# Marquette University e-Publications@Marquette

Bachelors' Theses

Dissertations, Theses, and Professional Projects

5-1942

# A Chromium Plating Bath Containing Sodium Benzenesulfonate Instead of Sulfuric Acid

Edward Burleigh

Follow this and additional works at: https://epublications.marquette.edu/bachelor\_essays

Part of the Chemistry Commons

A CHROMIUM PLATING BATH CONTAINING SODIUM BENZENESULFONATE INSTEAD OF SULFURIC ACID

BY

# EDWARD BURLEIGH

A Thesis Submitted to the Faculty of the College of Liberal Arts, Marquette University, in Partial Fulfillment of the Requirements for the Degree of Bachelor of Science

Milwaukee, Wisconsin

MARQUETTE UNIVERSITY LIBRARY

# TABLE OF CONTENTS

1	DRFFACE	Page
+•	INSTRUM	-T
2.	NTRODUCTION	-2-6
Fig:	ddition Agents	-2
3.	EXPERIMENTAL RESULTS	-7-21
Fig	Appartus- Treatment of Electrodes- General Procedure- Particular Procedure- Results- Discussion of Figure One- Discussion of Figure Two- Appendix- Discussion of Figure Four- Discussion of Figure Six- Discussion of Figure Six- Discussion of Figure Seven- Discussion of Figure Eight- Discussion of Figure Ten- Discussion of Figure Ten- Discussion of Figure Eleven- Discussion of Figure Ten- Discussion of Figure Ten- Discussion of Figure Ten- Discussion of Figure Ten-	-7 -9 -11 -12 -14 -16 -18 -22 -23 -23 -23 -23 -23 -29 -29 -32 -32 -32 -32 -32 -32
	Discussion of Figure Fourteen Discussion of Figure Fifteen	-36 -36
	Suggestions for Further Work	-40
4.	SUMMARY	-44
	Energy of Salling Engenand Strate Day Lit	
5. Pig	ANNOTATED BIBLIOGRAPHY	-45-46
	Grams of Sudius Sansassolfonste Far Lit	
	9 The Fifeot of Ourrest Densloy on the Apr of a Osthode for an Pleatrolyte Containin Giams of Sector Persessulfonate Far Lis 4800.	er at
	10 The Effect of Current Density of the syn of a denhois for an Electrolyts Constants Grans of Sodium Benzenesblionste our Lit 4300.	earanae na Sova er at

i

# LIST OF ILLUSTRATIONS

- Fig. 1--- The Effect of Current Density and Concentration of Sodium Benzenesulfonate on the Bright Plating Range of Chromium at 48°C.----17
- Fig. 2--- The Effect of Various Temperatures on the Cathode Efficiency for an Electrolyte Containing Four Grams of Sodium Benzenesulfonate Per Liter-----20
- Fig. 3--- The Effect of Various Temperatures on the Plating Range for an Electrolyte Containing Four Grams of Sodium Benzenesulfonate Per Liter-----21
- Fig. 4--- The Effect of Current Density on the Appearance of a Cathode for an Electrolyte Containing One Gram of Sodium Benzenesulfonate Per Liter at 48°C.----24
- Fig. 5--- The Effect of Current Density on the Appearance of a Cathode for an Electrolyte Containing Two Grams of Sodium Benzenesulfonate Per Liter at 48°C-----25
- Fig. 6--- The Effect of Current Density on the Appearance of a Cathode for an Electrolyte Containing Three Grams of Sodium Benzenesulfonate Per Liter at 48°C.----26
- Fig. 7--- The Effect of Current Density on the Appearance of a Cathode for an Electrolyte Containing Four Grams of Sodium Benzenesulfonate Per Liter at 480C.-----28
- Fig. 8--- The Effect of Current Density on the Appearance of a Cathode for an Electrolyte Containing Five Grams of Sodium Benzenesulfonate Per Liter at 48°C.-----30
- Fig. 9--- The Effect of Current Density on the Appearance of a Cathode for an Electrolyte Containing Six Grams of Sodium Benzenesulfonate Per Liter at 48°C.-----31

- Fig. 11 -- The Effect of Current Density on the Appearance of a Cathode for an Electrolyte Containing Eight Grams of Sodium Benzenesulfonate Per Liter at
- Fig. 12 -- The Effect of Current Density on the Appearance of A Cathode for an Electrolyte Containing Nine Grams of Sodium Benzenesulfonate Per Liter at 48°C. \_\_\_\_\_35
- Fig. 13 -- The Effect of Current Density on the Appearance of a Cathode for an Electrolyte Containing Ten Grams of Sodium Benzenesulfonate Per Liter at 48°C.-----36
- Fig. 14 -- The Effect of Current Density on the Appearance of a Cathode for an Electrolyte Containing Twelve Grams of Sodium Benzenesulfonate Per Liter at
- Fig. 15 -- The Effect of Current Density on the Appearance of a Cathode for an Electrolyte Containing 2.5 Grams of Sulfuric Acid Per Liter at 480C-----40

# LIST OF TABLES

Table 1 .-- The Effect of Current Density on the Cathode Efficiency for an Electrolyte Containing Four Grams of Sodium Benzenesulfonate, Per Liter at 480C.----41 MART PLANT

Table 2.-- The Effect of Current Density on the Cathode Efficiency for an Electrolyte Containing Four Grams of Sodium Benzenesulfonate Per Liter at on the elect 48°C.----41

20

Table 3 .-- The Effect of Current Density on the Cathode Efficiency for an Electrolyte Containing Four Grams of Sodium Benzenesulfonate Per Liter at 

debtedness to be. Herbark setter on whole susteen, on led to

#### PREFACE

At the present day chromium plated articles are saving the country many tons of badly needed metals. The beautiful, bright luster that chromium has is no longer the prime quality that makes its use so extensive. Today its extreme hardness has taken the foremost place. Parts worn by use and re-claimed with chromium, not only wear longer than the original ones but they also save valuable metal and time put into new ones. New articles plated with chromium have increased life, and thus the time and metal needed for replacement is greatly reduced. 1

The present chromium plating baths containing sulfuric acid as the active agent in electrolysis presents many problems leading to investigation and experimentation as far as the throwing power, plating range, and efficiency is concerned. Many addition agents have been tried with different degrees of success. The purpose of this investigation is to improve on the above factors and show that bright deposits can be obtained using an organic addition agent such as sodium benzenesulfonate.

