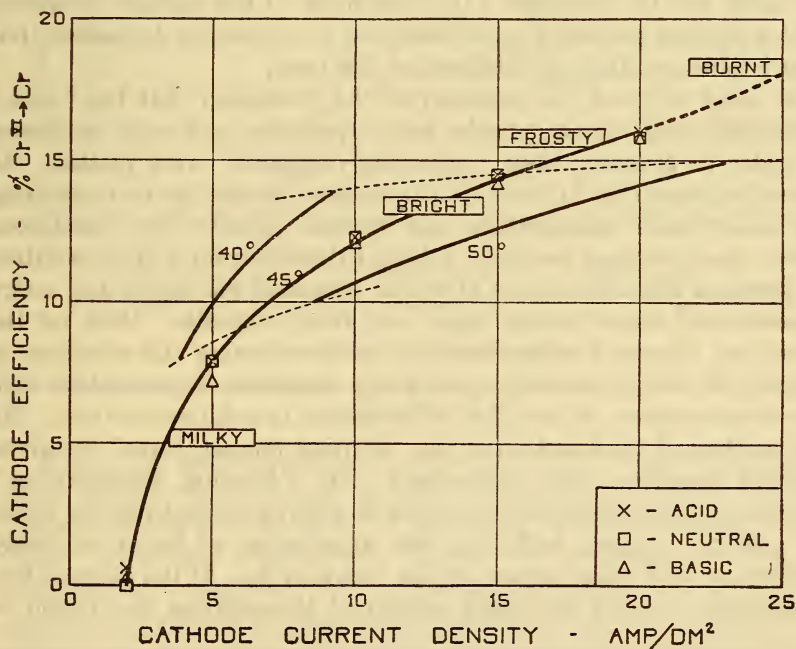FIG. 2.—*Polarization curves in chromium deposition from baths 2.5 M in CrO₃ and 0.05 N in SO₄*

FIG. 3.—*Cathode efficiency curves in chromium deposition from baths 2.5 M in CrO₃ and 0.05 N in SO₄*

In plotting Figure 2, it was assumed that the measured potential (e_h) of the passive gauzes ($+1.25$ V in all three solutions) was that of an oxygen electrode and the logical origin of the anode polarization curves. It was further assumed that the origin of the cathode polarization curves was the potential of a hydrogen electrode in the solutions which must then [20] be $+0.02$ V. Measurements of the hydrogen ion concentration of dilute [21] chromic acid solutions made by Britton [22] confirm the accuracy of these values. He found the potential of a hydrogen electrode against a 0.02475 M CrO₃ solution to be approximately -0.10 V. The 0.12 V difference between this value and $+0.02$ V for a 2.50 M solution is approximately what might be predicted on the basis of the 100-fold difference in their concentrations.

The fact that the potentials of the gauze electrodes in the three solutions are identical means that there is no measureable difference in their acidity. This is readily explained when it is considered, as indicated by Figure 2, that the chromic acid plating bath has an acidity of pH -0.3 and is therefore an exceedingly strong acid, more than normal in hydrogen ions; in consequence, a change in the acidity of only 0.05 N can have no appreciable effect on the pH.

The break in the cathode polarization curves is coincident with the initiation of gassing. At current densities below the gassing point no metal can be deposited. It is the belief of the authors, however, that hydrogen evolution is not essential to chromium deposition, but that it is unavoidable in solutions of this type.

In order to check the accuracy of the prediction that the "acid," "neutral," and "basic" baths were equivalent not only in theory but also in practice, their "operating diagrams" were plotted. In these diagrams (fig. 4) in which the coordinates are the two operating variables—bath temperature and current density—the conditions which must be used to obtain a bright deposit from a given solution lie between two curves, one of which separates the bright and milky deposits and the other the bright and frosty deposits. Data for the operating diagrams were obtained by electrolyzing the solutions in exactly the same manner as previously described in connection with the determination of the effect of a change in sulphate content. By the method of trial and error the "limiting temperatures" for given current densities were determined. By "limiting temperatures" are meant those temperatures which at a given current density result in a bright deposit with the first appearance of burnt or frosty corners, or of a milky center, as the case may be. If the cathode had completely covered the cross section of the solution the region of

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[20] It has been well established that in any aqueous solution the true equilibrium potential of a hydrogen electrode is always 1.23 V more negative (less noble) than the true equilibrium potential of an oxygen electrode in that solution.

[21] The hydrogen electrode does not function as such in concentrated solutions of chromic acid.

[22] J. Chem. Soc., **125**, p. 1572, 1924.

bright deposits would have been slightly broader, but the results given are more closely indicative of what would be obtained in actual practice.

Regardless of which of the three solutions was used, the same results were obtained both as regards the character of deposit and the efficiency of deposition, which was determined at the points indicated on the curves. The results of these comparative studies of the "acid," "neutral," and "basic" baths are not so surprising when it is considered that heretofore the basis of distinction between them has been a difference in acidity—a difference which recently available information, on the *actual* acidity of such baths, has shown to be so slight as to be negligible. The distinction between these three types of bath has thus proved psychological rather than real.
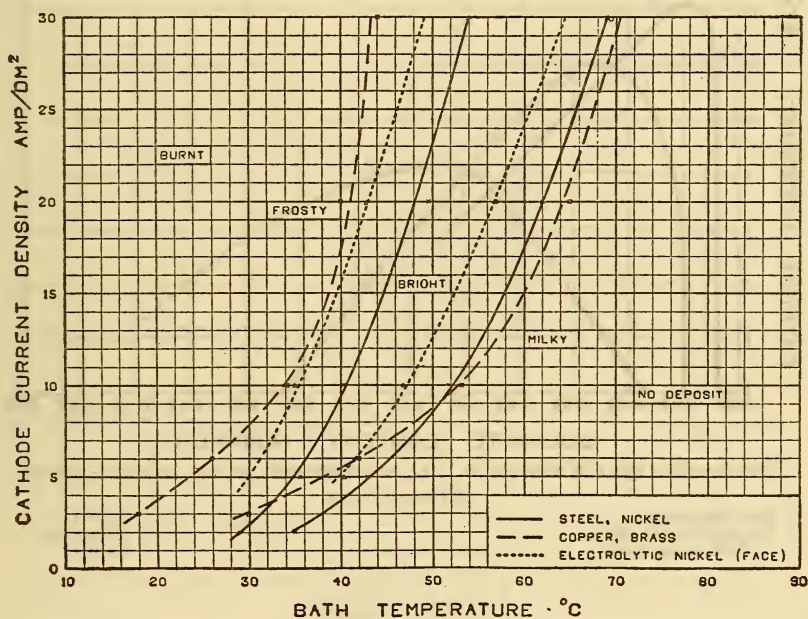

Fig. 4.—*Operating diagrams on different metals for a bath 2.5 M in CrO₃ and 0.05 N in SO₄*

If then no real change has been effected in the chromium plating bath since it was first used in 1856, it is evident that the industrial success of the process must be attributed solely to careful control. Many years ago results fully as good as the best of to-day were undoubtedly obtained [23] but apparently not maintained. Maintenance of quality is, of course, prerequisite to commercial application. Chromium plating is, and always will be, a process which must be very carefully controlled for best results. It has been a realization of

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[23] For example, as previously mentioned, Carveth and Curry stated that some of their deposits "without finishing by buffing, etc., resemble the very finest work done with silver."

this fact, induced by the rapid advances which have been made recently in all lines of plating as the result of more careful control, that has made chromium plating an industrial factor.

