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AF TECHNICAL REPORT 5692
SUPPLEMENT 3

**AN INVESTIGATION OF ELECTRODEPOSITED ALLOYS
FOR PROTECTION OF STEEL AIRCRAFT PARTS**

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BATTELLE MEMORIAL INSTITUTE

NOVEMBER 1952

WRIGHT AIR DEVELOPMENT CENTER

2

**AN INVESTIGATION OF ELECTRODEPOSITED ALLOYS
FOR PROTECTION OF STEEL AIRCRAFT PARTS**

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Battelle Memorial Institute

November 1952

*Materials Laboratory
Contract No. AF 33(038)8750
RDO No. 611-11*

**Wright Air Development Center
Air Research and Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio**

FOREWORD

This report was prepared by the Battelle Memorial Institute under Contract No. AF 33(038) 8750, Supplemental Agreement No. 3. The contract was initiated under the research and development Order No. 611-11, "Electrodeposition and Electrochemical Treatments," and was administered by Materials Laboratory, Directorate of Research, Wright Air Development Center, with Major L. E. Michael acting as project engineer. This is the last report of a series to be published on this project. The period of work covered by this report dates from 4 April 1951 to 3 July 1952.

Authors at Battelle Memorial Institute responsible for the report were Messrs. A. B. Tripler, Jr., C. R. Konecny, W. C. Schickner, and Dr. C. L. Faust.

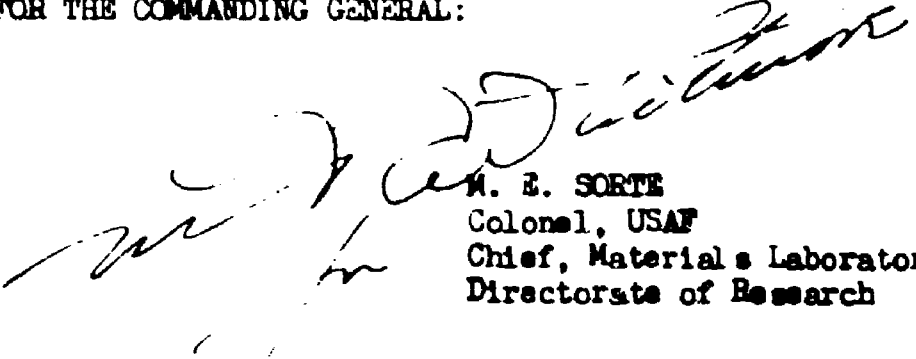
ABSTRACT

Previous work reported under this AFTR No. 5692 indicated that binary metallic systems, having manganese as one of the elements, might afford good cathodic protection to steel and be a superior coating to that of zinc or cadmium. Following a literature search, methods for electrodepositing various alloys of manganese were investigated. Manganese-zinc and manganese-tin coatings were prepared and tested under exposure conditions of alternate condensation and drying. Certain compositions of the two alloys protected steel longer than pure zinc coatings, however, they were inferior to pure cadmium coatings. The plating processes were not completely developed, and are not ready for practical application. Methods for plating manganese-nickel, manganese-chromium, manganese-iron, and manganese-molybdenum were also studied but with less success.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDING GENERAL:



M. E. SORTE
Colonel, USAF
Chief, Materials Laboratory
Directorate of Research

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FINAL REPORT

on

AN INVESTIGATION OF METHODS FOR ELECTRODEPOSITING CERTAIN BINARY MANGANESE ALLOYS AS PROTECTIVE COATINGS FOR STEEL PARTS OF AIRCRAFT

INTRODUCTION

In a temperate climate, electrodeposited zinc or cadmium keeps steel from rusting for periods of ten years or more. In the tropics, zinc and cadmium coatings deteriorate rapidly and the steel then corrodes. In many cases, this occurs in less than a year. During World War II, this condition became a menace to aircraft which were operating in the tropics. In addition, the storage of steel aircraft parts and components in the tropics could not be accomplished with safety.

In 1946, the Air Force contracted with Battelle Memorial Institute to conduct an exploratory research for substitutes for zinc and cadmium coatings for steel parts of aircraft. When the experimental work was being planned for this project, two restrictions were established for the substitute coatings. One, the coating must provide sacrificial (cathodic) protection for SAE 4130 steel. Two, the coating must be capable of being electrodeposited.

When one looks at a practical galvanic series of metals and alloys, he is struck by the fact that, of the metals which can be electrodeposited from aqueous solutions, there are only three that are more active than iron. These three metals are zinc, cadmium, and manganese.

This limited the search to alloys of cadmium or zinc, and pure manganese and its alloys. In order to keep the problem from becoming too complex, the study was further limited to binary alloys.

The work with the alloys of cadmium and zinc was reported in three final reports dated November 30, 1947, June 28, 1949, and February 23, 1951.

The report of February 23, 1951, also contained results of experiments, which showed diffusion-formed manganese-zinc alloys to have promise as protective coatings for steel. Even pure manganese appeared to be better than zinc.

As a result, a new project was set up for investigation of the electrodeposition of binary-manganese alloys. The systems to be studied were:

- (a) Manganese-zinc
- (b) Manganese-tin
- (c) Manganese-chromium
- (d) Manganese-nickel
- (e) Manganese-iron
- (f) Manganese-molybdenum
- (g) Manganese-copper (5% and less copper).

The main effort in this research program was centered on the manganese-zinc and manganese-tin alloy electrodeposits. Alloy deposits of Type c through g were to be investigated as time permitted.

The results of the work are reported herein.

The same contract covered tests on diffusion-formed manganese-zinc, and electrodeposited zinc-tin and pure manganese coatings on steel at the inland exposure site of the Battelle North Florida Research Station. The results of this test will be given in a separate final report to be prepared after approximately 24 month's exposure.

SUMMARY

Manganese-zinc alloys and manganese-tin alloys have been electrodeposited from aqueous solutions. X-ray diffraction studies revealed the presence of distinct alloy phases, although they were not the ones expected for a given alloy composition.

The electrodeposited manganese-zinc coatings, with 75 per cent manganese protected the underlying steel in the "wet-dry" cabinet for longer periods than did coatings having 25 per cent or 50 per cent manganese. Only the 75 per cent manganese coating was better in this test than pure zinc coatings of like thickness. The Mn75-Zn25 coating had an average corrosion index of 1014 compared with 439 for pure zinc. This does not necessarily mean that the manganese-zinc coating is twice as good as the zinc coating but it does indicate an improvement. Potential measurements were not made on the Mn75-Zn25 alloys. The Mn50-Zn50 alloy is over 400 millivolts more electronegative than SAE 4130 steel. The Mn75-Zn25 alloy would have a potential equal to or more negative than the Mn50-Zn50 alloy and would, therefore, provide sacrificial protection for the steel.

The manganese-tin coatings (approximately 50-50) had a slightly higher index (593) than pure zinc coatings (439) when tested in the "wet-dry" cabinet. The potential for manganese-tin was also 400 millivolts more electronegative than SAE 4130 steel, showing that it too would provide sacrificial protection.

The most satisfactory manganese-zinc coatings were obtained from a sulfate-citrate bath and a sulfate-borocitrate bath. Both of these baths suffered from a common shortcoming, this being the poor plate-composition throwing power (as contrasted to thickness throwing power). This resulted in a nonuniform alloy plate. The effect was minimized by special anode arrangements, but it was never eliminated.

In addition, each of the baths had individual faults. The surfaces of the deposits from the sulfate-citrate solution had numerous, uniformly distributed microholes, so called because they are not visible without magnification, but are apparent at 10X or 20X magnification. The microholes did not penetrate to the basis metal, but came within probably a few hundred thousandths of an inch of doing so. All attempts to eliminate the microholes were unsuccessful.

The sulfate-borocitrate solution plated at a lower efficiency than the sulfate-citrate bath. The deposits from the former were free of microholes however. Plate-density studies revealed the deposits from both baths to have densities far below those predicted on theoretical grounds. The microholes accounted for this in the sulfate-citrate plates, but no explanation was found for the low density of the sulfate-borocitrate plates.

The electrodeposition of manganese-zinc from fluoborate, fluoride, gluconate solutions and others was investigated, but none of them appeared promising.

The best deposits of manganese-tin were obtained from a sulfate-tartrate solution. The efficiency of this bath was low (of the order of 5 per cent), and little was known of the factors controlling the composition of the plate. A statistical study (a factorial experiment followed by an analysis

of variance) did not disclose any way to raise the efficiency, but it did reveal which factors influenced the plate composition. Also, purely as a result of the analysis of variance, predictions were made on formulation of twelve new bath composition for producing plates of a certain composition, quality rating, and at a given efficiency. An experimental test verified the predictions.

In performing the statistical experiment, the method was evaluated as a tool for the study of alloy plating baths. We believe it to be a valuable method, although its greater value lies in application to baths which have been developed more fully than the one chosen for this trial.

The electrodeposited manganese-tin alloy coatings, like the ones prepared by diffusion (see Final Report, dated February 23, 1951), underwent a strange transformation within a few weeks after being plated. At first, the $MnSn_2$ phase was present along with pure tin, but after a time the $MnSn_2$ disappeared, and finally by X-ray diffraction only tin and some $Mn(OH)_2$ were shown. No explanation is known for the disappearance of the $MnSn_2$ phase.

The sulfate-fluoride solution looked promising for manganese-tin deposition, because it operated at relatively high current efficiencies (up to 80 per cent), but no way was found to make the deposits entirely acceptable. Investigations of other solutions for manganese-tin alloy deposition were carried out, but none appeared practical.

Four of the minor alloy systems were studied in preliminary investigations. Manganese-copper alloys, however, were not touched upon. Available was a Navy report of research* during which no advantage was observed for manganese-copper alloy coatings (under five per cent copper) relative to zinc or cadmium coatings.

Manganese-nickel and manganese-iron alloy coatings were electrodeposited. For the most part, they had low (10 per cent or less) manganese contents. None of the plates were acceptable. The manganese-iron deposits with 10 per cent manganese were anodic (more active) than SAE 4130 steel, but the manganese-nickel plates with 10 per cent manganese were more noble than SAE 4130 steel.