The writer takes this opportunity to acknowledge his indebtedness to Dr. Herbert Heinrich whose suggestion led to the subject of this research, and to whose assistance and advice much of the success of this investigation is due. INTRODUCTION

addition of TESH of TA , or the Mary Discol aband in the

There in a second second second

suffer and an and the set of the

The full post is a screek of a screek of the state of the

#### ADDITION AGENTS

The following is a summary of addition agents to the chromium plating bath tried and published since 1935. For addition agents used previous to this date, see Ernest Curshmann's B.S. thesis, Marquette University 1935.

2

Wilfred W. Scott, Attilio A. Bissiri and Wm. C. Gregory1 deposited chromium from a solution of chromic acid in the presence of an amount of compounds of Se. and Te. providing a proportion of Se and Te of about 1 part to each 250 to 1000 parts of chromic acid.

Muller and Dreschel<sup>2</sup> list the advantages secured by substituting HF for H2SO4 in the standard chromium plating bath . The advantages are shown by comparison tables for a series of conditions.

The society of electro-chemistry and electro-metallurgy<sup>3</sup> in Germany published an article which stated that objects were plated from a bath consisting essentially of sodium tetrachromate, using a current of 3000 to 1000 amperes per square dm. The strength of the solution was maintained by addition of NaOH or Na Cr04 to keep the mol proportions of Na<sub>2</sub>0 to CrO<sub>3</sub> between the limits of 1:4 and 1:6 at a temperature below 40° C.

A. Pollack<sup>4</sup> plated black deposits, having improved hardness

- Belgian Patent 403,918, 1 Z. Elektrochem. 40,707-13, German Patent, 608,757, Chem. Ztg. 59,56, ( 1934 1.
- 2. 1934 1935
- 3. (1935)4.

and wear by replacing H SO in the usual chromium plating 2 4 bath by AcOH and using a higher current density. 3

Oscar Kramer<sup>5</sup> obtained bright deposits using a chromic acid bath containing over 2% sulfate radical (based on the amount of chromic acid in solution) and also 5% KCN and 5% potassium tartrate.

Dwight E. Ewing<sup>6</sup> used as an electrolyte for the deposition of chromium, a solution containing principally chromic acid and relatively small amounts of Ce oxalate and  $Na_2SeF_6$ .

Bornhauser<sup>7</sup> replaced the Na tetrachromate introduced into the chromic acid bath wholly, or partly, by equivalent amounts of other metals e.g. Al. Fe. and Cr and particularly metals whose hydroxides had a solubility increasing with the chromic acid content of the bath.

christian Wickenhiser<sup>8</sup> claims an increase in the "throwing power" of the bath by depositing chromium from a bath containing  $H_2^0$ ,  $Cro_3$  and about 2% the weight of chromic acid of a hydrous basic carbonate such as "magnesium alba".

N. D. Biryukov<sup>9</sup> deposited chromium from a bath of  $H_2CrO_4$ , Cr<sub>2</sub>(SO<sub>4</sub>)3, ZnCrO<sub>4</sub>, and MnCrO<sub>4</sub> and also CaCO<sub>3</sub> or CaO in such

5.	U. S. Patent, 2,016,677,	1935
6.	Canadian Patent, 345,121,	1934
7.	French Patent 45,020,	1934
8.	U. S. Patent, 2,050,478	1936
9.	Russian Patent, 37,956,	1934
0.	U. S. Patent, 2,040,881,	1936

proportions that the ratio by weight of the Ca, Zn, and Mn is 1:1:0:3.

Floricel A. Rojas<sup>10</sup> made up a chromium plating bath consisting of an aqueous solution such as may be prepared by use of Cr03 and Al(OH)3 in water.

Richard Schneidewind<sup>11</sup> increased the throwing power of the chromium plating bath by adding a quinone such as .5% or less of anthraquinone, hydroquinone or napthaquinone to the bath.

Again in 1937, Richard Schneidewind<sup>12</sup> deposited chromium on steel, copper or nickel at a temperature of 35° or higher from a bath containing chromic acid, a sulfate compound in small proportion, and boric acid to approximately saturation.

K. R. Rao<sup>13</sup> obtained bright deposits from a bath containing  $K_2Cr_2O_7$  and AcOH at a current density of .075 amperes per square cm. and efficiency of 21. 88%. NaOH was also added to the bath and this gave satisfactory results in one-half hour, with a current density of .2 amps./in.sq. and efficiency of 1.16%. Of the two baths, the AcOH gave the best results.

Oscar Kramer<sup>14</sup> used as electrolytes for the electrodeposition of chromium from CrO<sub>3</sub>, solutions containing small proportions of Co, Ni, or Cd, but practically free from H2SO<sub>4</sub>.

11.	U.S	. Patent.	2.020	.382	1936
12.	U. S	. Patent.	2.063	197	1937
13.	J. 0	smania Un	iv. 3.	9-15	(1935)
14.	Germa	an Patent	, 655,	494	1938

The solutions also contained an organic substance capable of forming complex compounds with Co, Ni, or Cd. e.g. sucrose glucose or fructose. The proportion of Co., Ni, or Cd was about 1% calculated on the amount of Cr03. 55

Kramer<sup>15</sup> also increased the efficiency of the chromic acid bath by adding a reaction product of chromic acid, a chromium salt such as chromium chromate, an alkali metal hydroxide, and an alkali metal salt of an organic acid oxidizable by chromic acid.