IV. BATH CONCENTRATION

In order to determine the effect of changes in concentration on the character of deposit and the efficiency of deposition, a comparative study was made of baths which were, respectively, 0.75, 2.50, and 5.00 M in CrO_3. Sulphate-efficiency curves for these three solutions are plotted in Figure 5. The sulphate was added as chromic sulphate,
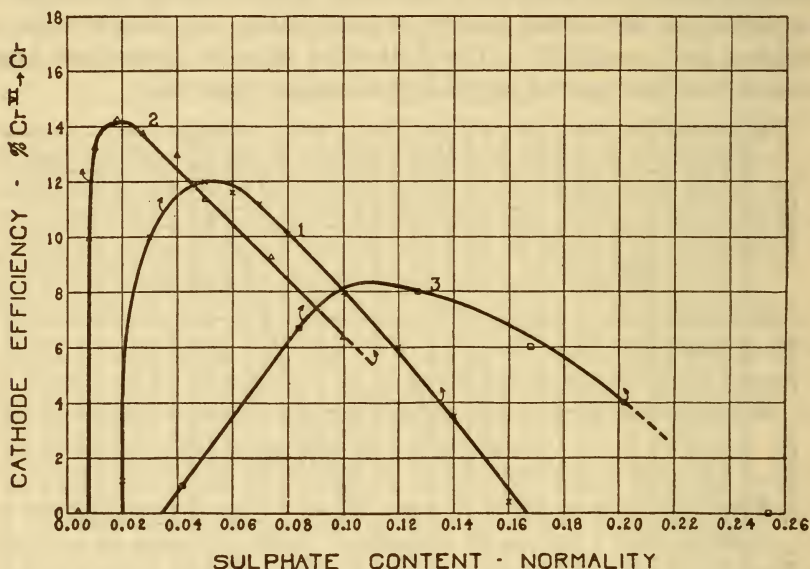

FIG. 5.—*The effect of changes in CrO_3 concentration on the sulphate-cathode efficiency curve*

Bath temperature... 45±1° C.
Cathode current density.. 10 amp./dm².
Cathode composition... Steel.

Curve	CrO_3 (molarity)
1	2.50
2	.75
3	5.00

"Bright" deposits are formed between the arrows.

although as has been stated, the form in which it was added is of no consequence. It will be observed that in all cases the optimum sulphate content bears a definite relation to the CrO_3 content. This relation may be expressed as $\dfrac{CrO_3 \text{ molarity}}{SO_4 \text{ normality}} = 50$. For CrO_3 and H_2SO_4 it is equivalent to a weight ratio of 100 to 1. This proportionality does not necessarily apply to conditions widely different from those used in these experiments.

A decrease in the CrO_3 concentration is accompanied by a desirable increase in efficiency, but also by an undersirable increase in resistivity; and conversely. It is not surprising then that baths of moderate concentration, such as 2.5 M, have been most frequently used in the past. Experience had shown that, in general, the use of dilute chromic acid baths requires higher plating voltages than are ordinarily available; but on the other hand, the low efficiency obtained with the concentrated bath did not seem necessarily objectionable when the greatly increased conductivity was considered. In order to determine how a bath 5.0 M in CrO_3 and 0.10 N in sulphate, would compare in practice with the one 2.5 M in CrO_3 and 0.05 N in sulphate, their operating diagrams were plotted. (Fig. 6.)
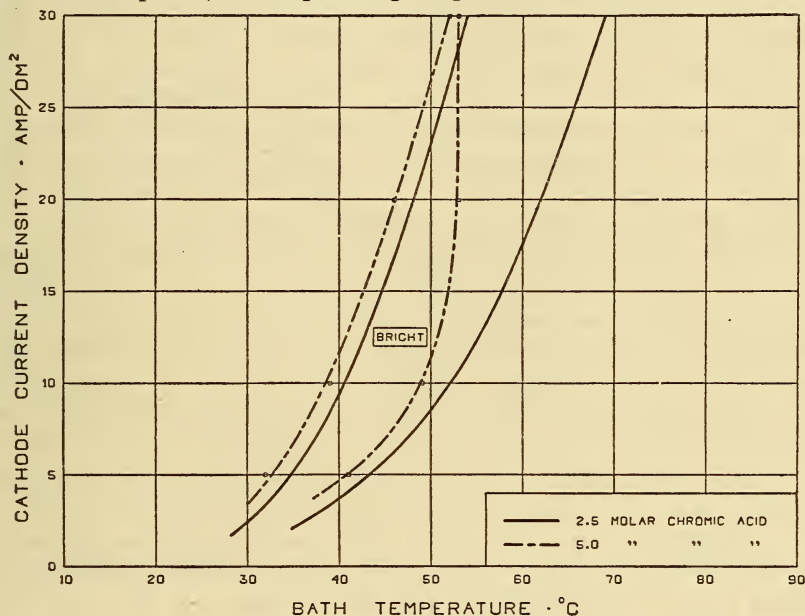
Fig. 6.—*The effect of bath concentration upon the operating diagram on steel*

The conditions under which a bright deposit can be obtained in the 5.0 M bath are so limited that it seems undesirable for plating purposes.

In the light of these results, it seems likely that chromic acid plating baths of moderate concentration, such as 2.5 M, will continue to be most generally useful.

V. "FREE" AND "COMBINED" CHROMIC ACID

In the type 3 or "basic" bath previously discussed, the concentration of free chromic acid was slightly decreased as the result of combination of a part of it with chromic carbonate to form the supposedly desirable chromium dichromate. In like manner, the free chromic acid is decreased and a dichromate is formed by the

48448°—27——3

addition to the bath of any basic or reducing substance or merely by the electrolytic reduction, which is an unavoidable accompaniment of chromium deposition. In any case an equivalent amount of that component of the bath which carries practically all of the current (the first hydrogen of chromic acid) is neutralized and as a result the resistivity is proportionally increased. It has already been demonstrated that chromium dichromate has no beneficial effect on a bath, and since its presence involves a corresponding decrease in free chromic acid, it is undesirable. In practice, chromium plating baths have frequently been rendered practically inoperable at the available voltages simply because of the accumulation of a large amount of this colloid. The resistivity of chromic acid baths is extremely low in comparison with the resistivities of other plating baths, but because of the relatively great current densities required it is still of real importance. Under ordinary plating conditions, however, it is practically impossible to prevent the formation in the bath of a limited amount of chromium dichromate as a by-product of chromium deposition, but as will be shown later, it is readily possible to prevent objectionable accumulations of it.

In order to determine whether the increased resistivity resulting from a decrease in the free chromic acid content of a bath would be compensated by practical advantages arising from the presence of a dichromate, a series of experiments was made with solutions 0.75 and 1.25 M in free chromic acid and 1.75 and 1.25 M, respectively, in "combined" chromic acid in the form of sodium dichromate, and the results were compared with those obtained with the solution 2.50 M in free chromic acid. Sulphate-efficiency curves for these solutions were first determined. In these experiments the sulphate was added in the form of Na_2SO_4. The results which are plotted in Figure 7 show that the optimum sulphate content is again determined by the concentration of free chromic acid and that the 50:1 ratio of CrO_3 to SO_4 still applies. A comparison of curve 3 (fig. 7) with curve 2 (fig. 5) shows that aside from a few minor changes in the form of the curves the only effect of the presence of the dichromate was to slightly lower the efficiency.

The operating diagrams for the three solutions containing in each case the optimum amount of sulphate were found to be practically coincident.

As a result of these experiments it seems reasonable to conclude that combined chromic acid in either soluble or insoluble form serves no useful purpose in a chromium plating bath.

VI. BATHS CONTAINING COMPOUNDS OTHER THAN SULPHATES

Carveth and Curry demonstrated that sulphate is, of itself, not an essential ingredient of the chromic acid bath. Small amounts of compounds, such as chlorides, nitrates, fluorides, phosphates, and borates have been proposed, and in some cases shown to be satisfactory substitutes. Experiments made by the authors indicated that the fluoride was one of the most promising of these additions.
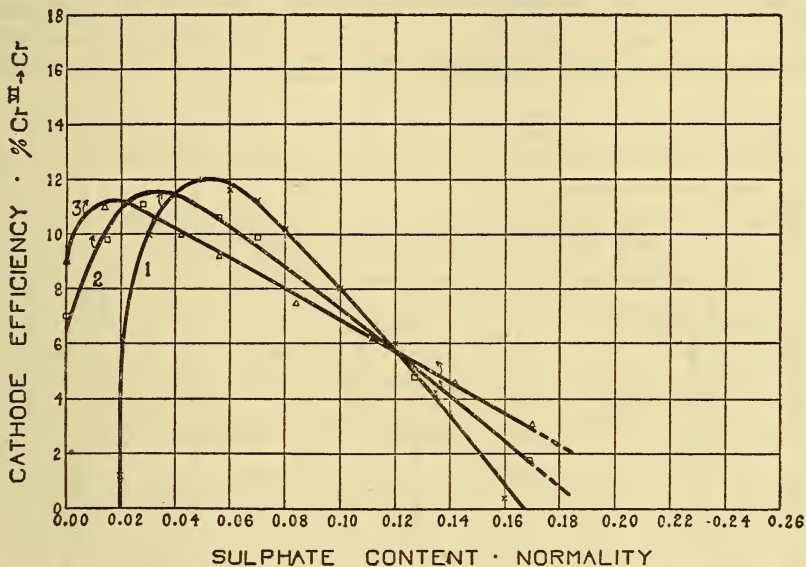
FIG. 7.—*The effect of "free" CrO_3 concentration on the sulphate-cathode efficiency curve*

Bath temperature_____ 45±1° C.
Cathode current density_____ 10 amp./dm².
Cathode composition_____ Steel.