The manganese-chromium and manganese-molybdenum plates were poor generally.

Cadmium-tin (75-25) coatings which were developed by another laboratory (reference 71, Appendix I) were tested in the "wet-dry" cabinet. Although not quite so good as pure cadmium coatings, they are superior to anything else yet tested in the "wet-dry" cabinet.

Any further work on manganese alloy plating should be undertaken only on the basis of a long-range project. In searching the literature,

*"Investigation of the Corrosion Resistance of Cuproferous Manganese Plating on Steel". Report No. AML NAM 41-1117, Part One.

prior to beginning experimental work reported herein, not a single work of practical importance was found. In the present work, the "surface has merely been scratched". Much lies beyond.

DISCUSSION OF ESSENTIAL DATA — LITERATURE SEARCH

The experimental work was preceded by a literature search. The indexes of Chemical Abstracts were first searched under numerous headings. The pertinent abstracts were then consulted, and following this, many of the original papers were studied. Where the original paper was not available, the abstract had to suffice.

Discussion of References

The review by Faust^{(1)*} covers the principles of alloy plating adequately. A revision⁽²⁾ of this review will soon appear, and the manuscript was available for this search. It was apparent from the beginning of the search that little published material was available on manganese-alloy electrodeposition.

Fink and Kolodney⁽³⁾ experimented with acid sulfate solutions containing ammonium ion and glycerol in the pH range 2.5 to 3.0. They made exploratory tests on the deposition of manganese-iron and manganese-zinc alloys by adding salts of these metals to their manganese bath. They reported the codeposition of the metals with manganese, but gave no quantitative data.

Agladze and Gdzeshvili⁽⁴⁾ were able to deposit alloys of manganese-nickel, manganese-iron, and manganese-zinc from simple sulfate solutions at "room temperature" (in the USSR).

Table 1 summarizes their findings as reported in Chemical Abstracts. A copy of the original publication was sought, but was not found. The alloy deposits which were obtained in this work had relatively low manganese contents. No data were given on pH.

Gritsan and Tsvetkov⁽⁵⁾ described a sulfate solution for depositing manganese-nickel alloys. This paper was available, and a translation was made. Five copies of the translation have been sent to WCRT-3 under separate cover. The authors made a systematic study of the effects of variations in plating conditions. They found that an increase in the $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ content above 150 g/l made no change in the deposit composition, a

*The numbers in parentheses correspond to the literature references found in Appendix I.

TABLE 1. RESULTS OF MANGANESE-ALLOY ELECTRODEPOSITION EXPERIMENTS
PERFORMED BY AGLADZE AND GDZESHVILI*

Alloy Deposit	Solution Composition							C.D. (ASF)	Current Efficiency, %	Composition of Deposit, % Mn
	MnSO ₄ , g/l	(NH ₄) ₂ SO ₄ , g/l	NiSO ₄ , g/l	FeSO ₄ , g/l	ZnSO ₄ , g/l	H ₃ BO ₃ , g/l				
Mn-Ni	38	75	1	-	-	-	4.4	23.7	23.7	9.53
	"	"	3	-	-	-	"	36.5	36.5	7.21
	"	"	5	-	-	-	"	45.6	45.6	6.18
	"	"	8	-	-	-	"	47.6	47.6	5.01
	"	"	10	-	-	-	"	56.6	56.6	3.86
	"	"	15	-	-	-	"	74.8	74.8	3.62
	"	"	20	-	-	-	"	82.1	82.1	3.42
Mn-Ni	7	-	6	-	-	25	2.7	33.9	33.9	11.45
	"	-	7	-	-	"	"	37.7	37.7	10.31
Mn-Fe	10	75	-	10	-	-	1.9	-	-	0.29
	20	"	-	"	-	-	"	-	-	0.37
	30	"	-	"	-	-	"	-	-	0.71
	"	"	-	"	-	-	2.85	-	-	4.41
	"	"	-	"	-	-	4.8	-	-	8.03
	"	"	-	"	-	-	8.5	-	-	9.33
Mn-Zn	40	75	-	-	40	-	8.5	-	-	0.62
	"	"	-	-	"	-	14	-	-	0.71
	"	"	-	-	"	-	16	-	-	1.54

*Reference (4), Appendix 1.

maximum of seven per cent manganese being obtained. At a given current density, increase in the ammonium-ion concentration caused a decrease in the manganese in the deposit. This fits in with the knowledge that manganese forms a complex with ammonium ion. As complexing increases, the deposition potential of the manganese becomes more electronegative, making it more difficult for manganese to deposit. Current-density changes had little effect. Changes in pH brought about very pronounced changes in the composition of the deposit. In general, increase in pH increased the manganese content of the deposit. Gritsan and Tsvetkov were able to get deposits containing almost any desired amount of manganese by small changes in pH. This naturally requires a strongly buffered solution for prolonged deposition.

Graham, Crowley, and Associates, Incorporated*, have deposited a manganese-copper alloy containing 2+% copper from a slightly alkaline sulfate solution.⁽⁶⁾

Shaffer⁽⁷⁾ patented a chromium-plating process that may involve the deposition of a chromium-manganese alloy. The bath contained manganese dioxide equivalent to about 10% of the chromic oxide content of the bath.

A solution from which tungsten-manganese alloys could be deposited was claimed by Armstrong and Menefee⁽⁸⁾. This alloy is not one of interest to this work as such, but the type of solution used might provide a clue for other baths. Armstrong and Menefee used a bifluoride-citric acid-type bath.

Manganese and tin were codeposited from pyrophosphate solutions and thiocyanate solutions, during earlier phases of this project. In both cases, however, the tin content of the deposit was very low.⁽⁹⁾ Later experiments showed a tartrate-oxalate bath to give deposits with higher tin content, but the reproducibility of the results was poor.

Codeposits of manganese and nickel were also obtained at Battelle, using a sulfate-type manganese-plating bath with small additions of nickel sulfate. The deposits contained about 13% manganese.

In the absence of much direct information on the deposition of binary manganese alloys, a search was made for methods of deposition of the individual metals. Data on both the usual and unusual types of solutions were sought. Most of the work on the deposition of pure manganese has been with sulfate or chloride solutions. Much of it is repetitious.

The work of the Bureau of Mines Laboratories^(10,11) provides reliable data for the sulfate and chloride solutions, respectively. Bradt and

*407 South Dearborn Street, Chicago 5, Illinois.
475 York Road, Jenkintown, Pennsylvania.

Oaks^(12,13) also investigated the conditions for depositing manganese from sulfate and chloride electrolytes. In general, the solutions contain $MnCl_2$ or $MnSO_4$, and the corresponding ammonium salt. A small amount of sulfite is also added. The presence of ammonium ion appears desirable. Bradt and Taylor⁽¹⁴⁾ made a survey of several electrolytes and found that manganese could be deposited from solutions of manganese sodium citrate, manganese benzoate, manganese acetate, manganese fluoborate, and sodium citrate-containing solutions of manganese dithionate, manganese tartrate, manganese formate, manganese fluosilicate, manganese lactate, and manganese acetate. The best quality deposits were obtained from the benzoate, sodium citrate, and mixed lactate-sodium citrate solutions. Manganese was deposited at Battelle from pyrophosphate solutions.⁽⁹⁾ The efficiency was quite low, however.

Thompson⁽¹⁵⁾ describes two soluble manganese cyanide complexes. During the work by Graham, Crowley, and Associates⁽⁶⁾, unsuccessful attempts were made to deposit manganese from a cyanide solution. This does not rule out the possibility of using manganese cyanide for alloy deposition. In the presence of other metals, depolarization of the manganese may take place.

Piontelli⁽¹⁶⁾ was able to deposit manganese from a sulfamate bath. He has also used sulfamate solutions for binary-alloy deposition⁽¹⁷⁾, but none of the alloys contained manganese.

The deposition of zinc from acid sulfate and cyanide solutions is too well known to require references. Rogers and Bloom⁽¹⁸⁾ plated zinc from an alkaline zincate solution containing ammonium sulfate. This type of bath corresponds to the manganous sulfate bath. Piontelli^(19,20) and Choguill⁽²¹⁾ obtained good zinc deposits from sulfamate solutions.

Gernsb, Lorenz, and Montillon⁽²²⁾ obtained zinc deposits from thio-sulfate solution. The conditions for plating zinc from a fluoborate solution were described by Narcus.⁽²³⁾ Senter and Taft⁽²⁴⁾ investigated twenty-five addition agents for use with the acid zinc bath and found that any one of nine agents improved the deposit. Zinc can be deposited from a pyrophosphate solution. This information was privately communicated.

The two most well-known tin-plating solutions are the alkaline stannate solution and the acid sulfate solution. Recently, the fluoborate solution has come into use for depositing tin. Narcus⁽²³⁾ has given the conditions for obtaining sound deposits.

Kern⁽²⁵⁾ published a review of known tin-plating methods in 1913. Among the more or less successful baths were stannous ammonium oxalate, pyrophosphate, ammonium chloride, cyanide-carbonate, tartaric acid, fluosilicate, and fluoride.

In more recent years, Mathers and Johnson⁽²⁶⁾ and Hothersall and Bradshaw⁽²⁷⁾ obtained tin deposits from stannous ammonium oxalate solutions. Mathers and Cockrum⁽²⁸⁾ reported the deposition of tin from pyrophosphate solutions.

Binary manganese alloys have been prepared pyrometallurgically, and, in some cases, their chemical properties were studied. Several references reporting these results have been found. Tammann and Vaders⁽²⁹⁾ studied the electrolytic behavior of binary alloys of manganese with copper, nickel, cobalt, and iron. They made potential measurements and studied the displacement of various metals from their solutions by the alloys.