The Rojas Chemical Works<sup>16</sup> made up a  $H_2CrO_4$  plating bath containing a solution of aluminum compounds to the extent of 5-15% calculated as Al(OH)<sub>3</sub> of the  $CrO_3$  and was substantially free from inorganic materials.  $H_2SO_4$  as an impurity was kept below .5%.

Elmore M. Relitz<sup>17</sup> deposited chromium on bright nickel from a bath containing cyanide equivalent to 6-12 oz./gal. of NaCN.

Muller and Pietsch<sup>18</sup> studied the effect of adding  $H_2O_2$ solutions to solutions containing 278 grams of  $CrO_3/$ liter by determining the change in  $CrO_3$  concentration and amount of  $O_2$  evolved. The addition of  $H_2O_2$  resulted in a definite improvement in the throwing power of the bath and also the yield.

15.	U. S. Patent 2,114,002	1938	
16.	British Patent, 480,945	1938	
17.	Canadian Patent 378,303	1938	
18.	Korrosion u Metallschultz	15, 122-6	(1939)

John R. Mardick<sup>19</sup> plated from a solution containing chromic acid, 60-300 grams, Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, 100-350 grams per liter and some sulfate as an impurity whithin the range of .5 to 12 grams per liter. 6

Frank H. Beall<sup>20</sup> plated bright adherent chromium from an aqueous solution of chromic acid in free part and as an alkali salt, the free acid constituting 20-40% of the total and not less than approximately .5 oz. per gallon and sulfate to the amount of not over approximately .4% of total chromic acid.

In view of the many and varied compounds that have been used as addition agents in the deposition of chromium from aqueous solutions of chromic acid, it appears as though the best results that have been obtained are those that contain the sulfate radical present in one form or another. Apparently no organic substances have been tried that contain the sulfate radical. If it is the sulfate radical that is the deciding factor in the electroplating of chromium, it seems as though water soluble sodium benzenesulfonate should produce results comparable to other sulfate containing electrolytes.

19. U. S. Patent, 2,177,392194020. U. S. Patent, 2,182,2441940

# EXPERIMENTAL RESULTS

antipertories in the same is a set of the se

# APPARATUS

The vessel containing the chromic acid solution was a rectangular glass jar with a capacity of approximately sevenhundred and fifty cubic centimeters. Two anodes were so constructed that they fitted snugly and covered the entire ends of the jar. The vessel was covered with a loose fitting wooden cover, waxed on the bottom to prevent any attacking of the wood by the chromic acid. A hole was drilled in it for the entrance of a thermometer, and another square hole was cut in the middle for the suspension of the cathodes. The cathodes were suspended into the solution by means of a heavy copper wire flattened on both ends and a small hole drilled in each end so that a bolt could be passed through and tightened. The opposite end of the surface to be plated was connected to a strip of copper bent at the bottom in the form of a square. This square fitted into the square cut in the wooden cover, which was also provided with a small slit to prevent the entrance of the cathode. Two such racking devices were used and so constructed, that each cathode suspended in the bath was in the same position, making a better and faster comparison of results. Suspending the cathodes in this manner prevented any movement of them during electrolysis which would cause a difference in appearance. Connections were rapidly made by connecting a spring clip to the copper strip.

The glass jar containing the chromic acid solution was placed in a large tin can filled with water. By careful control of the temperature of the water in the outside bath, the plating solution could be maintained at the proper temperature. It was necessary to have two thermometers because maintenance of the desired temperature of the water bath does not give the correct temperature in the plating bath, as the temperature has a tendency to rise while plating with higher current densities. The plating jar was raised from the bottom of the can by placing two pieces of lead beneath it. This helped to give a uniform temperature through-out.the bath.

8

In order to affect the correct current density, the cathodes were pre-heated to the temperature of the plating solution. This was accomplished by suspending the cathodes in a tin can provided with a cover and thermometer, and heating to the desired temperature. One cathode was heated while the other one was plating. Changes were made from the air bath to the plating bath very rapdily.

A twenty volt direct current was used and the amperage varied by means of apotentiometer. The applied current was measured by means of a Jewell D.C. voltammeter.

# TREATMENT OF ELECTRODES

The cathodes used in this research consisted of strips of copper, one inch wide and two inches long, providing a total area of four square inches. The corners were rounded so that the current would not collect at the points and cause burning. Each strip had a small hole drilled in it on one end in order that a small bolt could be put through and a good contact made while in the bath.

In order to secure the best possible results it is necessary that the base metal be free of dirt and grease. This made it necessary to polish the copper to a high luster by means of a soft buffing wheel using copper buffing compound. It was found that the same degree of brightness of the chromium could not be obtained if the strips were buffed with different buffing compounds. After polishing, the strips were cleaned free of dirt and grease by washing with alcohol and wiping dry with a clean cloth. After cleaning with alcohol, caution was taken not to touch the surface to be plated, because the hands are often greasy and this would cause a change in the quality of the deposit.

The strips to be plated were always polished immediately before use, and were never polished one day and used on the next, because of the different gases that are often given off by experiments performed by students have a tendency to oxidize the copper, which in turn would effect the deposit of chromium. 9

The anodes used consisted of an alloy of antimony and lead, and were approximately four times the area of the cathode. The area of the anodes covered the entire cross section of the bath.

Before the anodes were to be used, they were cleaned free of dirt by means of a rotating wire brush, washed with water and alcohol, after which they were ready for use. The lead chromate that precipitated out was allowed to remain in the bath and additions of sodium benzenesulfonate were made without cleaning the anodes. The lead chromate that formed on the anodes was negligible and the current retarded by this would be small and make cleaning of them before additions unnecessary.

a south outloas benefit hand in the determine the dould

tent at the set tetter comparing the short of the Astron

# GENERAL PROCEDURE

After cleaning the cathodes, they were placed in the air bath until they reached the desired temperature. They were then rapidly transferred to the plating bath and allowed to plate for exactly five minutes at the desired amperage. The amperage was varied in successive steps, onefourth, one half, etc., up to three amperes per square inch. The cathodes were struck at a low current density and raised to the amperage wanted. This prevented any burning along the lower edges. At times it was necessary to raise the current density beyond the desired until an evolution of gas appeared and then bring it back down. In order to save time, while one cathode was plating another was racked and placed in the air bath. After removal from the plating solution, they were washed, dried, and placed on a square piece of cardboard so that comparisons could be made. 111

Enough cathodes were on hand so that several runs could be made at the different concentrations of sodium benzenesulfonate. For the removal of chromium, the cathodes were suspended in a solution containing three parts of water to one part of concentrated hydrochloric acid. It was necessary to wash them thoroughly with water and dry after removal from the acid solution, or buffing was difficult.