	CrO_3 (molarity)	
Curve	Free	Combined ($Na_2Cr_2O_7$)
1_____	2.50	0.00
2_____	1.25	1.25
3_____	.75	1.75

"Bright" deposits are formed between
the arrows.

A fluoride-efficiency curve for a solution 2.5 M in CrO_3 containing increasing amounts of sodium fluoride is shown in Figure 8. The difference between the maximum efficiency obtained with such a solution and that obtained under the same conditions from a bath

2.5 M in CrO_3 containing sulphate (curve 2, fig. 8) may be considered as within the experimental error. The only real difference between the two curves has to do with their extent. At first glance it might seem that the fluoride solution is the superior bath because the permissible range of fluoride concentration is wider than that of sulphate concentration. However, this fact is probably of no practical significance. It merely indicates that a fluoride in solution is less concentrated in the active principle required than is a sulphate. The active principle is obviously the dissociated anion. If it were possible to plot anion normality as the abscissas in Figure 8, the two curves would probably coincide. This hypothesis is supported by
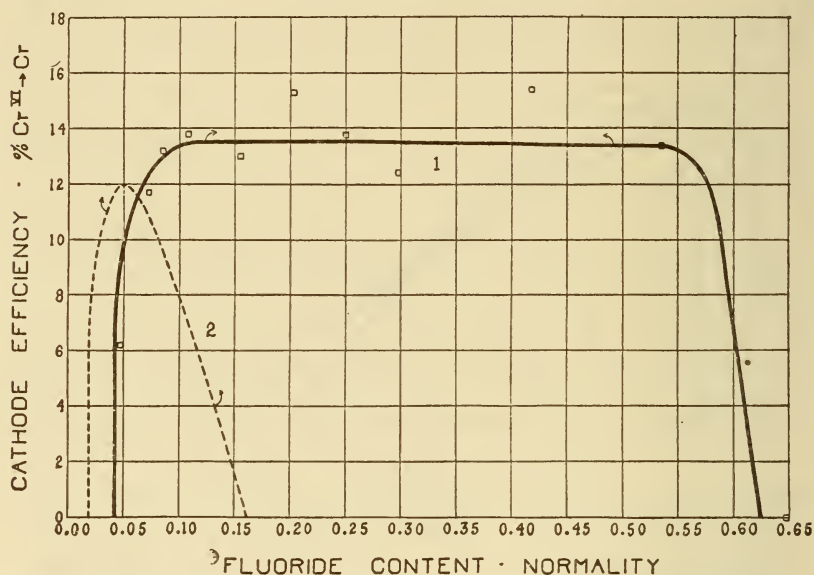

FIG. 8.—(1) *Fluoride-cathode efficiency curve.* (2) *Sulphate-cathode efficiency curve (plotted against sulphate normality)*

CrO₃ concentration -- 2.5 M.
Bath temperature --- 45±1°C.
Cathode current density -- 10 amp./dm².
Cathode composition -- Steel.

"Bright" deposits are formed between the arrows

the fact that the elongation of the fluoride curve is approximately proportional to the difference in the degree of dissociation of hydrofluoric and sulphuric acids.

Possible advantages or disadvantages of the fluoride as an addition can be determined only by an extensive study of the subject.

It seems logical to assume then that the only essential ingredients of a chromic acid plating bath (for depositing pure chromium) are CrO_3 and any anion which will not be decomposed or precipitated by chromium in any of its valences. The form in which this anion is added, whether in combination with hydrogen (as an acid) or with metals ordinarily considered as more negative or more positive than

chromium, seems theoretically to be of no consequence provided only that the metal added is not itself deposited.

Because of the limited number of anions which can be satisfactorily substituted for the sulphate ion no attempt was made to prove this theory. However, experiments made by the authors with solutions containing chromic acid and acetic acid in various concentrations definitely showed that chromium could be deposited from such solutions and that the most favorable concentration of acetic acid was approximately that which might be predicted from its low degree of dissociation.

VII. THE ANODE

The anodes used in chromium deposition have, in general, been of the insoluble type and the chromium content of the bath has been maintained by periodic additions of CrO_3. It has been demonstrated by Schwartz [24] and others that metallic chromium is readily soluble in baths containing chromic acid; however, probably because pure chromium has been decidedly less expensive in the form of CrO_3 than in the metallic state, chromium anodes have been rarely used commercially. In order that the composition of a chromic acid bath be satisfactorily maintained it is essential that the anode be of such composition and area as to permit the complete oxidation to chromic acid of the chromium dichromate formed at the cathode during electrolysis. Otherwise, as previously indicated, the bath may become inoperable on account of the gradual increase in resistivity resulting from the decrease in free chromic acid. Because there must be a finite distance between the electrodes, there will, of necessity, be a small amount of the colloidal dichromate in transit to the anode, unless free sulphuric acid is present, as may be the case under conditions exceedingly favorable to oxidation. If sulphuric acid is available, chromic acid and chromic sulphate will be immediately formed by its action on the chromium dichromate.

Both lead and iron anodes have been extensively used commercially, but practically no information as to their relative merits is available. A comparative study of their behavior was therefore made. For these experiments a previously used solution was selected which happened to be 2.8 M in total CrO_3 and which contained initially a relatively large amount of chromium dichromate. Two 600 cc samples of this solution were electrolyzed in series; in one bath lead anodes were used and in the other, iron anodes (in the form of sheet steel). A 24-hour run was made with the anode area one-third that of the cathode, and then, using fresh portions of the original solution, with an anode area three times that of the cathode. In each bath a cathode of sheet steel 5 by 5 cm was suspended midway between the

[24] Trans. Am. Electrochem. Soc., **44**, p. 451; 1923.

anodes that were in contact with the opposite sides of the electrolyzing vessel, which was a rectangular glass jar (9 by 9 by 13 cm). The electrolyses were conducted at a temperature of $45 \pm 1°$ C. and a cathode current density of 10 amp./dm ^{2}. The baths were covered to prevent loss in volume by evaporation or spray. The results of these experiments are given in Table 3.

TABLE 3.—*A comparative study of lead and iron anodes*

Ratio of electrode areas (anode: cathode)	Anode composition	Chromium dichromate normality (Cr III)		Percentage of total CrO_3 in "free" state	
		Initially	After electrolysis	Initially	After electrolysis
1:3	Lead	0.46	0.15	84	95
	Iron	.46	1.24	84	50
3:1	Lead	.46	.05	84	98
	Iron	.46	.93	84	65

It is apparent that the composition of the anodes is far more important than their area (which, of course, determines the anode current density). As could be predicted, the large anodes were most favorable to oxidation, but the figures show that regardless of area, the use of iron anodes resulted in a considerable increase in chromium dichromate which was objectionably high initially. On the other hand, the use of the lead anodes regardless of their area resulted in a considerable decrease in the concentration of chromium dichromate. Further electrolysis with the large lead anodes would probably have effected the complete removal of the colloidal dichromate and even possibly have oxidized some but not all of the chromic sulphate to chromic acid and sulphuric acid. In any case an equilibrium is eventually reached. In this connection it is of interest that the 1:2 ratio of anode and cathode areas previously used at the Bureau of Engraving and Printing was chosen because it permitted the maintenance of the original "chromium chromate" content of the bath, which was then considered desirable.

The difference in the behavior of lead and iron anodes can be attributed to differences in oxygen overvoltage. The overvoltage of oxygen on lead is high and on iron relatively low, and as a consequence lead, the metal upon which it is most difficult to evolve oxygen, is the one most favorable to oxidation of Cr^{III} to Cr^{VI}.