There were no sudden changes in the potentials of copper-manganese alloys until the manganese content reached 50 atomic per cent. The potential then suddenly changed to a very electronegative value, being about the same value as that of pure manganese. This indicates that at this composition the alloy becomes very active chemically. This was supported by experiments where alloys containing 46 mole per cent manganese displaced zinc from solution. Manganese-iron alloys showed no such marked changes in electrolytic properties at any composition. This is supported by the work of Wells and Warner.⁽³⁰⁾ Tammann and Vaders' experiments with manganese-nickel alloys showed no abrupt changes in potentials, but rather a uniform change with changes in composition.

Landau and Oldach⁽³¹⁾ did some work on the corrosion of binary alloys. Manganese-nickel and manganese-iron were included. Two solutions were used, aerated four per cent sodium chloride solution and 1 N air-free hydrochloric acid solution. All experiments were at 25 C. As the nickel in manganese-nickel alloy increased from zero to 40 atomic per cent, the corrosion in the sodium chloride decreased from 145 mdd* to 100 mdd. At 60 atomic per cent nickel, the corrosion had fallen to 15 mdd, and at 80 atomic per cent nickel the corrosion was the same as for pure nickel, or about 2 mdd. Of course, with the higher quantities of nickel, the alloy would no longer be electronegative to steel. Manganese-nickel containing 9 atomic per cent nickel corroded at the rate of 10 mdd in 1 N, air-free hydrochloric acid solution at 25 C. The rate decreased uniformly with increase in nickel until at pure nickel the rate was 10 mdd.

Experiments conducted here⁽⁵¹⁾ with cast manganese-nickel alloys revealed a very interesting point. Alloys containing 13.7 and 29.5 per cent nickel and coupled with steel were immersed in three per cent sodium chloride solution. The manganese-nickel alloy polarized so strongly that insufficient current flowed to protect the steel.

Landau and Oldach, in their experiments with manganese-iron, recorded a corrosion rate of 115 mdd for a manganese-iron alloy containing 40 atomic per cent iron in four per cent aerated NaCl solution. The rate decreased uniformly with increase in iron, until at 100 per cent iron the

*Milligrams per square decimeter per day.

rate was 80 mdd. In the HCl solution, the manganese-iron alloys with 40 atomic per cent iron corroded at about 30,000 mdd, and again this rate decreased uniformly to 500 mdd for pure iron.

Walters, in an article describing manganese-iron alloys⁽³²⁾, says that 30 to 50 per cent manganese produces a completely austenitic alloy, but the corrosion resistance is probably less than that of other austenitic alloys.

Since cathode polarization measurements will continue to be used for this investigation, two older papers have been reviewed, and two very recent papers have been consulted. Lustman⁽³³⁾ used such techniques in a study of zinc-nickel alloy deposition. He was able to correlate changes in cathode polarization with the equilibrium phase diagram of zinc-nickel alloys. Lustman first studied solutions containing single metal salts, and then proceeded to the more complex solutions. Parkinson⁽³⁴⁾ used polarization measurements in studying the deposition of tin-nickel alloys. Nambissan and Allmand⁽³⁵⁾ measured cathode polarization in their study of silver-cadmium alloys.

The so-called "direct method" was used for measuring the cathode potentials in the above three works. The potentials are measured with the plating current flowing. A reference electrode, such as the saturated calomel electrode, is used as the zero of reference. Glasstone⁽³⁶⁾, in his polarization studies of the deposition of alloys of zinc with iron, cobalt, and nickel, used the "commutator" method. Here, the plating current is periodically interrupted, and, in the interval when zero current is flowing, the cathode potential is measured several times over a total period of less than a second. The potential changes during this brief time, and the points are plotted. Extrapolation to zero time is supposed to give the true polarization value, and values obtained by this method do differ from those obtained by the "direct method". One disadvantage of the "commutator" method is the relatively complicated apparatus necessary. It is not believed necessary to have the "true" polarization values for alloy-plating work. What is needed is a method for showing the effects of changes in plating conditions in the cathode layer. The "direct" method is believed adequate for this purpose.

Thiel and Hammerschmidt⁽³⁷⁾ found the hydrogen overvoltage of manganese to be fairly high. They obtained 0.37 volt, compared with 0.48 for zinc. No data were found for manganese alloys.

Newbery⁽³⁸⁾ found the hydrogen overvoltage of manganese to be 0.57 volt in acid solution, and 0.33 volt in alkaline solution, as compared with 0.57 volt and 0.60 volt, respectively, for zinc.

Mellor⁽³⁹⁾ was consulted on the chemistry of manganese, zinc, tin, nickel, iron, chromium, and molybdenum. Prescott and Johnson⁽⁴⁰⁾ contained much of value insofar as the chemical reactions of these metals were concerned.

The review of alloy electrodeposition for the period 1930-1940 by Faust⁽⁵³⁾, and the literature survey on alloy deposition prepared by the Materials Laboratory⁽⁵⁴⁾ of the U. S. Air Force were also consulted and proved helpful.

X-ray diffraction analysis was used in this work for determining the phases present in the electrodeposited alloys. Table 2 contains references on X-ray data and/or constitution diagrams for each of the alloy systems.

Additional references are cited in the body of this report. Numerals in parenthesis will continue to refer to the list of references in the bibliography (Appendix I).

DISCUSSION OF ESSENTIAL DATA — MANGANESE-ZINC ALLOY DEPOSITION

Introduction

Previous work with manganese-zinc alloy coatings, prepared by diffusion of duplex deposits (see Final Report, dated February 23, 1951), indicated that coatings containing approximately 50 per cent manganese would provide good protection for steel. When tested in the "wet-dry" cabinet, these coatings provided protection for longer periods than did like thicknesses of pure zinc. The codeposition experiments described below were aimed at producing an acceptable manganese-zinc deposit, containing 50 per cent manganese.

Exploratory Plating Work

Simple Sulfate Solutions

Following the lead obtained from the literature survey, experiments began with simple sulfate solutions. These solutions proved unsuitable for two reasons. During electrolysis, the pH changed rapidly, and the manganese contents of the deposits were below five per cent. Details of the simple sulfate-solution experiments are recorded in Table 14, Appendix II. Clearly, a solution with better buffering qualities was needed, as well as one in which the cathode polarization was greater than in the simple sulfate solution. Figure 1 shows the cathode polarization for the simple sulfate solution to be insignificant.

**TABLE 2. REFERENCES ON CONSTITUTION
DIAGRAMS AND X-RAY DATA**

System	References
Mn-Zn	Metals Handbook (41), p 1229 Potter & Huber (42) Parravano & Montoro (43) Parravano & Caglioti (44) Hansen (45), pp 905-909
Mn-Sn	Tin Research Institute (46), pp 36-37 (Diagram according to 0.N121) Nowotny & Schubert (47) Hansen (45), pp 902-904
Mn-Fe	Metals Handbook (41), p 1210 Sekito (48) Hansen (45), pp 676-687 Walters (32)
Mn-Cr	Zwicker (49)
Mn-Cu	Metals Handbook (41), p 1198 Hansen (45), pp 576-584
Mn-Ni	Metals Handbook (41), p 1228 Koster & Rauscher (50) Coles & Hume-Rothery (52)
Mn-Mo	Hansen (45), p 883

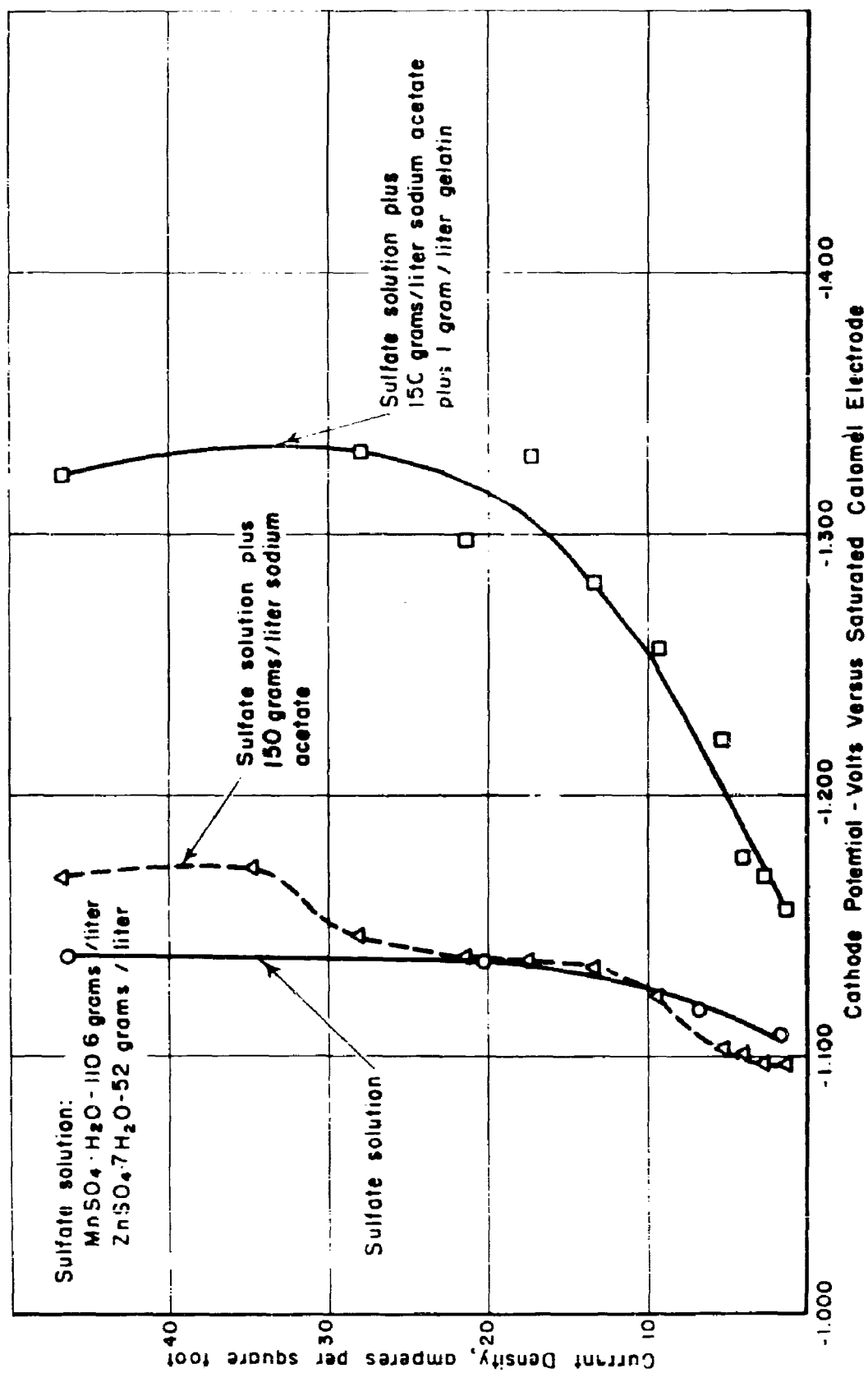


FIGURE 1. THESE CURVES SHOW THE EFFECT OF SODIUM ACETATE AND GELATIN ON THE CATHODE POLARIZATION

A-98

Sulfate-Acetate Solutions

Acetate solutions are known to provide buffer action, and have been used in pure-manganese deposition. Sulfate solutions containing either sodium acetate or ammonium acetate were tested in this series of experiments. The details are given in Table 15, Appendix II. As was expected, the solutions did not change pH appreciably during electrolysis. Yet, the cathode polarization for the sulfate-acetate mixtures was not much greater than for the simple sulfate baths. This is shown in Figure 1.