# Particular Proceeure

In order to see if there was enough sulfate as an impurity in the chromic acid to cause deposition of the chromium, a solution was made up containing 250 grams of chromic acid per liter of water. The current was varied in successive steps, a quarter ampere per squære inch at a time up to three amperes per square inch. No deposits were observable at a temperature of 48° C.

Next a solution was made up containing one gram of sodium benzenesulfonate and 250 grams of chromic acid per liter. At a temperature of 48° C., a copper cathode was placed in the bath and allowed to plate for twenty minutes. In previous runs it was noted that at the concentration of the best plating range could not be duplicated by making up a new bath at the same concentration. This necessitated plating of a cathode for twenty minutes before starting to vary the current density, and noting the current at which the best plates occurred. The temperature was kept constant at 48° C. and each cathode was plated for a period of exactly five minutes. The concentration of sodium benzenesulfonate was varied, a gram at a time, the current varied as before, and the plating range noted for each addition.

In order to have a comparison of results under the same conditions and technique, a solution containing 2.5 grams of sulfuric acid and 250 grams of chromic acid per liter was 12

made up. This is the recommended bath for the largest plating range. The current was varied as before, and the amperage noted at which the best deposits were obtained. Cleaning operations, temperatures, time, and the air bath were the same as those used in the bath containing sodium benzenesulfonate.

Files is like in the the torestic, of it would be the

#### RESULTS

The plates obtained from the sodium benzenesulfonate bath were compared with those of the standard sulfate bath containing 2.5g of sulfuric acid per 250g. chromic acid per liter. The extent of the bright plating ranges, the appearance of the chromium deposit, and the color of the solution were taken into account. The following results were obtained:

- 1. The appearance of the bright deposits are the same, both possessing the characteristic color of chromium.
- At concentrations of four, five and six grams of sodium benzenesulfonate, the bright plating range is greater than that of the sulfate bath.
- 3. The ratio of sodium benzenesulfonate to chromic acid is not as rigid as the sulfuric acid is to the chromic acid. Concentrations from four to eight grams of sodium benzenesulfonate give plating ranges equal, and in some cases greater than the sulfuric acid bath.
- 4. The sodium benzenesulfonate bath does not possess the characteristic dark brown color of the sulfate bath, which is largely due to the formation of chromium chromate or chromium dichromate.

14

Grams (C <sub>6</sub> H <sub>5</sub> So <sub>3</sub> )Na	Lowest C.D. at which bright plate was obtained AMPS/IN <sup>2</sup>	Highest C.D. at which bright plate was obtained <u>AMPS/IN</u>	Plating range AMPS/IN <sup>2</sup>
1			
2		terest Lente	
3	.75	1.25	.50
4	•50	1.75	1.25
5	.50	1.50	1.00
6	.50	1.50	1.00
7	.50	1.25	. 75
8	•50	1.00	.50
9	•50	1.00	• 50
10	.50	.75	.25

Gram Sulfuric Acid

2.5

.75

1

1.50

.75

.

#### FIGURE ONE

Figure one is a graphic illustration of the bright plating range using different concentrations of sodium benzenesulfonate in a bath containing 250 grams of chromic acid per liter. At a concentration of four grams perliter of sodium benzenesfulfonate, the largest plating range occurred. At concentrations below 3.5 grams per liter no burning could be observed but dark, moldy appearing deposits resulted. Concentrations of sodium benzenesulfonate between 3.5 and 7 grams per liter produce the best deposits, as shown by the shaded portion of the graph. Above this concentration, although the deposits are bright, there is a great tendency for burning to occur at lower current densities, until finally at a concentration of twelve grams per liter the plating range drops to almost zero. As can be seen by the curve there is no change in the lowest current densities at which bright plates occurred, going from a concentration of four grams per liter all the way up to ten grams per liter. There is no sharp decrease in the plating range with an increase in the concentration of sodium benzenesulfonate, showing that the ratio of chromic acid to sodium benzenesulfonate is not quite as strict for bright deposits as is the chromic acid sulfuric acid bath.

16

# FIGURE ONE

THE EFFECT OF CURRENT DENSITY AND CONCENTRATION OF SODIUM BENZENE SULFONATE ON THE BRIGHT PLATING RANGE OF CHROMIUM, AT 48° C.



#### FIGURE TWO

Figure two shows the effect of various temperatures on the cathode efficiency for an electrolyte containing four grams of sodium benzenesulfonate per liter.

At a temperature of thirty-eight  $^{\circ}$  C. the highest cathode efficiency was obtained but the plating range for chromium was very limited, it being only one-fourth amperes per square inch. At a current density of only three-fourths amperes per square inch, burning occured at the lower edges of the plate. At a current density of one and one-fourth amperes per square inch only a small portion in the center of the plate consisted of bright chromium. As the current was increased the frostiness increased until, at a current density of three amperes per square inch, (the one current density of the highest cathode efficiency--twenty-seven percent) the deposit was extremely frosty. The curve obtained at  $38^{\circ}$  C. does not level off as does the curves for  $48^{\circ}$ C. and  $58^{\circ}$  C.