In the light of these results it seems reasonable to conclude that the continual use of iron anodes will eventually reduce the concentration of free chromic acid in a bath to such an extent as to render it inoperable except at prohibitive voltages. Lead anodes, on the contrary, are perfectly satisfactory. They should have as large an area as is conveniently possible. Lead-coated iron anodes might sometimes be used to advantage.

A few experiments made by the authors with chromium anodes indicated that their use results in a rapid accumulation of chromium dichromate, undoubtedly due to the solution of chromium as Cr^{III}. If chromium anodes are to have any extensive commercial application, the free chromic acid content of the bath must be maintained either by the use of special operating conditions or conceivably by periodic chemical oxidation.

VIII. THE CATHODE. THROWING POWER AND THE "PLATING RANGE"

Chromium would be more extensively applied to-day were it not for the fact that it is difficult and often impossible to deposit it satisfactorily upon irregularly shaped objects. In any plating operation it is primarily essential that a deposit be obtained which has the desired physical properties, such as structure, color, and luster; the quantitative distribution of the deposit, although of importance, is secondary. In most plating processes, however, satisfactory deposits are obtained over such a wide range of operating conditions that their quality is usually accepted as a matter of course and quantitative distribution only is considered. In chromium plating, on the other hand, the range of conditions under which satisfactory deposits can be obtained is so limited that the question of metal distribution must be considered in both its qualitative and quantitative aspects.

The character of the deposit on various parts of a cathode, or, in other words, qualitative distribution is determined by the "plating range" which may be defined as the range of cathode current densities within which satisfactory deposits are formed. By satisfactory in this particular case is meant bright. For many purposes frosty or milky chromium deposits are also suitable, but it seemed logical to focus this investigation upon that type of deposit which is most generally applicable.

The quantitative distribution of metal on a cathode is determined by the "throwing power" of the solution used. It has been shown [25] that throwing power in metal deposition is the resultant of three factors: (1) The change in cathode polarization with current density; (2) the resistivity of the solution; and (3) the change in cathode efficiency with current density.

Figure 2 shows that although in chromium plating the cathode polarization is high, the change effected in it by a change in current density within the range of bright deposits (6 to 15 amp./dm²) is exceedingly small—only 0.01 V/amp./dm² as compared to 0.05 V/amp./dm² in the acid copper bath and 0.8 V/amp./dm² in the cyanide copper bath. From this fact alone it could be predicted

[25] H. E. Haring and W. Blum, "Current distribution and Throwing Power in Electrodeposition," Trans. Am. Electrochem. Soc., **44**, p. 313; 1923.

that there can be no appreciable positive throwing power in chromium deposition. There is, furthermore, no reason to believe from present indications, that the slope of the cathode polarization curve can be materially changed.

Although the resistivity of the chromic acid bath is relatively low, the necessary use of high-current densities makes the IR drop (which is a significant factor in throwing power) rather large and, hence, still further reduces the small effect of the relatively low change in polarization. There is no prospect of greatly reducing the resistivity of an otherwise satisfactory chromic acid bath. The use of higher concentrations of CrO_3 lowers the resistivity, but as previously noted the conditions under which a satisfactory deposit can then be obtained are so limited that such a change is undesirable.

The principal cause, however, of the very low and in fact decidedly negative throwing power in chromium deposition is the great decrease in cathode efficiency which accompanies a decrease in current density. For example, as shown in Figure 3, no deposit is obtained on steel at less than 2 amp./dm² from a 2.5 M CrO_3 solution at 45° C. and even at 6 amp./dm² the efficiency is less than 9 per cent.

The low efficiency in chromium deposition, especially at the lower current densities, can be attributed to the fact that the bath involved is essentially chromic acid, a powerful oxidizing agent. In consequence, reduction of the solution at the cathode must be effected before metal can be deposited and as a result those parts of the cathode upon which the current density is less than sufficient to accomplish this reduction, receive no deposit, and even on those parts upon which the current density is somewhat higher the efficiency is still extremely low. Because this condition is due to an inherent property of the solution it is doubtful whether the throwing power of the chromic acid plating bath can ever be decidedly improved by the necessarily limited changes which can be made in its composition.

It is therefore especially desirable that those operating conditions be selected which are most favorable to an improved throwing power. For example, an increase in bath temperature (which must, of course, be accompanied by a corresponding increase in cathode current density) results in a more nearly horizontal efficiency curve (fig. 3) at least within the region of bright deposits, and must, therefore, increase throwing power. Moderate agitation of the bath was found to be without effect on the efficiency of chromium deposition. It is quite conceivable, however, that a form of agitation which would cause a more rapid replacement of the solution in contact with the high-current-density areas of a cathode than of that in contact with the low-current-density areas would have a beneficial effect on throwing power. Such agitation might be afforded either by movement of the solution, or of the "work" as, for example, when mechanical conveyors are used.

It seems more probable that progress on the plating of recessed objects with chromium will be made as the result of an extension of the plating range rather than through any improvement in throwing power. In chromium deposition the lower limit of the plating range is a relatively high current density which varies widely with the conditions used. Whether an irregularly shaped article can be chromium plated depends, therefore, not merely on the actual extent of the plating range, but also on the ratio of its limiting current densities. For example, in a 2.5 M bath at 45° C. the plating range on steel extends from 6 to 15 amp./dm²; the ratio of the limiting current densities is then 1 : 2.5, and in consequence an entirely bright deposit can be obtained only on objects upon which the highest current density will not be more than 2.5 times the lowest current density.

Although the indications are that all of the 2.5 M chromic acid baths containing sulphate mentioned in this investigation have identical operating diagrams and, therefore, the same plating range, a change in bath concentration was found to have a marked effect. Comparison of the operating diagrams (for steel cathodes) of 2.5 and 5.0 M solutions (fig. 6) shows that at the lower temperatures the plating ranges are similar, but at temperatures above 50° the plating range of a 2.5 M bath continues to widen while the plating range of a 5.0 M solution rapidly narrows until at 53° it is no longer possible to obtain a bright deposit at any current density. The conclusion should not be drawn, however, that the plating range of a 2.5 M solution continues to increase until the boiling point of the solution is reached. A few experiments indicated that constriction of the zone of bright deposits for such a bath begins at about 65° for a steel cathode, and that the regions of burnt and milky deposits eventually merge just as in the case of the 5.0 M solution.

TABLE 4.—*Operating data for a bath 2.5 M in CrO₃ and 0.05 N in SO₄*

Cathode	Bath temperature	Ratio of limiting current densities	Optimum average current density	Approximate average efficiency	Time required to deposit average of 0.005 mm. or 0.0002 inch
	° C.		Amp./dm²	Per cent	Minutes
Steel or nickel	35	2.5	3.5	7	255
	40	2.5	6.5	10	96
	45	2.6	10.5	12	50
	50	2.7	16.0	13	30
	55	2.6	21.5	14	21
Copper or brass	35	2.6	7.5	11	76
	40	3.1	11.0	13	44
	45	4.7	20.0	15	21
	50	5.0	25.0	17	15
Electrolytic nickel face	35	3.2	6.0	9	116
	40	3.2	10.5	12	50
	45	2.7	15.5	14	29
	50	2.4	22.0	15	19

The effect of temperature and current density upon the plating ranges in chromium deposition can best be illustrated by a comparison of the ratios of their limiting current densities. Such a comparison is made in Table 4. The results illustrate the impossibility of defining in general terms the most satisfactory conditions for chromium plating. However, it may be concluded that a temperature favorable to a satisfactory deposit, on most metals, from a bath 2.5 M in CrO_3 and 0.05 N in SO_4 lies between 40 and 60° C. and that, in general, it will be found advisable, not only because of the beneficial effect on the plating range but also on the efficiency of deposition (see Table 4), to use high temperatures and high current densities.

The solution and operating conditions do not alone determine the plating range. The composition of the cathode is of extreme importance, as indicated by Figure 4 and Table 4. The plating range on copper and brass is approximately twice that on steel and nickel, and the lower current density limit of the bright deposit is practically the same for all of these metals. Obviously, then, as could also be predicted from Table 4 and as has been confirmed by experience, irregularly shaped objects of copper or brass can be much more readily chromium plated than those of steel or nickel.