The deposits from solutions containing ammonium acetate had very low manganese contents, while the deposits from the sodium acetate baths contained up to 36 per cent manganese, and the manganese content increased with increasing sodium acetate concentration. The deposits in both cases, however, were dark and flaky. Several types of addition agents were tried in an attempt to improve the deposits. Among the addition agents tried were a sulfonic acid, hide glue, gelatin, an amino sulfonic acid, and a proprietary agent. None of these had the desired effect. The data are given in Table 16, Appendix II.

Cathode-polarization measurements (Figure 1) with a solution containing gelatin revealed strong polarization. Analysis of a deposit from the gelatin-containing solution showed a lower manganese content than was expected on the basis of the polarization measurements. Efficiencies varied from below 10 per cent to slightly over 100 per cent. In general, where the cathode efficiency was high, the manganese content of the deposit was low.

Sulfate-Citrate Solutions

Sodium citrate proved to be both a good buffer and a good polarizer. Figure 2 shows the polarization curves for a simple sulfate solution and sulfate solutions with 50 g/l and 250 g/l sodium citrate, respectively. Very strong cathode polarization was observed at the 250 g/l concentration.

Further study of additions causing cathode polarization revealed the most promise for citrate. The results of extensive study with citrate-containing baths are reported in the following sections.

Sulfate-Borocitrate Solutions

Borocitrate complexes have been used with success in alloy plating.⁽⁵⁵⁾ There was a possibility that this type of complex would be more stable than the citrate, and that no precipitation would occur. Cathode polarization studies were started to learn the effect of varying quantities of boric acid. These results are given in Figure 3. The addition of boric acid did not increase the polarization to the desired degree. Actually, when boric acid is present, the polarization decreases with current densities exceeding

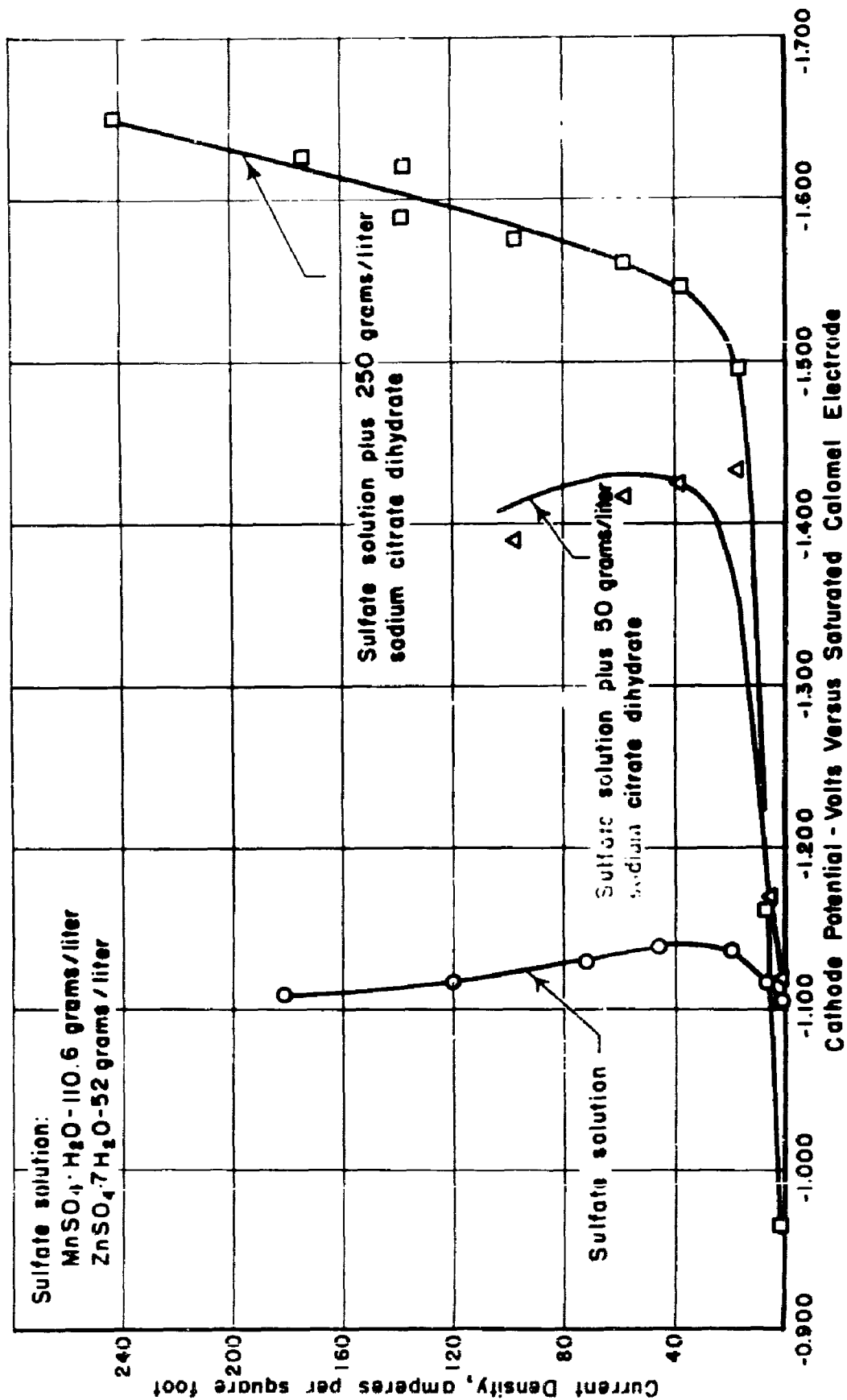


FIGURE 2. THESE CURVES SHOW THE EFFECT OF INCREASING CITRATE CONCENTRATION ON THE CATHODE POLARIZATION

A-2575

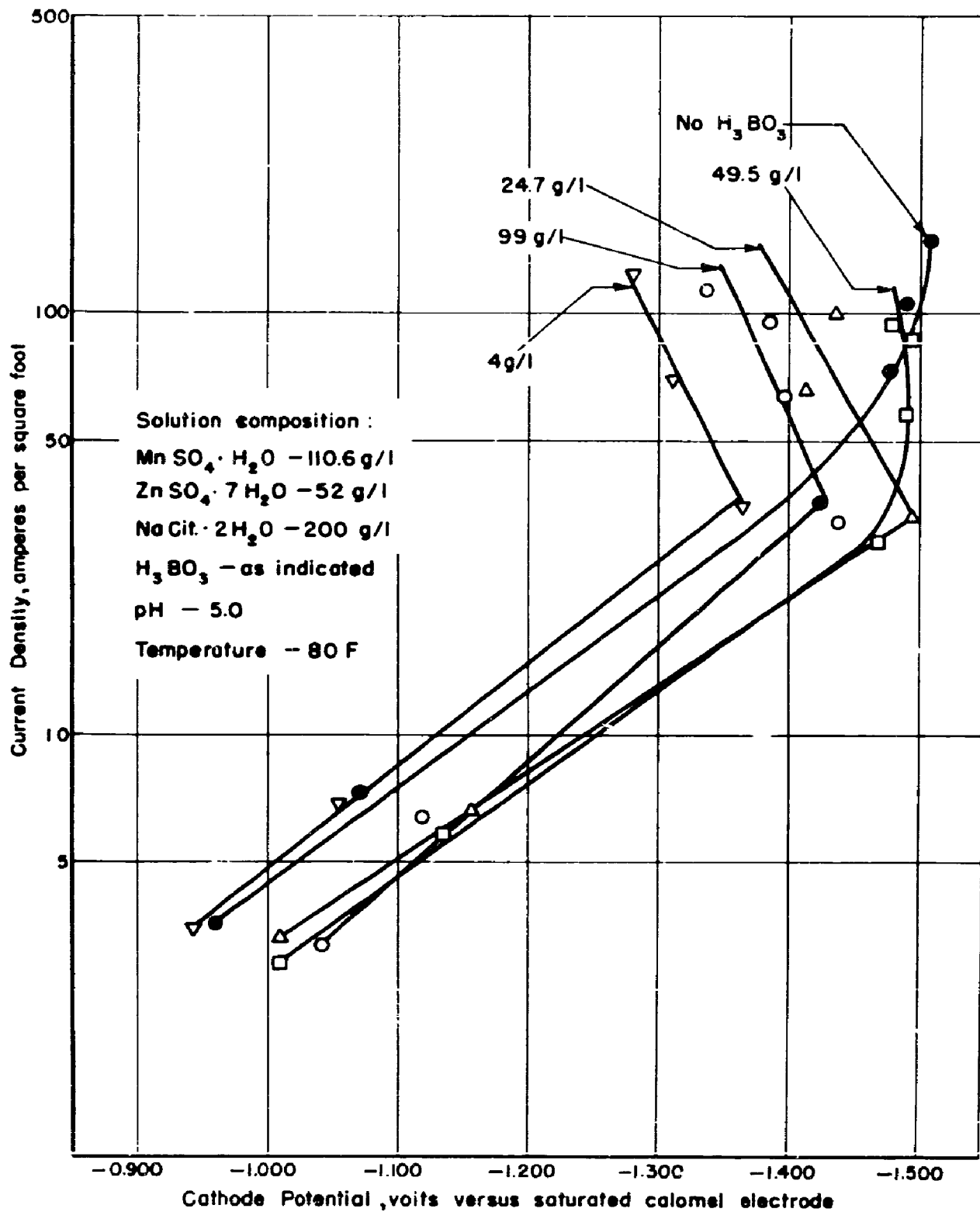


FIGURE 3. THE EFFECT OF BORIC ACID ADDITIONS ON THE CATHODE POLARIZATION IN MANGANESE - ZINC SULFATE - CITRATE SOLUTIONS

A-497

40 amp/sq ft. Solutions containing 99 g/l of boric acid showed no precipitate following electrolysis. Apparently the borocitrate complex is more stable. The manganese content of the deposits was about the same as those plated from the sulfate-citrate bath, but the efficiency was lower. The decrease in polarization may be connected with the lower efficiency.