At a temperature of 48° C. the cathode efficiency was lower than that of the 38° C. but is was at this temperature the best plating range was obtained, namely one and one-fourth amperes per square inch. The curve shows a gradual increase in efficiency and has a tendency to level off at a current density of three amperes per square inch. The efficiency gradually rises until it reaches nineteen percent and then begins to level off. The maximum efficiency that can be o btained and still get bright deposits is at about sixteen per-

# cent.

The efficiency at 58°C. is lower that that of the 48°C. although the bright plating range is about the same. The curve is similiar to that of the 48°C. in that it begins to level off at a current density of three amperes per square inch. The highest efficiency that could be used and bright deposits obtained, is at about two and one-half amperes per square inch. Deposits obtained below a current density of one and one-half amperes per square inch were milky in appearance and thin. The bright deposits that resulted at the higher current densities and lower temperature did not quite possess the characteristic color of the deposits resulting from the lower current densities and higher temperature. They possessed more of a bluish tint and had true bright chromium only on the lower edge.

# FIGURE TWO

# EFFECTS OF VARIOUS TEMPERATURES ON THE CATHODE EFFICIENCY FOR AN ELECTROLYTE CONTAINING FOUR GRAMS OF SODIUM BENZENESULFONATE PER LITER



59 Limit of bright plating range

20

..

#### FIGURE THREE

THE EFFECT OF VARIOUS TEMPERATURES ON THE PLATING RANGE FOR AN ELEC-TROLYTE CONTAINING FOUR GRAMS OF SODIUM BENZENESFULFONATE PER LITER



1.1

# APPENDIX

Results of the investigation are to be found on the following pages. They include in detail, the appearance of the cathode and the extent of the bright plating ranges for different concentrations of sodium benzenesulfonate. As a basis for comparison, the results of the appearance of the chromium plate and the bright plating range for a standard sulfate bath have been included. These results are in detail what has been summarized in the foregoing graphs.

the second s

Contraction of the second water provide the second s

#### FIGURE FOUR

Figure four shows the effect of current density on the appearance of a cathode for an electrolyte containing one gram of sodium benzenesulfonate per liter. No deposits of chromium were observable although the current density was varied from one-quarter amps per square inch to three amps per square inch. The dark deposits that marred the surface increased in intensity as the current was increased. The appearance of the cathode showed no improvement over a bath containing nothing but chromic acid and water. 23

# FIGURE FIVE

Figure five shows the effect of current density on the appearance of a cathode for an electrolyte containing two grams of sodium benzenesulfonate per liter. This bath showed some improvement over the one containing one gram per liter. Although the deposits were somewhat spotted and thin it showed that the electrolyte was beginning to show its effect. The best deposit was obtained at a current density of three-fourths amps per square inch. As the current density was increased, the spots increased and at a current density of two amps per square inch there was no chromium that could be detected. As a whole the deposits were poor and of no value.

# FIGURE SIX

Figure six shows the effect of current density on the appearance of a cathode for an electrolyte containing three

# FIGURE IV

THE EFFECT OF CURRENT DENSITY ON THE APPEARANCE OF A CATHODE FOR AN ELECTROLYTE CONTAINING ONE GRAM OF SODIUM BENZENESULFONATE PER LITER, AT 48° C.

3			
	C U	DARK DEPOSIT ON ENTIRE SURFACE.	
	R		51
	E		
	T		
2	D	DARK DEPOSIT ON ENTIRE SURFACE.	1000
	EN		
	ST	DARK DEPOSIT ON ENTIRE SURFACE.	
	T	DARK DEPOSIT ON ENTIRE SURFACE.	
ı	AMPS/IN <sup>2</sup>	DARK DEPOSIT ON ENTIRE SURFACE.	
	-	DARK DEPOSIT ON ENTIRE SURFACE.	
		DARK DEPOSIT ON ENTIRE SURFACE.	-
-		NO DEPOSIT	

Cr0<sub>3</sub> concentration-----250g/liter (C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>)Na concentration----lg/liter Composition of cathode-----Copper

# FIGURE V

THE EFFECT OF CURRENT DENSITY ON THE APPEARANCE OF A CATHODE FOR AN ELECTROLYTE CONTAINING TWO GRAMS OF SODIUM BENZENESULFONATE PER LITER, AT 48° C.



Cr03 concentration-----250g/liter

(C6H5S03)Na concentration-----2g/liter

Composition of cathode-----Copper

# FIGURE VI

THE EFFECT OF CURRENT DENSITY ON THE APPEARANCE OF A CATHODE FOR AN ELECTROLYTE CONTAINING THREE GRAMS OF SODIUM BENZENESULFONATE PER LITER, AT 48° C. 26

	- a	
3	U	
	R	
	R TR	
	E DT	
	IN	
	T	
	D	
2	E NT	JADOGET DADOGTE
2	IV C	FROSTI DEPOSIT
	D T	
	<u>т</u>	
	Ŷ	SLIGHTLY FROSTY DEPOSIT
	AMPS/IN <sup>2</sup>	BRIGHT DEPOSIT
1	hon na dela	BRIGHT DEPOSIT
		BRIGHT DEPOSIT
		DULL DEPOSIT
	218000 te	DULL THIN DEPOSTT

Cr0<sub>3</sub> concentration-----250g/liter (C<sub>6</sub>H<sub>5</sub>S0<sub>3</sub>)Na concentration---- 3g/liter CAthode compositon----- copper

grams of sodium benzenesulfonate per liter. At this concentration the first bright plates were noticable. At a current density of one-fourth and one-half amperes per square inch a deposit was noticable although they were somewhat dull in appearance and thin. Bright deposits were obtained a current densities of three-fourths one and one and one-fourth amperes per square inch. Above this current density frosty deposits were obtained. When the current was first varied in successive steps, a quarter ampere at a time, spots were noticeable at current densities of threefourths and one ampere per square inch. This was eliminated by allowing a copper cathode to plate at a current density of one-half ampere per square inch for one-half hour. This seemed to bring the bath to a sort of equilibrium and as a result bright deposits were obtained which otherwise wouldn't have been. The bright plating range was three-fourths amperes per square inch.