The overvoltages of hydrogen upon copper and brass are about equally high, while upon steel and nickel they are relatively low and about equal. The difference in the character of the deposit obtained on various metals can, therefore, be attributed to the difference in the overvoltages of hydrogen upon those metals, and the conclusion can be drawn that the higher the overvoltage of hydrogen upon a metal the less critical are the conditions under which it can be satisfactorily chromium plated.

These results suggest the possibility of increasing the plating range on such metals as steel and nickel by increasing the overvoltage of hydrogen upon them, for instance, by lightly plating them with copper. It was found that the operating diagrams for solid copper and copper-plated cathodes were identical, and practical experience has demonstrated that the expedient of flashing a metal of low hydrogen overvoltage with copper is of considerable value. In such a procedure it is essential to obtain good adherence of the copper coating, otherwise it may "peel" during the deposition of chromium.

To be complete, a study of metal distribution in chromium plating should include a consideration of the treatment of the cathode immediately prior to deposition. For example, (1) the plating circuit may be closed after the cathode has been immersed in the solution, (2) the plating circuit may be closed by the introduction of the cathode, or (3) the object to be plated may, with the aid of a reversing switch, be made anode and then after a short time, cathode.

The first method of treatment obviously can not be used on metals, such as brass and lead, that are attacked by chromic acid. It has also been found [26] to be undesirable, at least in so far as throwing power is concerned, for metals, such as iron and nickel, which are tendered passive by chromic acid. On the other hand, it was further found that metals which are attacked by chromic acid can be satisfactorily plated, and the throwing power obtained on metals which become passive can be greatly improved by the use of the second method. The third treatment has been used by some concerns as a method for cleaning iron, steel, and similar metals prior to plating. It can not, of course, be used for metals which are attacked by the bath. In addition to being an efficient cleaning method, the indications are that its use results in an improvement in metal distribution even greater than that afforded by method (2). Because the metal to be plated upon is rendered passive by such anodic treatment, these results may seem anomalous. However, any improvement in throwing power can be explained on the basis of a difference in the degree of passivity on various parts of the object. Those parts which are ordinarily most readily plated will as the result of brief anodic polarization contain oxygen in higher concentration than those recessed parts ordinarily difficult to plate, and then upon reversing the current, it must be at least momentarily easier to deposit metal in the recesses because of their lower oxygen content and, therefore, more negative (less noble) potential.

As indicated, it does not seem likely that the chromic acid plating bath will ever be particularly adapted to the plating of recessed articles, but careful investigation of all of the factors involved will undoubtedly extend its usefulness. For example, the results of this brief study of the subject indicate that a satisfactory distribution of chromium on an irregularly shaped object is favored by (1) the use of baths of as low a CrO_3 concentration as is otherwise convenient, (2) the use of relatively high temperatures and current densities, (3) selection whenever possible of a cathode metal upon which the overvoltage of hydrogen is high, or else the deposition of a thin coat of such a metal on the cathode prior to chromium plating, (4) the introduction of the cathode into the bath in such a manner that its immersion closes the plating circuit, or (5) polarizing it anodically for a minute or two previous to plating. (As stated, the latter treatment is applicable only to those metals which become passive in chromic acid.)

However, notwithstanding any improvements thereby effected, the successful plating of recessed articles with chromium will depend largely on so arranging the "work," racks, and anodes that the current density over the cathode surface will be as nearly uniform as possible. Results which would otherwise prove impossible can often be obtained by ingenious arrangements of this kind.

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[26] H. E. Haring, Chem. and Met. Eng., **32**, pp. 692 and 756; 1925.

In depositing chromium upon any object it is desirable to use that current density which is the mean of the limiting current densities for the bath temperature involved. A current density so chosen will be in the center of the plating range and in consequence will be the one most favorable to a uniformly satisfactory deposit. A few of these optimum current densities for different metals in the 2.5 *M* bath at different temperatures are shown in Table 4, together with the approximate efficiencies and the time required to deposit 0.005 mm (0.0002 inch) of chromium at those current densities. This thickness is probably the maximum that will be used on most commercial work.

Chromium deposits can be readily removed from practically all metals, including steel and nickel, by means of dilute hydrochloric acid.[27] Rapid action is, of course, favored by an increase in the temperature or concentration of the acid.

IX. BATH MAINTENANCE AND ANALYTICAL METHODS

The maintenance of a chromic acid plating bath is a relatively simple matter if lead anodes are used. No large amount of chromium dichromate can then accumulate in the bath, which will, hence, contain practically nothing but its initial constituents. Because about 99 per cent of the material dissolved in the bath is chromic acid, its approximate concentration can be readily determined by means of a hydrometer and a density table such as Table 5. Results so obtained are usually sufficiently accurate for all practical purposes. If, however, an appreciable amount of chromium dichromate is present, the method is no longer applicable. In any event the sulphate content must be occasionally determined and corrected in order to preserve the proper ratio of CrO_3 to SO_4.

TABLE 5.—*Density of chromic acid solutions as a function of the CrO_3 content* [a]

Density $\left(\frac{15°}{4°} C.\right)$	CrO_3 content			Density $\left(\frac{15°}{4°} C.\right)$	CrO_3 content		
	Molarity	g/L	oz./gal.		Molarity	g/L	oz./gal.
1.01	0.15	15	2.0	1.18	2.57	257	34.4
1.02	.29	29	3.9	1.19	2.72	272	36.4
1.03	.43	43	5.8	1.20	2.88	288	38.6
1.04	.57	57	7.6	1.21	3.01	301	40.3
1.05	.71	71	9.5	1.22	3.16	316	42.3
1.06	.85	85	11.4	1.23	3.30	330	44.2
1.07	1.00	100	13.4	1.24	3.45	345	46.2
1.08	1.14	114	15.3	1.25	3.60	360	48.2
1.09	1.29	129	17.3	1.26	3.75	375	50.2
1.10	1.43	143	19.1	1.27	3.90	390	52.2
1.11	1.57	157	21.0	1.28	4.06	406	54.5
1.12	1.71	171	22.9	1.29	4.22	422	56.5
1.13	1.85	185	24.8	1.30	4.38	438	58.7
1.14	2.00	200	26.8	1.31	4.53	453	60.7
1.15	2.15	215	28.8	1.32	4.68	468	62.7
1.16	2.29	229	30.6	1.33	4.84	484	64.8
1.17	2.43	243	32.6	1.34	5.00	500	67.0

[a] From data compiled by J. A. Beattie for International Critical Tables. (The McGraw-Hill Book Co., New York.)

[27] The Application of Chromium Plating to Printing Plates, Bureau of Standards Letter Circular No. 177; 1925.

The chromium content of the bath is gradually decreased as the result of chromium deposition and of mechanical losses of the solution. On the other hand the sulphate content is decreased by mechanical losses only. In consequence, in order to restore a used bath to its original composition the proportion of CrO_3 and SO_4 which must be added is somewhat greater than the initial ratio of $\dfrac{CrO_3 \text{ molarity}}{SO_4 \text{ normality}} = 50$. If it were possible to prevent mechanical losses the bath could be maintained by the addition of CrO_3 alone. "Drag out" can be minimized by using the rinse water to replace that lost by evaporation. "Spray losses," however, can not be so readily eliminated. The chromium lost in the spray at the Bureau of Engraving and Printing is about equal to that deposited. In consequence, it is necessary to add the CrO_3 and H_2SO_4 approximately in the ratio, by weight, of 200:1 instead of 100:1 as in the preparation of the baths. Mechanical losses of solution may vary greatly, however, depending on circumstances and, therefore, no safe generalization can be made.

It might be possible to secure commercial CrO_3 containing as an impurity about 1 per cent of SO_4. Such a grade of acid dissolved in water would make an ideal plating bath, but its use for replenishing purposes would, in time, result in an objectionable accumulation of SO_4. Hence, for general use the CrO_3 should not contain more than 0.5 per cent of SO_4. The presence of even several per cent of alkali salts, such as dichromates, which might be present in the absence of H_2SO_4, is apparently not detrimental, as has sometimes been claimed. It is desirable that the CrO_3 be free from insoluble matter. Experience at the Bureau of Engraving and Printing has shown that the commercially available "98 per cent chromic acid" is quite satisfactory for all purposes. Typical analyses of this grade of acid are given in Table 6.