Figure 4 shows the effect of lowering the pH on the cathode polarization. The magnitude of the polarization is unchanged, but the shape of the curve is different. The significance of the difference in shape is unknown. The fact that the magnitude is the same indicates that there would be no appreciable change in composition due to the change in pH. It appears from Figures 3 and 4 that the limiting current density is about 40 amp/sq ft.

The Sulfate-Citrate Bath

Introduction

As a result of the preliminary work, the standard sulfate-citrate bath for depositing manganese-zinc alloys was as follows:

MnSO ₄ · H ₂ O	110 g/l
ZnSO ₄ · 7H ₂ O	52 g/l
Na Citrate	250 g/l
pH	5.3

The plating cells contained either 250 or 500 ml of solution and were operated with carbon rod anodes enclosed in porous Alundum cups. Usually, one anode (and its cup) was on each side of the cathode.

In general, this bath gave the best results. Any composition variations will be made with reference to it.

Fairly good plates, containing up to 85 per cent manganese, were obtained in these experiments, which are described in detail in Table 17, Appendix II. On the 2-inch x 1/2-inch cathodes, the plates were fairly uniform, but showed a slight edge effect. The per cent manganese in the plates was proportional to the citrate content of the bath. This is in agreement with the cathode-polarization results. The manganese content of the alloy plate also became greater with increasing current density, and at the same time the cathode efficiency decreased. Increase in temperature resulted in inferior deposits. Cathode agitation seemed to have little effect on the deposit.

X-ray diffraction measurements on a 30 per cent manganese alloy showed only the epsilon phase to be present. The phase designations used here follow the constitution diagram for manganese-zinc according to Potter and Huber⁽⁴²⁾. Figure 5 is a reproduction of this diagram. X-ray measurements of the 50% alloy also showed only the epsilon phase to be present. According to the phase diagram, one would expect beta manganese plus alpha at room temperature for both alloys. At 50 per cent manganese, epsilon phase is stable down to 1025 F, while the 30 per cent alloy is stable down to 575 F.

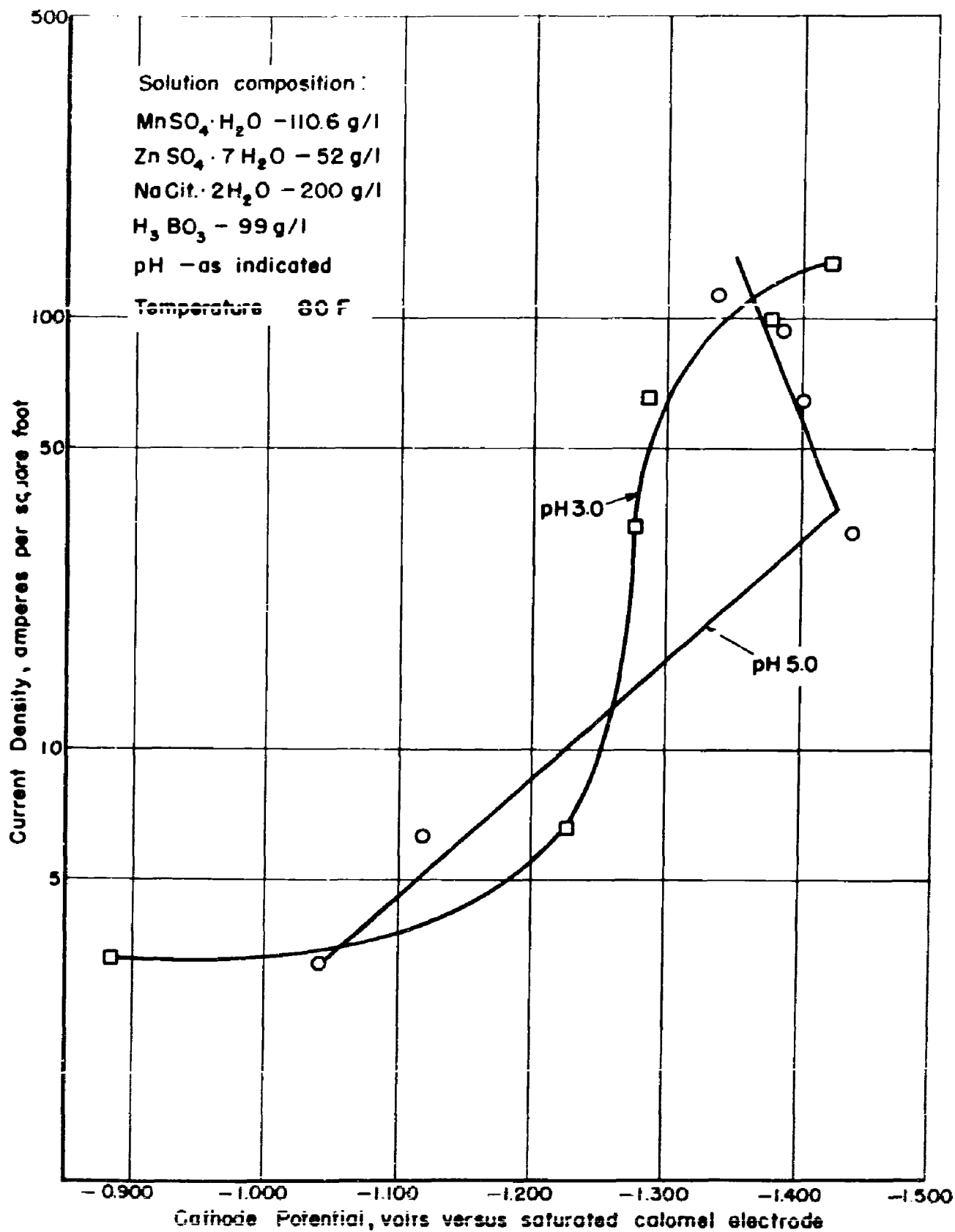


FIGURE 4. EFFECT OF pH CHANGE ON THE CATHODE POTENTIAL IN THE SULFATE BOROCITRATE SOLUTION

A-498

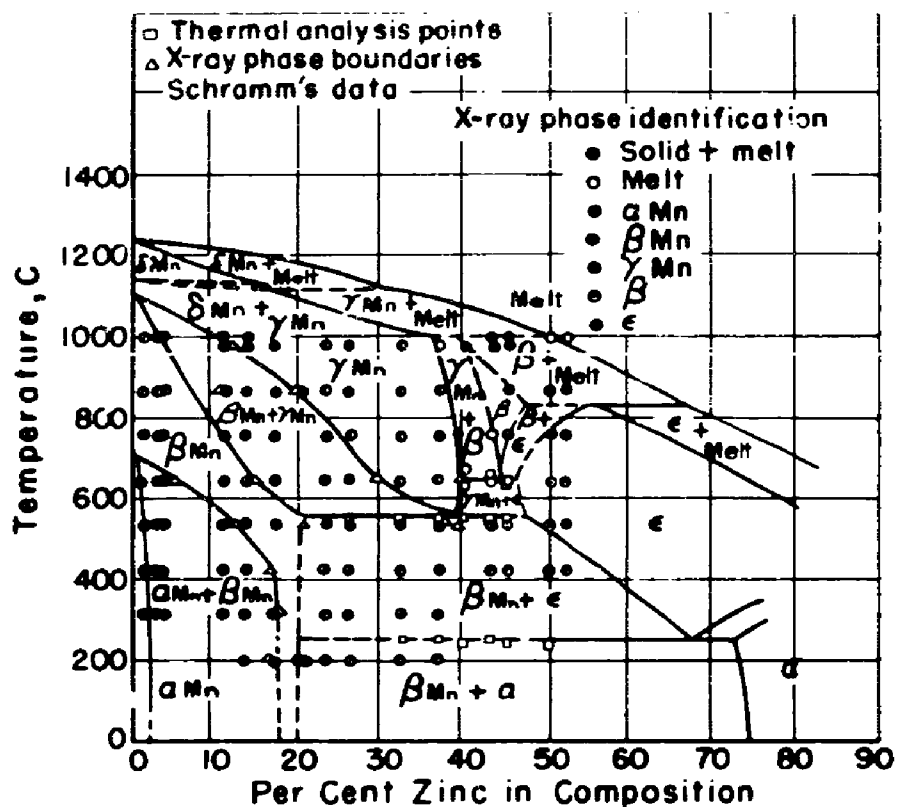


FIGURE 5. MANGANESE-ZINC CONSTITUTION
 DIAGRAM
 (Reference 42, Appendix I)

A-2576

Manganese-zinc (50-50) alloy coatings, prepared by diffusion (see Final Report dated February 23, 1951), failed to agree with the phase diagram. In this case, however, X-ray diffraction detected beta manganese plus epsilon. These phases are stable down to about 550 F. Slow cooling of the diffusion coating failed to produce the expected beta manganese plus alpha. The discrepancy between the phases predicted by the phase diagram and those in the electrodeposited alloys has not been explained. Discrepancies also have appeared in work by other investigators of alloy electroplates.