#### FIGURE SEVEN

Figure seven shows the effect of current density on the appearance of a cathode for an electrolyte containing four grams of sodium benzenesulfonate per liter. At this concentration the best results were obtained. Bright deposits were obtained using current densities varying from one-half ampere per square inch to one and three-fourths amperes per square inch. At a current density of one-fourth ampere per square inch, a dull milky deposit was obtained. Burning at the lower edge took place at a current density of two amperes per square inch. Although no frosty deposits were

27

# FIGURE VII

THE EFFECT OF CURRENT DENSITY ON THE APPEARANCE OF A CATHODE FOR AN ELECTROLYTE CONTAINING FOUR GRAMS OF SODIUM BENZENESULFONATE PER LITER, at 480 C.

4		
3	U	BRIGHT DEPOSIT BURNED ALONG EDGES
	R R	BRIGHT DEPOSIT EDGES BURNED
-	E N	BRIGHT DEPOSIT EDGES BURNED
	T D	BRIGHT DEPOSIT EDGES SLIGHTLY BURNED
2	<b>N</b>	BRIGHT DEPOSTT SLIGHTLY BURNED ON EDGES
	SI	BRIGHT DEPOSIT
	T Y	BRIGHT DEPOSIT
-	AMPS/IN <sup>2</sup>	BRIGHT DEPOSIT
1		BRIGHT DEPOSIT
		BRIGHT DEPOSIT
		BRIGHT DEPOSIT
		DULL DEPOSIT

Gr03 concentration-----250g/liter

(C6H5SO3)Na concentration-----4g/liter

Cathode composition ----- Copper

obtained when the current was raised to three amperes per square inch, there was still burning along the lower edges. During the one trial run a bright plating range of two and one-half amperes per square inch was obtained at this concentration but could not be duplicated in several different trial runs. This may have been due to a rise in temperature which would allow bright deposits at higher current densities as is shown on the graph.

#### FIGURE EIGHT

Figure eight shows the effect of current density on the appearance of a cathode for an electrolyte containing five grams of sodium benzenesulfonate per liter. The bright plating range for this concentration is from one-half amperes per square inch to one and one-half ampere per square inch. This is not an appreciable change from a bath containing four grams of sulfonate per liter. The lower current densities produced the same results, while at the higher current densities burning was noticed at a current density of one and three-fourths amperes per square inch. An increase of current densities produced deposits with burning along the lower edges more pronounced than the previous bath.

#### FIGURE NINE

Figure Nine shows the effect of current dnesity on the appearance of a cathode for an electrolyte containing six grams of sodium benzenesulfonate per liter. The bright plating range at this concentration of sodium benzenesulfonate was the same as that of the previous one. Con-

# FIGURE VIII

THE EFFECT OF CURRENT DENSITY ON THE APPEARANCE OF A CATHODE FOR AN ELECTROLYTE CONTAINING FIVE GRAMS OF SODIUM BENZENESULFONATE PER LITER, AT 48 C.

3	C	
	R	
	E	BRIGHT DEPOSIT EDGES BADLY BURNED
	Т 	BRIGHT DEPOSIT BURNED ON EDGES
2	E	BRIGHT DEPOSIT BURNED ON EDGES
	SI	BRIGHT DEPOSIT EDGES SLIGHTLY BURNED
	T	BRIGHT DEPOSIT
	AMPS/IN2	BRIGHT DEPOSIT
l		BRIGHT DEPOSIT
		BRIGHT DEPOSIT
		BRIGHTDEPOSIT
	-	DULL DEPOSIT

Cr0<sub>3</sub> concentration-----250g/liter (C<sub>6</sub>H<sub>5</sub>S0<sub>3</sub>)Na concentration----5g/kiter Cathode domposition----Copper

# FIGURE IX

THE EFFECT OF CURRENT DENSITY ON THE APPEARANCE OF A CATHODE FOR AN ELECTROLYTE CONTAINING SIX GRAMS OF SODIUM BENZENESULFONATE PER LITER, AT 48° C. 31

	and the second se	
3	C U	BRIGHT PLATE EDGES BADLY BURNED
	R R	to a well and south and interview, the service of
2	EN	The startistics of the president end the set
	T D	BRIGHT PLATE EDGES BURNED
2	E N	BRIGHT PLATE EDGES BURNED
	S	BRIGHT PLATE EDGES SLIGHTLY BURNED
	T T	BRIGHT PLATE
	AMPS/in?	BRIGHT PLATE
1		BRIGHT PLATE
		BRIGHT PLATE
		BRIGHT PLATE
		DULL PLATE

Cr03 concentration-----250 g/liter

(C6H5S03)Na concentration-----6g/liter

Cathode composition ----- Copper

ditions remained the same and the appearance of the deposits was essentially the same. This shows that the concentration of the sodium benzenesulfonate bath is not quite as rigid as that of the sulfate bath.

# FIGURE TEN

Figure ten shows the effect of current density on the appearance of a cathode for an electrolyte containing seven grams of sodium benzenesulfonate per liter. At this concentration of sodium benzenesulfonate, the bright plating range was smaller than that of the previous bath, it being three-fourths amperes per square inch. As in the previous figures, bright deposits were obtained in the lower current densities, with the burning moving to one and three-fourths amperes per square inch. Frosty deposits were obtained at current densities above two and one-half amperes per square inch.

#### FIGURE ELEVEN

Figure eleven shows the effect of current density on the appearance of a cathode for an electrolyte containing eight grams of sodium benzenesulfonate per liter. The bright plating range for this concentration was only onehalf ampere per square inch. The burning occurred at a current density of one and one-fourth amperes per square inch.

# FIGURE TWELVE

Figure twelve shows the effect of current density on the

# FIGURE X

THE EFFECT OF CURRENT DENSITY ON THE APPEARANCE OF A CATHODE FOR AN ELECTROLYTE CONTAINING SEVEN GRAMS OF SODIUM BENZENESULFONATE PER LITER, at 48° C. ..