TABLE 6.—*Typical analyses of "98 per cent chromic acid"*

	(1)	(2)	(3)
	Per cent	Per cent	Per cent
CrO_3	97.7	97.5	97.7
SO_4	.46	.20	.42
Alkali salts [1]	.78	.38	.62
Insoluble matter	.06	.00	.04
Solution in water	Slightly cloudy.	Clear.	Slightly cloudy.

[1] Soluble salts, chiefly sodium or potassium sulphate and chromate, extracted from the insoluble residue obtained by ignition of the acid to Cr_2O_3.

It is, of course, essential that the sulphate content of the chromic acid used be known or determined and that sufficient sulphuric acid or sulphate be added to bring the sulphate content of the bath to the optimum. It has been found most convenient to introduce the sulphate in the form of sulphuric acid, although chromic sulphate which has usually been employed is equally satisfactory. If

chromic sulphate is used, its sulphate content should be known and calculations made on that basis. To be most effective it should be readily soluble in cold water.

If a chromic acid bath is properly operated only a small amount of chromium dichromate will accumulate and periodic adjustments of composition can be made solely on the basis of specific gravity and sulphate content. However, if chromium dichromate is present in considerable quantity, a complete analysis of the solution is necessary. The presence of an undesirable amount of this colloid is made evident by the fact that a much higher voltage is required to produce a certain current density than is warranted by the apparent CrO_3 concentration as measured with the hydrometer. The opacity of the bath is also dependent on the chromium dichromate content and, therefore, furnishes another indication of whether a complete analysis is desirable. Such an analysis involves the determination of Cr^{VI}, Cr^{III}, and SO_4. The results can be conveniently expressed in terms of (1) the molarity of free or uncombined CrO_3; (2) the molarity of combined CrO_3, which is the same as the normality of chromium dichromate to which the formula $Cr^{III}(HCrO_4)_3$ may tentatively be assigned; and (3) the normality of SO_4.

The molarity of free CrO_3 equals the total molarity of CrO_3 (which is determined by the Cr^{VI} content of the bath) minus the molarity of combined chromic acid. The molarity of combined chromic acid is equal to the normality of $Cr(HCrO_4)_3$, which in turn is equal to the Cr^{III} normality of the bath minus the normality of Cr^{III} equivalent to the SO_4 present.

DETERMINATION OF Cr^{VI} AND Cr^{III}.—These analyses can be made either by electrometric or chemical titrations. The electrometric method is the most convenient, but it requires special equipment which is not available in the average plant laboratory. The chemical method will, therefore, be described in this paper.[28] The following reagents are required:

Dichromate solution.—Exactly 5.884 g of $K_2Cr_2O_7$ ("C. P.," recrystallized, powdered, and dried) is dissolved in water and diluted to 1 liter. This solution is 0.0400 M in CrO_3.

Ferrous ammonium sulphate solution.—Approximately 40 g of $FeSO_4.(NH_4)_2SO_4.6H_2O$ and 75 cc of H_2SO_4 (sp. gr. 1.84) are dissolved in water and diluted to 1 liter. This solution must be standardized immediately before use.

Potassium permanganate solution.—Approximately 3.2 g of "C. P." $KMnO_4$ is dissolved in water and diluted to 1 liter.

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[28] The electrometric method is identical with the chemical method except that the Cr^{VI} is determined by direct electrotrometric titration rather than by a back titration as in the chemical method. A permanganate solution is therefore unnecessary.

Manganese sulphate solution.—Approximately 1 g of $MnSO_4.4H_2O$ is dissolved in 100 cc of water.

Silver nitrate solution.—Approximately 2.5 g of $AgNO_3$ is dissolved in 1 liter of water.

Ammonium persulphate solution.—About 10 g of $(NH_4)_2S_2O_8$ is dissolved in 100 cc of cold water. This solution decomposes readily and should be made immediately before use.

The determination of Cr^{VI} involves (1) reduction of Cr^{VI} to Cr^{III} with an excess of the standardized ferrous sulphate solution and (2) titration of the ferrous sulphate not used in the reduction, with the permanganate solution of which the ferrous sulphate equivalent is known. The volume of ferrous sulphate solution actually required for the reduction of Cr^{VI} and the total CrO_3 content of the bath are then readily calculated.

The ferrous sulphate equivalent of the permanganate solution is first determined. Exactly 25 cc of the ferrous sulphate solution is diluted to about 300 cc in a 600 cc beaker and 25 cc of concentrated H_2SO_4 is added. This solution is titrated with the permanganate to the first appearance of a pink color which persists for one minute.

The ferrous sulphate solution is next standardized against the standard dichromate solution. A 25 cc sample of the latter which is equivalent to exactly 0.001 mole of CrO_3 or 0.1000 g CrO_3 is diluted to about 300 cc and 25 cc of concentrated H_2SO_4 is added. After cooling to room temperature, 50.0 cc of ferrous sulphate, which is considerably more than sufficient to reduce the Cr^{VI}, is added, and the excess is titrated with the permanganate to an end point which persists 1 minute. Although somewhat masked by the color of the solution, the end point is readily detected. A correction for the volume of permanganate required to produce the end point can be made by boiling the solution for 10 minutes (which destroys the excess of $KMnO_4$) cooling to room temperature and again titrating to the same end point. The small volume of permanganate required the second time is the "color correction" which when subtracted from the volume used the first time gives the true permanganate equivalent of the excess ferrous sulphate. The ferrous sulphate actually required for the reduction of Cr^{VI} and, hence, the equivalent of the ferrous sulphate in moles of CrO_3 can then be readily calculated.

If the bath to be analyzed is approximately 2.5 M in CrO_3, a 0.50 cc sample (which would contain about 0.001 mole of CrO_3) will be found convenient. Such a sample may be obtained by diluting a 10.00 cc sample of the bath to exactly 500 cc and using a 25.0 cc aliquot. The procedure is identical with that employed in the standardization of the ferrous sulphate. The molarity of total CrO_3 in the bath is equal to 2,000 times the number of moles of CrO_3 found in the sample.

The determination of Cr^{III} involves (1) its oxidation to Cr^{VI}, and (2) titration of total Cr^{VI}. The Cr^{VI} found after oxidation minus the Cr^{VI} found before oxidation is equivalent to the Cr^{III} present in the bath. The Cr^{III} normality is equal to three times this difference in the molarity of the CrO_3.

The same sized sample is taken as in the determination of Cr^{VI} and is likewise diluted to about 300 cc. Approximately 25 cc of concentrated H_2SO_4 and a few drops of the manganese sulphate solution are added and the solution is brought to the boiling point. (The introduction of several glass beads will prevent excessive "bumping".) Ten cc of the silver nitrate solution is then added and *after that* 20 cc of the persulphate solution. Complete oxidation is indicated by the formation of permanganic acid. If this is not formed, more of the persulphate must be added. The solution is boiled for 10 minutes, and while still boiling 5 cc of dilute HCl (1:3) is added and the boiling is continued until the color of the permanganate has disappeared. After cooling to room temperature, the solution is titrated for Cr^{VI} in the same manner as before. The difference between the number of moles of CrO_3 found in this oxidized sample of the bath and in the unoxidized sample previously titrated, multiplied by 6,000 equals the Cr^{III} normality of the bath.

DETERMINATION OF SO_4.—This analysis can be made in the usual way, by precipitation with barium chloride in the presence of sufficient hydrochloric acid to prevent the formation of barium chromate. It is, however, extremely difficult to completely free the barium sulphate so obtained from traces of chromate and the following more accurate method, which involves the precipitation of barium sulphate in the presence of Cr^{III} only, is therefore suggested.

If the bath to be analyzed is approximately 0.05 N in SO_4, a 10 cc sample will be found convenient. After dilution to about 125 cc, 10 cc of HCl (sp. gr. 1.18) is added and next 10 cc of 95 per cent ethyl alcohol. The solution is then boiled until the excess alcohol and the aldehyde formed are removed. Ten cc of a barium chloride solution containing 50 g/L of $BaCl_2$ is slowly added and boiling is continued for a few minutes more. After standing for several hours in a warm place (for example, overnight on a steam bath) the solution is filtered and the precipitate washed, dried, and weighed as $BaSO_4$. The weight of $BaSO_4$ precipitated from the 10 cc sample divided by 1.167 equals the SO_4 normality.

Example

Standardization of solutions—

(1) 25.0 cc $FeSO_4$ required 20.0 cc $KMnO_4$. Hence, 1 cc $KMnO_4$ = 1.25 cc $FeSO_4$.