The baths and deposits from it had certain faults. The plates were not uniform in appearance ("edge effect") and composition, and plates containing 50 per cent or less manganese had relatively poor corrosion resistance (caused by microholes) on steel. Plates containing about 75 per cent manganese held up better than pure zinc in the "wet-dry" test. Part of the material in the baths precipitated, showing the bath to be unstable. The results of the studies toward attempting to eliminate those undesirable qualities are given in the following sections.

Static Potential Measurements on Electrodeposited Manganese-Zinc Alloy Coatings

Table 3 contains the static potential measurements for three specimens of manganese-zinc alloy coatings. Two of these are of the Mn25-Zn75 type, and the third is of the Mn50-Zn50 type. The measurements were made in 3 per cent sodium chloride solution at 90 F. The two specimens with the lower manganese contents had about the same potential as pure zinc. These two panels had been plated at different times and from different baths (although of the same composition). The potentials were fairly close, as they should have been.

The coating with the higher manganese had a potential of 80 to 100 millivolts more negative than the others. All three coatings should give sacrificial protection to steel under most corroding conditions.

Tests on Mn-Zn Alloy Plated Steel in "Wet-Dry" Exposure.*

A series of six SAE 4130 steel panels were coated with 0.3 mil of the approximately 50-50 manganese-zinc alloy. Table 18, Appendix II, gives details of the plating conditions in preparing these panels and the ones used

*The conditions are described in the experimental section.

TABLE 3. STATIC POTENTIAL MEASUREMENTS
OF MANGANESE-ZINC ELECTRO-
DEPOSITED ALLOYS IN THREE PER
CENT NaCl SOLUTION AT 90 F

Elapsed Time, minutes	Potential Versus Saturated Calomel Electrode in Volts		
	6429-78E Mn24-Zn76	6606-2I Mn26-Zn74	6429-30C Mn45-Zn55
1	-1.012	-1.079	-
10	-1.020	-1.076	-1.165
20	-1.045	-1.064	-1.137
30	-1.055	-1.049	-1.137
40	-1.053	-1.035	-1.133
50	-1.053	-1.030	-1.132
60	-1.052	-1.028	-1.133
90	-1.049	-1.033	-1.132
120	-1.050	-1.035	-1.135
180	-1.053	-1.038	-1.140

for X-ray study. The panels were exposed in the "wet-dry" cabinet. Iron rust appeared after two cycles, and the advance of rusting was rapid. The specimens were removed after 40 cycles. Table 4 gives the results of the test. This table also contains "wet-dry" data for manganese-zinc coatings having two other compositions, for manganese-tin coatings, and for cadmium-tin coatings. These will be discussed in their proper place in the report. The reason for putting all the "wet-dry" results in a single table is for ease of comparison of one set of data with another.

The index system of comparison (first described in the Final Report, dated February 23, 1951) is used here, and the electrodeposited manganese-zinc alloys are compared on the basis of this index with those prepared by diffusion. The average index for a 50-50 diffused alloy was 878. The average for the codeposited alloy is 234. Plain zinc coatings have averaged 439. The larger the index number, the better is the corrosion resistance.

The question immediately arises, why the difference? The iron rust first appeared on the codeposited specimens in pinpoints distributed with fair uniformity over the surface. It was thought that the coatings were porous. Metallographic examination of a cross section showed the trouble to be not with porosity but with what appeared to be voids. Rough density measurements were then made. The average coating weight for eight test pieces having 0.3-mil coatings was 0.1531 gram. The theoretical weight of a uniform 0.3-mil deposit of a 50-50 manganese-zinc alloy is 0.2420 gram. In making the theoretical calculation, no weight of coating was added for the edges. The apparent density of the electrodeposited coatings clearly is low.

Further "wet-dry" tests were made on manganese-zinc deposits containing approximately 25 per cent and 75 per cent manganese, respectively. Reference to Table 4 shows the corrosion resistance of the manganese-zinc coatings to be proportional to the amount of manganese in the deposit. With 75 per cent manganese, the coatings are more resistant than pure zinc coatings when tested in the "wet-dry" test.

The first thought was that basic manganese compounds were precipitating on the cathode with the metals. When the compounds dry, they shrink, causing voids in the deposit. Later this hypothesis was discarded.

If basic compounds codeposited with the metals, they were formed in the cathode layer as the pH increased. Ammonium sulfate was added to the standard sulfate-citrate solution with the thought it might buffer the cathode layer. (See Table 19, Appendix II.)

The pH of the cathode layer was estimated by the so-called drainage method, which is performed as follows: After plating for a given time, the cathode is withdrawn, allowed to drain for five seconds, and a piece of indicator test paper is pressed against the cathode, but is not touched to the drop clinging to the lower edge of the cathode. With the ammonium

TABLE 4. "WET-DRY" TEST RESULTS FOR VARIOUS
BINARY ALLOY PLATES ON SAE 4130 STEEL

Specimen Number	Type of Plate and Nominal Composition, weight %	Type of Bath Used in Preparing Plate	Thickness of Plate, mil	Cycles to First Rust	Cycles to 50% Rust	Index	Average Index for Type Plate	Remarks
6106-2B	Mn28-Zn74	Sulfate-Citrate	0.3	2	92	368	399	No special comment
-2E	Ditto	Ditto	0.35	4	72	288		
-2F	"	"	0.3	2	178	618		
-2J	"	"	0.3	2	78	320		
6145-46E	Mn50-Zn50	"	0.4	4	See footnote (1)	202	234	No special comment
-56B	Mn45-Zn55	"	0.3	2	Ditto	242		
-56C	Ditto	"	0.3	2	"	303		
-56A	"	"	0.3	2	"	202		
-56B	"	"	0.25	4	"	220	633	No special comment
6106-24C	Mn50-Zn50	Sulfate- Borocitrate	0.2	6	94	491		
-24D	Mn45-Zn55	Ditto	0.4	6	136	775		
6106-10E	Mn79-Zn21	Sulfate-Citrate	0.3	4	171	1088	1014	Initial rust no longer visible at 6 cycles; rust reappeared at 86 cycles. Removed from cabinet by mistake after 92 cycles (10% rust). No special comment.
-10F	Ditto	Ditto	0.3	4	--	--		
-10G	"	"	0.3	6	164	930		
6530-22C	Mn55-Sn45	Sulfate-Tartrate	0.3	2	92	475	593	No special comment.
-22G	Ditto	Ditto	0.3	14	78	412		
-22J	"	"	0.3	2	118	668		
-24B	"	"	0.3	2	170	815		

TABLE 4. (Continued)

Specimen Number	Type of Plate and Nominal Composition, Weight %	Type of Bath Used in Preparing Plate	Thickness of Plate, mil	Cycles to First Rust	Cycles to 50% Rust	Index	Average Index for Type Plate	Remarks
5350-35A	Cd77-Sn23	Fluoborate	0.3	156	---	---	---	No special comment
-35B	Ditto	Ditto	0.3	100	---	---	---	
-35C	"	"	0.3	---	---	---	---	
-35D	"	"	0.3	---	---	---	---	
5350-36A	Cd	Cyanide	0.3	---	---	---	---	The cadmium coated panels are being used as comparison standards for the Cd-Sn-coated panels. The former show no rust after 394 cycles, at which time the test was concluded
-36B	Ditto	Ditto	0.3	---	---	---	---	
-36C	"	"	0.3	---	---	---	---	
-36D	"	"	0.3	---	---	---	---	

(1) These panels were removed from the "wet-dry" cabinet before 50% of their surfaces were covered with iron rust. The index for each one was obtained by extrapolating to 50% rust.

sulfate concentration at 135 g/l, the manganese content of the deposit fell to about one per cent. This is due to the formation of a tight manganese-ammonium complex. The cathode film pH was 6 to 7. The pH of the bulk of the solution was 5.3.

With the ammonium sulfate concentration at 50 g/l, the manganese in the deposits varied between five and ten per cent, and the pH of the cathode film was 6 to 8. This is about the same pH as the cathode layer in a sulfate-citrate solution with no ammonium ion present. The cathode was agitated in an effort to keep the pH of the cathode layer lower, but this depressed the manganese content further. The ammonium ion is undesirable, then, because it suppresses the manganese so strongly.

Direct evidence for the absence of basic manganese compounds was uncovered by the determination of oxygen in Specimen Number 6606-38B (Table 20, Appendix II) which had an oxygen content of 0.14 per cent. Assuming that a compound of the type Mn(OH)_2 is formed, this compound would be present only to the extent of 0.39 per cent. If the Mn(OH)_2 undergoes dehydration, and a compound of the type MnO results, it would be present in the deposit to the extent of 0.62 per cent. These small amounts do not account for the discrepancies observed in the densities of the deposits.

Bath-Stability Studies

As made up, the sulfate-citrate solution is stable and develops little or no precipitate on standing. Once it has been electrolyzed, some unknown change occurs which causes a fairly heavy white precipitate to form after several hours. The precipitate contains manganese, but no zinc. X-ray analysis did not disclose the nature of the precipitate.

In an effort to increase the stability of the solution, a bath was prepared which contained 200 g/l methyl alcohol. This was not altogether successful, since manganese still precipitated, although to a lesser degree. Fairly good deposits were obtained from the bath containing alcohol when agitation was used.

Another attempt to stabilize the solution consisted of preheating the solution for four or more hours at 160 F. The solution was then cooled to 80 F, and electrolyzed. The idea behind this was to hasten the reaction between the metal and the citrate in forming a complex. Preheating did not stabilize the solutions, nor was any change in the subsequent deposits detected.

Dilution of the solution was also tried. This did not prevent the precipitation, but the electrodeposition efficiencies were somewhat higher. Table 21, Appendix II, records the results of the dilution experiments. A coating containing 57 per cent manganese was produced at a current

efficiency of 31 per cent. This compared with about 20 per cent for the more concentrated solutions. The deposits were powdery on the edges, however.