	C	
3	U	
	R	
	R	
	E	
	N	BRIGHT DEPOSIT EDGES BADLY BURNED
	Т	
	D	
	E	
2	N	BRIGHT DEPOSIT EDGES SLIGHTLY BURNED
10	S	
+	<u> </u>	BRIGHT DEPOSIT EDGES SLIGHTLY BURNED
	Т	
+	<u> </u>	BRIGHT DEPOSIT EDGES SLIGHTLY BURNED
	, 2	
+	AMPS/IN	BRIGHT DEPOSIT
-		
4		BRIGHT DEPOSIT
		DDTOIT DTDOGTH
ł		BRIGHT DEPOSIT
		TATE DETOCTE
+		BRIGHT DEPOSIT
		DITT T DEPOST
		DOUT DELODIT

Cr03 concentration----------250g/liter (C6H5S03)Na concentration----7g/liter

CATHODE composition-----Copper

# FIGURE XI

THE EFFECT OF CURRENT DENSITY ON THE APPEARANCE OF A CATHODE FOR AN ELECTROLYTE CONTAINING EIGHT GRAMS OF SODIUM BENZENESULFONATE PER LITER, AT 48° C.

3	C U	
	R R	
	E	
2	T	
	E	BRIGHT DEPOSIT EDGES BADLY BURNED
	S	BRIGHT DEPOSIT EDGES BURNED
	T	BRIGHT DEPOSIT EDGES SLIGHTLY BURNED
1	AMPS/IN <sup>2</sup>	BRIGHT DEPOSIT EDGES SLIGHTLY BURNED
ı		BRIGHT DEPOSIT
+		BRIGHT DEPOSIT
+		BRIGHT DEPOSIT
1		DULL DEPOSIT

Cr03 concentration-----250g/liter

(C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>)Na concentration00000-----8g/liter CAthode composition----Copper

# FIGURE XII

THE EFFECT OF CURRENT DENSITY ON THE APPEARANCE OF A CATHODE FOR AN ELECTROLYTE CONTAINING NINE. GRAMS OF SODIUM BENZENESULFONATE PER LITER, AT 48° C.

-		
3	U U U	
	R	
	E	
	N	
	T D	•
2	E N	BRIGHT DEPOSIT EDGES BADLY BURNED
1	SI	BRIGHT DEPOSIT EDGES BURNED
	T Y	BRIGHT DEROSTT EDGES SLIGHTLY BURNED
	AMPS/IN <sup>2</sup>	BRIGHT DEPOSIT EDGES SLIGHTLY BURNED
l		BRIGHT DEPOSIT
	danette Contra	BRIGHT DEPOSIT
	The second	BRIGHT DEPOSIT
		DULL DEPOSIT

Cr03 concentration----250g/liter

(C6H5S03)Na concentration-----9g/liter

Cathode composition-----Copper

appearance of a cathode for an electrolyte containing nine grams of sodium benzenesulfonate per liter. The bright plating range remained the same as the previous one with the deposits of chromium the same in appearance.

# FIGURE THIRTEEN

Figure thirteen shows the effect of current density on the appearance of a cathode for an electrolyte containing ten grams of sodium benzenesulfonate per liter. The plating range at this concentration is very limited at being only one-fourth ampere per square inch. At the higher current densities (above one and three-fourths amperes per square inch) frosty deposits were obtained. This concentration indicated that ten grams of sodium benzenesulfonate is the maximum amount that can be used and bright deposits still be obtained.

#### FIGURE FOURTEEN

Figure fourteen shows the effect of various current densities on the appearance of a cathode for an electrolyte containing twelve grams of sodium benzenesulfonate per liter. This concentration is the poorest for obtaining bright deposits. Only one bright deposit was obtained showing that we are now entirely out of the range of usefulness.

# FIGURE FIFTEEN

Figure fifteen shows the effect of various current densities on the appearance of a cathode for an electrylyte containing 2.5 grams of sulfuric acid per liter. The figure shows that the bright plating range for this electrolyte is very limited, it being only three fourths amperes per square inch. Milky deposits are obtained below a current density of three-fourths amperes per square inch and burning can be noticed at a current density above one and one-half amperes per square inch.

## FIGURE XIII

THE EFFECT OF CURRENT DENSITY OF THE APPEARANCE OF A CATHODE FOR AN ELECTROLYTE CONTAINING TEN GRAMS OF SODIUM BENZENESULFONATE PER LITER, AT 48° C.



Cr0<sub>3</sub> concentration-----250g/liter (C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>)Na concentration-----10g/liter Cathode composition-----Copper

# FIGURE XIV

THE EFFECT OF CURRENT DENSITY ON THE APPEARANCE OF A CATHODE FOR AN ELECTROLYTE CONTAINING TWELVE GRAMS OF SODIUM BENZENESULFONATE PER LITER AT 48° C.

C U	
R	
E	
T	
E	BRIGHT DEPOSIT EDGES BADLY BURNED
S	
T	
AMPS/3	IN <sup>2</sup> BRIGHT DEPOSIT EDGES BURNED
	BRIGHT DEPOSIT EDGES SLIGHTLY BURNED
	BRIGHT DEPOSIT
	SLIGHTLY FROSTY DEPOSIT
inna h	DULL DEPOSIT

CrO<sub>3</sub> concentration-----250g/liter (C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>) concentration-----l2g/liter Cathode composition-----Copper

# FIGURE XV

THE EFFECT OF CURRENT DENSITY UPON THE APPEARANCE OF A CATHODE FOR AN ELECTROLYTE CONTAINING 2.5 GRAMS OF SULPHURIC ACID PER LITER AT 48° C. 40

C	EDGES VERY FROSTY AND BURNED
υ	
R	
R	
E	
N T	
D	DTAIL DEDACTO DECISA MADE EDACOT
E	BRIGHT DEPUSIT-EDGES MORE FROSTY
N	
T	
Ţ.	BRIGHT DEPOSIT-EDGES SLIGHTLY BURNED
Ÿ	
	BRIGHT DEPOSIT
	BRIGHT DEPOSIT
	MTODOTIO MILLION
	BRIGHT DEPOSIT
	SLIGHTLY MILKY DEPOSIT
AMPS/IN <sup>2</sup>	BRIGHT ON EDGES-NO DEPOSIT IN CENTER
Cr03	concentration250g/liter
J	2

H<sub>2</sub>S0<sub>4</sub> concentration-----2.5g/liter

CATHODE composition----copper.