(2) 50.0 cc $FeSO_4$ was added to 25.0 cc of 0.04 M CrO_3 or 0.001 mole CrO_3 (as $K_2Cr_2O_7$). The excess of $FeSO_4$ required 18.0 cc $KMnO_4$. Therefore, the excess of $FeSO_4 = 18.0 \times 1.25 = 22.5$ cc $FeSO_4$; and 0.001 mole CrO_3 required $50.0 - 22.5 = 27.5$ cc $FeSO_4$. Therefore, 1 cc $FeSO_4 = \frac{0.001}{27.5} = 0.0000364$ mole CrO_3.

Cr^{VI} determination—

To a 0.50 cc sample of the bath, 50.0 cc of $FeSO_4$ was added, and the excess required 12.0 cc of $KMnO_4$, equivalent to $12.0 \times 1.25 = 15.0$ cc $FeSO_4$. Hence, $50.0 - 15.0 = 35.0$ cc of $FeSO_4$ was used by the CrO_3 in 0.50 cc, which was, therefore, $35.0 \times 0.0000364 \times 2000 = 2.55$ M, or 255 g/L total CrO_3.

Cr^{III} determination—

To a 0.50 cc sample, after oxidation, 50.0 cc of $FeSO_4$ was added. The excess required 11.0 cc $KMnO_4$, equivalent to $11.0 \times 1.25 = 13.8$ cc $FeSO_4$. Hence, $50.0 - 13.8 = 36.2$ cc $FeSO_4$ was used by the total Cr as CrO_3 in 0.50 cc. Therefore, the total Cr as CrO_3 is $36.2 \times 0.0000364 \times 2000 = 2.64$ M. The Cr^{III} originally present is then equivalent to $2.64 - 2.55 = 0.09$ M CrO_3. Hence, the normality of the Cr^{III} is equal to $3 \times 0.09 = 0.27$ N.

SO_4 determination—

A 10 cc sample yielded 0.0595 g $BaSO_4$, and the SO_4 content is therefore $\frac{0.0595}{1.167} = 0.051$ N.

Calculation of bath composition—

Total $CrO_3 = 2.55$ $M = 255$ g/L
     $Cr^{III} = 0.27$ N
     $SO_4 = 0.051$ $N = 3.3$ g/L $Cr_2(SO_4)_3$

Hence, Cr^{III} present as $Cr^{III}(HCrO_4)_3 = 0.27 - 0.05 = 0.22$ N, and "combined" $CrO_3 = 0.22$ M or 22 g/L. Then "free" $CrO_3 = 2.55 - 0.22 = 2.33$ M or 233 g/L.

X. EQUIPMENT, POWER, AND COSTS

The equipment required for chromium plating is, in general, quite similar to that required for the electrodeposition of other metals. The tank must, of course, be constructed of a material which will not be attacked by chromic acid and which will withstand the elevated bath temperatures. Stoneware tanks have proved satisfactory at the Bureau of Engraving and Printing. Iron and lead-lined iron tanks have also been used commercially with apparent success.

Facilities must be available for heating and cooling the bath. Temperature control can be facilitated by immersing the plating

tank in water in a larger tank. The heating and cooling coils can be placed either in the plating bath or in the water jacket. Thermostatic control may be feasible, but will be difficult if there are large fluctuations in the current and, consequently, in its heating effect.

Provision must be made for the removal of the fine spray of chromic acid which is evolved from the bath during the plating operation. This spray is injurious to the tissues of the respiratory tract. A suction flue, preferably of sheet iron, with a slot located immediately above the back edge of the bath, so as to draw the gases and spray across the surface of the solution, will eliminate any danger to the operators. A mixture of oxygen and hydrogen, the gases which are evolved at the electrodes during electrolysis, is explosive. The practice of covering a chromium plating bath to prevent the discharge of spray is, therefore, dangerous.

Most plating processes are conducted with 6-volt generators, but a generator of higher voltage is desirable for chromium deposition. Traces of chromium can be deposited on steel from a solution 2.5 M in CrO_3 and 0.05 N in SO_4 at a temperature of 45° C., at about 3 volts, but in order to obtain satisfactory deposits, especially on irregularly shaped articles, a considerably higher voltage is required. Figure 9 furnishes a graphic analysis of the total voltage drop under the conditions mentioned, between two plane, parallel electrodes spaced 10 cm. apart. This diagram shows that 4.5 volts must be applied in order to obtain the optimum current density (10 amp./dm²) for a bright deposit at the temperature specified. If the cathode surface is the "face" of an electrodeposit as when electrolytic intaglio plates, or electrotypes, are plated, approximately twice this current density is employed, necessitating about 6 volts.

Inspection of Figure 9 shows that of the 4.5 V which is required to produce a current density of 10 amp./dm², 27 per cent must be applied to initiate and maintain electrolysis (decomposition voltage), 33 per cent is used in overcoming the resistance of the solution (IR drop), and 40 per cent is electrode polarization. It seems probable that the IR drop is the only one of these three components which can be materially decreased, for example, by decreasing the distance between anode and cathode or by increasing the anode area. In some cases such a change may permit the use of 6-volt generators, but in view of the fact that the tendency in chromium deposition is apparently toward higher bath temperatures and current densities, which require higher voltages, it does not seem likely that 6-volt generators will prove useful for miscellaneous chromium plating. In general, it is desirable to have about 10 volts available at the tanks.

At the present time metallic chromium in the form of CrO_3 suitable for use in plating baths, is about the same price as nickel in the form of anodes. The intrinsic value of a deposit of either metal, 1 square

foot in area and 0.0002 inch thick or 10 square decimeters in area and 0.005 mm. thick, is less than half a cent. On the other hand, the cost of power for chromium plating may be 30 times as much as for nickel plating. The power cost, at 4 cents a kilowatt-hour at the tank for a chromium deposit of the above dimensions is from 2 to 3 cents as compared to 0.1 cent for nickel.

However, the factor which largely determines the total costs of both chromium and nickel plating is not power but labor; that is, the work involved preparatory to, during, and subsequent to the actual metal deposition. For example, in a particular case which is
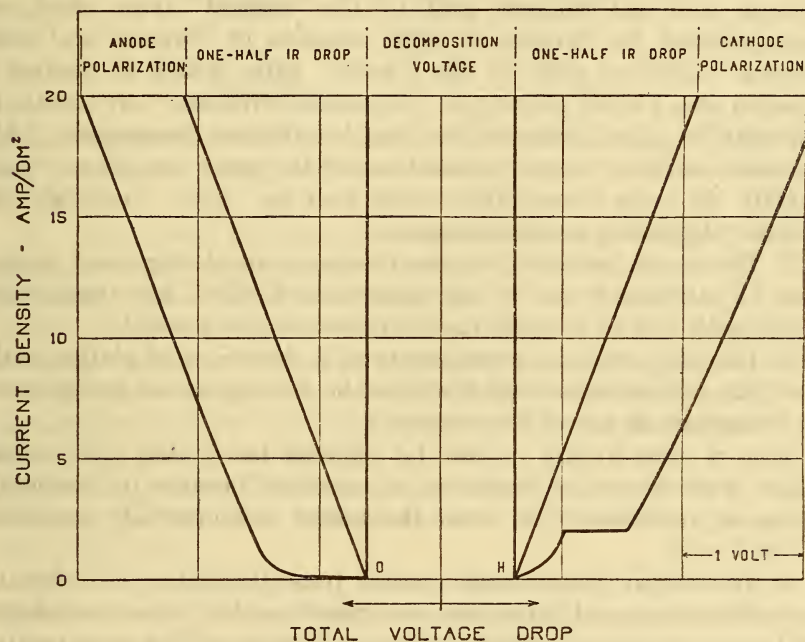

Fig. 9.—*Graphic analysis of the total voltage drop in chromium deposition*

Bath composition_____ CrO$_3$, 2.5 *M;* SO$_4$, 0.05 *N.*
Bath temperature_____ 45° C.
Anode composition_____ Lead.
Cathode composition_____ Steel.
Distance between electrodes_____ 10.0 cm.

probably typical, it has been found that the cost of buffing and polishing before and after nickel plating constitutes three-fourths of the total cost of the process. Labor costs in connection with chromium deposition vary widely. Considerable experimentation, far more than with nickel, is frequently necessary before the proper conditions for plating a given article are determined and greater personal attention is then required to maintain these conditions. On the other hand, the labor cost subsequent to the chromium plating may be much less than for most nickel plating. This statement is based on the assumption that a chromium deposit which requires little or no buffing is obtained.