There was the possibility that oxidized material from the anolyte was diffusing through the single Alundum diaphragm and initiating precipitation in the catholyte. To eliminate this possibility, a double diaphragm cell was used. The anolyte was a solution of $(\text{NH}_4)_2\text{SO}_4$ and the catholyte was purified with activated carbon. The cell had only one anode. The experiments are detailed in Table 22, Appendix II. The cathode surface facing the anode had a gray mat center with lighter edges, but the surface away from the anode had a light-gray mat center with darker edges. X-ray diffraction results for plate structures are given in Table 5. The data show no change in structure of the plate due to absence of oxidation products.

TABLE 5. X-RAY DIFFRACTION RESULTS
FOR PANELS PLATED IN
DOUBLE DIAPHRAGM CELL

Specimen No.	Results
6429-28A	Strong epsilon phase, both sides
-28B	Ditto
-28C	"

The catholyte from these tests showed no precipitate after standing one week. Apparently, either the activated-carbon treatment, or the absence of anodic-oxidation products, or both, prevented precipitation. Hydrogen peroxide in dilute acid solution is known to reduce oxidized manganese to the divalent state. The precipitate redissolved when a few milliliters of H_2O_2 were added and the solution was heated to 180 F. Boiling expelled the excess H_2O_2 . Subsequent experiments disclosed that the precipitate would redissolve if the solution merely was boiled, no H_2O_2 being present. This knowledge was valuable in that it enabled making the bath aging studies described later.

"Edge-Effect" Studies

In this work, "edge effect" denotes a very narrow border around the edge which apparently differed from the rest of the plate in color only. The standard panel for use in the "wet-dry" cabinet measures 3 inches x 1 inch (plated area). The first alloy deposits on the larger panels showed a marked "edge effect". The borders at the lower extremity of the panels measured as much as 1/2 inch. This was thought to be related to throwing power. The carbon rod anodes were then replaced with two flat carbon anodes measuring 2 inches x 4 inches, and placed in porous, rectangular Alundum cups. This innovation resulted in minimizing the "edge effect", but not in its elimination.

Panels showing sufficient "edge effect" to be measure were studied by X-ray diffraction. Table 6 gives the results of these tests. The difference between the center and edge was demonstrated to be more than one of color. Two separate structures were found. The center is composed of epsilon phase and the edge contains gamma manganese. A spot check of the literature has revealed no reference to the fact that zinc will stabilize manganese in the gamma form. It is known that iron, nickel, cobalt, and copper will stabilize manganese in the gamma form.

TABLE 6. RESULTS OF X-RAY DIFFRACTION TESTS
ON SEVERAL MANGANESE-ZINC ALLOY
ELECTRODEPOSITS

Specimen No.	Per Cent Manganese in Deposit ⁽¹⁾	Area Examined	Phases Identified ⁽²⁾
6245-44C	87	Edge	S gamma ⁽³⁾ Mn + VF epsilon phase
-46D	90	Center	S epsilon ⁽⁴⁾ phase
-48F	90	Edge	S gamma Mn + F Fe ⁽⁵⁾
-56G	45	Center	S epsilon phase
-56G	45	Edge	S gamma Mn

(1) Nominal.

(2) The letters S, F, and VF (strong, faint, and very faint) refer to the relative intensities of the phases' diffraction patterns.

(3) Gamma Mn is a face-centered tetragonal structure according to Potter and Huber, Trans. ASM, 41, 1001 (1949).

(4) Epsilon phase is a hexagonal close-packed structure also reported by Potter and Huber.

(5) The Fe in this pattern came from the basis metal.

The difference in structure and composition was confirmed by potential measurements of the two areas, using 3 per cent NaCl solution, at 80 F. The potentials, after two minutes, showed a difference of 162 millivolts, the edge being the more negative or active. The values for the edge and center, respectively, were -1.170 and -1.008 volts on the saturated calomel scale. After 38 minutes, the difference had diminished to 116 millivolts.

The effect of variations in the anode to cathode spacing in the sulfate-citrate solution was studied. Table 23, Appendix II, contains the details. A long rectangular cell was used, and the cathodes were of two types. The dimensions of one of these was such that it did not fill the cross section of the cell, and the other type did fill the tank.

Edge effects were present on those panels whose edges were not in contact with the cell walls. Where the cathode filled the cross section of the cell, the deposits were uniform except for an "edge effect" at the air-liquid interface. Regardless of edge effects, all plates formed at 95 or 100 amp/sq ft had microholes. One of the plates was deposited at 28 amp/sq ft and while it had no microholes, it did show high and low areas. The composition of the plates varied, but in no apparent regular way.

The results of further changes in the number and arrangement of anodes are recorded in Table 24, Appendix II. (The term "standard" used in referring to the anode arrangement means one flat 4" x 2" x 1/4" anode on each side of the cathode.) The panels were plated at current densities up to 150 amp/sq ft, instead of the usual 100 amp/sq ft, thus accentuating the current-density effects. Each of the cathodes was surrounded by a robber. The edge effect persisted at 150 amp/sq ft regardless of the number or arrangement of anodes. When the current density was reduced to 115 amp/sq ft, the edge effect diminished, but did not disappear.

Using the standard anode arrangement, the agitation effect was increased by holding the cathode at an angle to the flat anodes while the work rod moved it back and forth. The edge effect did not disappear (Table 25, Appendix II). Finally, using the standard anode arrangement and a robber, it was possible to get a uniform deposit at 90 amp/sq ft which contained about 22 to 25 per cent manganese. If the current density was raised in an attempt to increase the manganese content in the deposit, then the edge effect returned.

A number of additional runs using robbers (see Table 26, Appendix II) confirmed the earlier findings. A uniform deposit was possible at 90 amp/sq ft. The manganese contents of the deposits ranged from 26.3 per cent to 30.3 per cent. Considering the weight versus thickness (or density) relationship, the plates apparently are more dense than those reported in Table 18, Appendix II.

Many of the so-called "chemically pure" reagents contain significant amounts of organic material, which would certainly influence cathodic processes. Table 27, Appendix II, records the observations made on solutions purified with activated carbon. For comparison, plates were also made from untreated baths. The small decrease in "edge effect" that was observed was thought due to aging of the bath, rather than to the activated-carbon treatment.

The deposit was somewhat more dense when plated from a treated solution. The manganese content was about 43 per cent for the untreated solutions and about 29.5 per cent for the treated solutions. Apparently the carbon does remove small quantities of organic material which polarize the cathode. The lower manganese content of the deposits from the treated baths supports this belief.

The edge effect is less on successive deposits. This indicated a possible beneficial "aging" effect. Accordingly, a series of aging tests are described in detail in Table 28 in Appendix II. The test was run over a period of nine days. In most cases, two specimens were run each day. The duration of each electrolysis was thirty minutes. Any precipitate which formed was redissolved by boiling just prior to electrolysis.

The deposits showed less edge effect on the third test, but thereafter the edge effect became more or less pronounced on successive panels. Except for one test (42E), the manganese contents of the deposits were above 40 per cent. The efficiencies averaged about 30 per cent, which is to be expected with this type of bath. From this test, the only conclusion is that no beneficial effects can be expected from aging.

The Hull cell* has proved useful in studies of single-metal plating baths, and for the control of commercial plating solutions. Very little appears in the literature on its use in developing alloy-plating solutions. Its use for this work was in the nature of a trial. Because the Hull-cell cathode is subjected to a wide spread (but of known values) of current densities, it was thought that it might be useful in studying the causes of edge effects. Table 29, in Appendix II, contains the results of the tests.

Most clearly demonstrated was the fact that the sulfate-citrate solution is susceptible to changes in current density. This is evident from the large number of distinct areas across the panel. The schematic drawings in Table 29 do not give all the areas which were actually present on the panels. To have done so would have made the diagrams very complicated. Various treatments combined with an addition agent showed that, while the areas shifted, there were usually as many of them.

Using the activated-carbon-purified baths, the effect of various basis metal surfaces on the nature of the deposit was studied. Table 30, Appendix II, shows that copper or zinc undercoatings, or electropolishing the steel surface, were of no consequence as far as reducing the edge effect was concerned. The deposits on the undercoated and electropolished panels had nonuniform center areas.

Experiments were run to see if a bath not treated with activated carbon would show the same effects. Deposits were made over zinc plate, copper plate, and electropolished steel, as before. Table 31, Appendix II, records the results of these experiments. The deposits were no different from those produced from the treated baths.

Addition-Agent Studies

Table 32, Appendix II, contains data on the effects of hide glue. Two grams per liter of hide glue made it possible to obtain a deposit with 53 per cent or 78 per cent manganese (depending on whether work-rod agitation was used or not) at 40 amp/sq ft. However, the efficiency dropped below 4 per cent. The efficiency was not increased by cutting the bath concentration in half. At 40 amp/sq ft, the deposit contained 47 per cent manganese. The glue caused black edges in most cases.

*R. O. Hull and Company, Incorporated, Rocky River 16, Ohio.

The results of other tests with hide glue in the sulfate-citrate bath are recorded in Table 33, Appendix II. This series of experiments showed that the age of the hide glue influenced the results. With a hide glue suspension which was two months old, efficiency varied from 15 to 24 per cent (depending on current density), but the manganese content of the deposit was not over 20 per cent. With a glue suspension that was two days old, the efficiency dropped to 5 per cent and the manganese content rose to 36 per cent.

Table 34, Appendix II, records the results of the use of hide glue and other addition agents in a bath in which all constituents were at half the standard concentrations. The efficiency was higher but the deposits showed marked "edge effect".

Table 41, Appendix II, contains the results of experiments where gelatin and urea were used as addition agents in the standard bath. The deposits were not acceptable.

Studies on the Elimination of Microholes

Microscopic (about 20X) examination of the surfaces of the manganese-zinc coatings, deposited from sulfate-citrate baths, revealed numerous tiny, evenly distributed holes. These holes are believed not to go through to the basis metal. The microholes (as they shall be called henceforth) account for the low density of the deposits.