THE EFFECT OF VARIOUS TEMPERATURES ON THE CATHODE EFFICIENCY FOR AN ELECTROLYTE CONTAINING FOUR GRAMS OF SODIUM BENZENESULFONATE PER LITER

	I	TABLE I (TEMPERATURE - 38°C.)		
AMPERES	SECONDS	OBSERVED WEIGHT	CALCULATED WEIGHT	CATHODE EFFICIENCY
1	300	.0012	.0269	4.46
2	300	.0054	.0539	10.02
3	300	.0102	.0808	12.62
4	300	.0194	.1077	18.01
5	300	.0258	.1346	19.17
6	300	.0326	.1616	20.18
7	300	.0408	.1885	21.65
8	300	0482	.2154	22.39
9	300	.0598	.2424	24.68
10	300	.0694	.2693	25.72
11	300	.0804	.2962	27.15
12	300	.0798	.3232	24.7

AMPERES	SECONDS	TABLE II (T OBSERVED WEIGHT	EMPERATURE - CALCULATED WEIGHT	48°C.) CATHODE EFFICIENCY
1	300	.0010	.0269	3.72
2	300	.0046	.0539	8.54
3	300	.0094	.0808	11.63
4	300	.0106	.1077	9.84
5	300	.0188	.1346	13.97
6	300	.0248	.1616	15.36
7	300	.0302	,1885	16.03
8	300	.0348	.2154	16.16
9	300	.0418	.2424	17.25
10	300	.0472	.2693	17.53
11	300	.0536	.2962	18.1
12	300	.0600	.3232	19.00

41

~ 6 mm

AMPERES	SECONDS	OBSERVED WEIGHT	CALCULATED WEIGHT	CATHODE EFFICIENCY
1	300	.0008	.0269	. 3.11
2	300	.0012	.0539	2.23
3	300	.0058	.0808	5.70
4	300	.0090	.1078	8.35
5	300	.0136	.1346	10.1
6	300	.0190	.1616	11.76
7	300	.0246	.1885	13.06
8	300	.0270	.2154	12.54
9	300	.0310	.2424	12.8
10	300	.0370	.2693	13.74
11	300	.0414	.2962	13.97
12	300	.0468	.3232	14.48

.

TABLE III (TEMPERATURE 58°C.)

..

SUGGESTIONS FOR FURTHER WORK

Due to the success of the bath containing sodium benzenesulfonate as the active agent in the deposition of chromium, it seems reasonable to assume that other organic compounds with essentially the same structure could be used. It seems probable that such compounds as ortho and para phenol sulfonic acids, which are strong acids readily soluble in water, would have great possibilities as an electrolyte. The probability is not limited to the phenol sulfonic acids as there are many other sulfonic acids that would appear to have equal capabilities.

43

Further work could be done with the sodium benzenesulfonate  $b_a th$ , which is very peculiar in its appearance. It does not possess the characteristic color of the sulfate bath nor is the evolution of hydrogen the same. The sulfate bath evolves gases with uneven sizes of bubbles while the sodium benzenesulfonate bath evolves the hydrogen with a rolling smoothness.

# SUMMARY OF RESULTS

- Bright deposits are obtained using a pure organic compound as an electrolyte.
- 2. The widest plating range occured at a temperature of 48°C and a concentration of four grams of sodium benzene sulfonate per liter
- 3. A temperature of 38°C produces the highest cathode efficiency but the bright plating range is very limited.
- 4. The sodium benzenesulfonate bath does not possess the characteristic brown color of the sulfate bath.
- 5. Concentrations between four and six grams of sodium benzenesulfonate do not produce a marked change in the bright plating range.
- 6. A bright plating range of one ampere per square inch is obtained at a temperature of 58<sup>0</sup>C.
- 7. A cathode must be plated a minimum of twenty minutes before the sodium benzenesulfonate bath is put into use.

#### ANNOTATED BIBLIOGRAPHY

1. BLUM & HOGABOOM Principles o Electroformiz

Principles of Electroplating and Electroforming, McGraw-Hill Book Co., New York, 1930.

A book devoted to electroplating with an extensive chapter devoted to chromium plating, mentioning the operating conditions, methods of analysis, etc.

2. BURNS & SCHULTZ Pro

Protective Coatings for Metals, Reinhold Publishing Corporation, New York, 1939.

A discussion of the various methods for the deposition of metals with a special chapter devoted to chromium.

3. BROCKMAN

Electrochemistry, Principles and Practice, D Van Nostrand Co., New York, 1931.

A book entirely of electrochemistry with several pages given to chromium plating, regarding the general conditions for plating bath.

4. ELECTROPLATING By the Editorial staff of Popular Science Publishing Company, New York, 1936.

A practical handbook of diagrams, formulas, processes, and instructions showing how to set up an amateur electroplating apparatus.

5. FIELD & WEILL

Electroplating, Including Nickel Cadium and Chromium, Sir Isaac Pitman and Sons, Ltd. London 1930.

A survey of modern practice of chromium plating including types of deposits, throwing power, current efficiency, annodes etc.

#### 6. FREEMAN & HOPPE

Electroplating with Chromium Copper and Nickel, Methuen and Co., Ltd., London, 1930.

Gives some of the more practical methods of chromium plating with a detailed discussion on racking of the cathodes.

7. RICHARDS

Chromium Plating, Charles Criffin andnCo., London, 1936.

A discussion of practical plating giving the methods of cleaning of the cathodes, the equipment in the plating shops, and the racking of the cathods. Approved

Henbert Keineich Major Professor

hl.J. Kreques ?

Date May 11 1942 "