In general, it will probably be found that chromium plating is somewhat more expensive than nickel plating. Any such difference in cost should not, however, prevent its application in any cases where properties such as extreme hardness and resistance to tarnish are particularly desirable.

XI. CONCLUSIONS

1. The three principal types of chromic acid plating bath which have been employed in the past, namely (1) the "acid" type which as definitely proposed in 1905 by Carveth and Curry contains chromic acid and sulphuric acid, (2) the "neutral" type, which, as recommended by Sargent in 1920, consists of chromic acid and chromic sulphate, and (3) the "basic" type, which is Sargent's solution plus a small amount of "chromium chromate;" are identical, not only in initial behavior but also in ultimate composition. All of these solutions when operated under the same conditions reach exactly the same composition, which may be "acid," "neutral," or "basic," depending on circumstances.

2. The recent industrial success of chromium plating must, therefore, be attributed, not to any improvement which has been made in the bath, but to its more careful operation and control.

3. The only essential constituents of a chromic acid plating bath are CrO_3 and any anion which will not be decomposed or precipitated by chromium in any of its valences.

4. It is most logical to use the sulphate ion (unless some other anion is subsequently shown to be superior) because it invariably exists as an impurity in even the purest commercially available chromic acid.

5. To exclude nonessential cations from the bath, the sulphate should be introduced in the form of sulphuric acid or chromic sulphate. Of the two, sulphuric acid is preferable because of its known purity.

6. The CrO_3 employed in the preparation and maintenance of chromic acid baths should contain not more than 0.5 per cent of SO_4. A number of samples of the so-called 98 per cent chromic acid of commerce have been found to satisfy this requirement. It is, of course, also desirable that the CrO_3 be free from insoluble matter.

7. If chromic sulphate is used to furnish the SO_4 ion, its sulphate content should be determined and additions made on that basis. It should be readily soluble in cold water.

8. To insure not only a bright chromium deposit but also maximum efficiency the CrO_3 and SO_4 should be present in the bath in the approximate ratio of $\dfrac{CrO_3 \text{ molarity}}{SO_4 \text{ normality}} = 50$. Expressed in terms of concentrations by weight of CrO_3 and H_2SO_4 this proportionality becomes $\dfrac{CrO_3}{H_2SO_4} = 100$.

9. The CrO_3 content of the bath decreases more rapidly than the SO_4 content, and to restore a used bath to its original concentration it is therefore necessary that the ratio of CrO_3 to SO_4 added be greater than that used in the preparation of the bath.

10. Baths of moderate concentration, for example, 2.5 M in CrO_3 and 0.05 N in SO_4 are most suitable for general purposes. Formulas for such a bath in terms of chemicals of 100 per cent purity are given below:

	g/L	oz./gal	
CrO_3	250	33. 5 ⎱	(1)
H_2SO_4	2. 5	. 34 ⎰	

or

	g/L	oz./gal	
CrO_3	250	33. 5 ⎱	(2)
$Cr_2 (SO_4)_3$	3. 3	. 44 ⎰	

Both of these solutions have been in use at the Bureau of Engraving and Printing for a long period and have yielded equally satisfactory results.

11. "Chromium chromate," or more properly chromium dichromate, serves no useful purpose in a chromium plating bath. The formation of this colloid is accompanied by a corresponding decrease in free chromic acid and, hence, in conductivity; any appreciable accumulation of it is therefore objectionable and should be avoided.

12. Chromic carbonate and similar basic compounds and also reducing agents have been added to chromic acid plating baths for the express purpose of forming "chromium chromate." In view of the fact that this colloid should be excluded from the bath rather than included in it, such additions are not only unnecessary but actually detrimental.

13. The chromium plating bath originally used at the Bureau of Engraving and Printing [29] gave results equal to any which are now obtained, not because it contained "chromium chromate," but because as was subsequently learned, sulphate was present as an impurity in the chromic carbonate used in preparing the bath, in exactly the right concentration to raise the sulphate content of the bath to the optimum for the conditions used.

14. Insoluble anodes composed of a metal upon which the overvoltage of oxygen is high are most suitable for use in chromic acid baths.

15. The anode area should be as large as is conveniently feasible.

16. Lead anodes are entirely satisfactory. If they are of sufficient area their use is accompanied by the formation of at most only a negligible amount of "chromium chromate."

17. Continued use of iron anodes results in an objectionable accumulation of "chromium chromate."

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[29] Chem. and Met. Eng., **32**, p. 692; 1925; and also Bureau of Standards Letter Circular No. 177; 1925.

18. If chromium anodes are to be used in chromic acid baths some means of preventing excessive formation of "chromium chromate" must be found.

19. In the absence of an appreciable amount of "chromium chromate" analysis of a chromic acid bath involves only the determination of its specific gravity and sulphate content. If a large quantity of the colloid is present, however, a complete chemical analysis is necessary.

20. In the deposition of bright chromium as well as of other metals, the optimum operating conditions (bath temperature and cathode current density) are determined not only by each other, but also by a number of variable factors, such as bath composition and concentration, and the composition and structure of the cathode. In consequence, it is impossible to specify a definite range of operating conditions which will give universally satisfactory results. Any statement as to the optimum operating conditions for chromium plating is therefore meaningless unless properly qualified.

21. If a bath 2.5 M in CrO_3 and 0.05 N in SO_4 is used, most metals can be satisfactorily plated at temperatures ranging from 40 to 60° C. (104 to 140° F.) providing that a suitable current density is employed in each case.

22. If it is desired to deposit bright chromium the optimum average current density for the bath temperature involved should be employed. By "optimum average current density" is meant that current density which lies halfway between the lowest current density resulting in a frosty area on the "work" and the highest current density resulting in a milky area. (Such data must be determined empirically for any given conditions. Typical data are included in Table 4.)

23. The optimum average current density for a given bath and temperature varies widely, depending upon the nature of the metal which is being chromium plated. For example, if a bath 2.5 M in CrO_3 and 0.05 N in SO_4 is employed at 50° C. (122° F.), the optimum average current density for steel or nickel is 16 amp./dm² (149 amp./sq. ft.), while for copper or brass it is 25 amp./dm² (232 amp./sq. ft.).

24. The cathode efficiencies at which bright chromium deposits are produced are nearly equal, regardless of whether a low temperature and current density are used or a high temperature and correspondingly higher current density. The time required to deposit a given thickness of chromium is therefore approximately inversely proportional to the cathode current density. For maximum production it is hence desirable to use current densities and bath temperatures as high as are otherwise permissible.

25. It is doubtful whether the throwing power of the chromic acid plating bath can ever be decidedly improved by the necessarily limited changes which can be made in its composition.

26. Irregularly shaped articles composed of metals upon which the overvoltage of hydrogen is high can be more readily completely plated with bright chromium than those composed of metals upon which the overvoltage of hydrogen is low. For example, recessed articles of copper or brass are decidedly easier to plate with a bright chromium deposit than are those of steel or nickel.

27. When chromium is plated upon even a thin electrolytic coating of some other metal, the results obtained are identical with those which would be obtained if the cathode consisted entirely of that metal. In other words, the character of a chromium deposit is influenced by the nature of the cathode surface, and not of the underlying metal.

28. Irregularly shaped articles composed of metals of low hydrogen overvoltage, such as steel, can be more readily completely plated with bright chromium if they are first lightly coated with a metal of high hydrogen overvoltage, such as copper.

29. To prevent the attack of metals, such as brass and copper, by the chromic acid, it is essential that the cathode be introduced into the bath in such a manner that its immersion closes the plating circuit. This procedure also improves the throwing power on metals, such as iron and nickel, that become passive in chromic acid. The throwing power upon the latter metals can be still further improved if the article to be plated is polarized anodically for a minute or two previous to plating.

30. Although minor improvements may be effected in the distribution of chromium upon objects of irregular shape by variation of numerous factors in the process, the successful plating of such articles will probably continue to depend chiefly upon ingenious arrangements of the "work," the racks, and the anodes.