The microholes observed in the manganese-zinc deposits are different from the pits caused by clinging hydrogen bubbled in nickel plate. Possibly, however, the gas could be responsible for the microholes. Wetting agents eliminate the pits in nickel plate, so a similar remedy was indicated here. Two types of wetting agents, in spite of markedly lowering of the surface tension (see Table 35, Appendix II), did not eliminate the microholes.

Since linear agitation with flat cathodes appeared to have no effect in eliminating the holes, rotating cylindrical cathodes were tried next. The conditions and results of rotation tests are given in Table 36 in Appendix II. Rotating the cathode at 50 rpm had no effect in eliminating the microholes. No significant change was observed due to the increased length of plating time.

In connection with this series of experiments, both manganese and zinc in the deposits were determined by chemical analysis. Formerly, only manganese was determined by analysis, the zinc content being obtained by difference. If relatively large quantities of basic manganese compounds were present, it should become apparent, because the sum of the per cent manganese and the per cent zinc would be appreciably less than

one hundred. In all cases, except one, reported in Table 36, the total metal added up to practically one hundred per cent. Further evidence in contradiction to the basic compound hypothesis was presented earlier in this report.

The formation of the microholes was studied by plating a series of panels, each one of the series being plated for a different time. Table 37, Appendix II, shows that no microholes are visible after one minute at 100 amp/sq ft. The second panel, which was plated for two minutes, had microholes just visible on the center of the panel. After a three-minute plate, the microholes were visible over the entire panel. No further changes were observed as the time increased. For these experiments, polished and buffed steel panels were used. Microscopic examination of the two- and three-minute panels did not show any correlation between the scratches or other imperfections in the basis metal and the microholes.

Effect of Sulfate

Solutions were made by dissolving electrolytic manganese and mossy zinc in separate portions of citric acid solution. When dissolution was complete, the separate solutions were mixed. The purpose of preparing the bath this way was to study codeposition from a sulfate-free bath. Table 38, Appendix II, gives the results of the experiments. The cathode efficiencies were about one per cent, and, although the manganese contents were high, the deposits were unsatisfactory. Worthy of note was the fact that the deposits were bright in spots. A few tests were made with a citrate solution at pH 13, but no manganese was found in the deposit.

Effect of Superimposed Alternating Current

Alternating current superimposed on direct current in electrodeposition has, in some cases, improved the deposit. Table 39, Appendix II, shows the results of superimposing alternating current on the direct current in manganese-zinc, sulfate-citrate solutions. The ratio of ac to dc was varied at several levels. The edge effect did not disappear. With the higher ratios, the percentage of manganese in the deposit increased. The largest amount was 87 per cent. The efficiencies varied between 17.5 and 32 per cent. Table 40, Appendix II, contains data on the preparation of "wet-dry" test panels using alternating current.

Miscellaneous Tests

Table 41, Appendix II, contains the details on a group of miscellaneous experiments. The first of these was performed at 52 F. This was the lowest practical temperature for plating. Below this, the salts crystallized out. The plate was not improved by the low temperature.

Four experiments in Table 40 were made to test the effect of anode material on the deposit. The first two of the plates were made using a Pb99-Ag1 alloy anode. The second two were made with carbon anodes and were the control experiments. No significant difference was observed due to the difference in anodes.

The Sulfate-Borocitrate Bath

Introduction

The exploratory work on the sulfate-borocitrate solutions has already been described.

The bath which gave the best results, and which was chosen as a standard, had the following composition:

MnSO ₄ · H ₂ O	110.6 g/l
ZnSO ₄ · 7H ₂ O	52.0 g/l
Na Citrate · 2H ₂ O	250.0 g/l
H ₃ BO ₃	99.0 g/l
pH	5.3

Carbon anodes enclosed in porous Alundum cups were also used with this bath.

The borocitrate bath did not precipitate following electrolysis, and the deposits from it did not have microholes. There were faults to be remedied nevertheless. The cathode efficiencies were low, the deposits showed edge effect, and the reproducibility was poor.

A discussion of what was done to improve the process and the deposits is given in the following sections.

Tests on Mn-Zn Alloy Plated Steel in "Wet-Dry" Exposure

The coatings from the borocitrate solution were somewhat more resistant in the "wet-dry" test than sulfate-citrate bath coatings of the same composition. Table 4 contains the data. The absence of microholes no doubt accounts for the better resistance. Since there were only two panels sufficiently uniform and having the right composition (50-50), the comparison is subject to some question.

Cathode-Efficiency Studies

Table 42, Appendix II, lists several experiments designed to increase the cathode current efficiency. Decreasing the concentration of all bath constituents to one-half the standard values increased the current efficiency of the sulfate-citrate solution. Only a small increase was observed when this was done to the borocitrate solution.

When the bath concentration was reduced to one-quarter of the original value, still no increase in current efficiency was observed. During these tests, only two acceptable deposits were produced. One of them, a uniform mat deposit, came from the standard (higher concentration) solution. The efficiency was low, however. The other good deposit came from the bath whose concentration was halved and which contained hide glue. This was a uniform, fairly bright deposit, but it contained only 9 per cent manganese.

Very small additions of arsenic trioxide have been observed to raise the hydrogen overvoltage in some solutions. No increase in efficiency accompanied the arsenic trioxide additions to the sulfate-borocitrate bath.

Small additions of sulfite in the simple sulfate manganese-plating bath result in large increases in efficiency, and in improvement of the deposit. Na_2SO_3 additions up to 0.5 g/l had no effect in the manganese-zinc borocitrate solution at pH 5.3. Current efficiency, manganese content of the deposit, and appearance of the deposit were the same as for solutions containing no sulfite (Table 43, Appendix II). With the pH at 6.2, the efficiency was close to one per cent, but was raised to 7.0 per cent by the presence of 5 g/l of Na_2SO_3 . At a pH of 6.2, however, the deposits were poor, as the edge effect was quite pronounced. Comparison of two tests run at different times but under the same apparent conditions again reveals a discrepancy. Specimen 6429-44A (Table 42) was coated at 12.8 per cent efficiency and contained 23.8 per cent manganese, and the deposit had a uniform, mat-gray center, with darker edges. On Specimen 6429-66A (Table 43), the deposit, at 26.7 per cent efficiency, contained 20.2 per cent manganese, and was a uniform mat gray.

Sodium thiosulfate was added to the borocitrate solution in various concentrations (Table 44, Appendix II). At a pH of 5.3, the results were quite erratic. As the thiosulfate concentration increased, the cathode efficiency was fairly steady between 22 and 26 per cent, but the manganese content fluctuated irregularly from 10 to 22 per cent. With increase in thiosulfate, the deposit became powdery. At a pH of 6.2, there appeared to be greater regularity. The efficiency increased with the concentration of $\text{Na}_2\text{S}_2\text{O}_3$, and the manganese content of the deposits was as high as 88 per cent. No metal deposited on the edges of the panels in the majority of the tests.

A group of experiments was then performed with the thiosulfate content held constant at 0.5 g/l and the pH at 6.2, with the time and current density variable (Table 45, Appendix II). Again, the results were somewhat erratic. The deposits described in Table 45 were nonuniform for the most part. The best deposits came after the bath containing $\text{Na}_2\text{S}_2\text{O}_3$ remained idle for two days, but even then there was small edge effect. An increase in time did not result in a proportionate increase in thickness, other conditions being constant. For example, Panel Number 6429-54E, where the time was 15 minutes, had more than 1-1/2 times as much deposit as Number 6429-54F where the time was 10 minutes.

The addition of hide glue lowered the cathode efficiency. Lowering the pH from 5.3 to 3.5 caused an increase in the current efficiency but the manganese content of the deposit dropped from approximately 25 to 10 per cent. (See Table 42, Appendix II.)

Edge-Effect Studies

As with the sulfate-citrate bath, the edge effect was minimized by the use of flat anodes having approximately twice the area of the cathodes. But the flat anodes did not eliminate the edge effect. Robbers appeared to have no value when used in the borocitrate solution (Table 46, Appendix II). Edge effects were present even at low current densities.

Aging tests were run on the borocitrate solution also. Reference to Table 47, Appendix II, discloses that, there, too, the edge effect did not lessen significantly with bath age. Of interest is the fact that there were no microholes in these deposits. The prevalence of powdery deposits during this run points to the lack of reproducibility for the borocitrate solution. This is supported by the low efficiencies and high manganese contents. Previous experience with this solution, under the same operating conditions, showed the efficiency to be 12 to 15 per cent, rather than the approximate average of four per cent obtained in this run, and the deposits were much more sound in the preceding work.

Two panels measuring 4 inches by 2-3/4 inches (the usual cathode size was 3 inches by one inch) had 1/2-inch bands along all four edges (both sides) stopped off with lacquer. Stopping off the edges did not prevent edge effect. (See Table 41, Appendix II.) The deposits had no microholes and were fairly uniform except for the edge effect so they were used in the "wet-dry" test.

Addition-Agent Studies

Table 48, in Appendix II, records the results of adding various addition agents to the sulfate-borocitrate solution at pH values of 5.3 and 7.5. Poor deposits were obtained at pH 7.5. X, a proprietary addition agent, whose composition has not been disclosed and is still in the development stage, improved the deposit, but the edges of the flat panels remained unplated. X also increases the manganese in the deposit. Urea gave results only slightly inferior to those obtained with X, and the edges remained unplated here, too. The first test in this series was run as a control, with no addition agent present. The cathode efficiency of this test was 11.5 per cent and the deposit contained 29 per cent manganese. These values are in accord with the best results obtained from this type of bath.

A series of tests was run then on borocitrate solutions containing X (10 g/l) (Table 49, Appendix II) with the current density at 30 amp/sq ft,

rather than the 40 amp/sq ft used in the preceding run. A deposit was obtained on the edges as well as at the center, but the deposits were nonuniform in appearance.

Further exploratory tests, under varying conditions of agitation, current density, and time, were made using the borocitrate solution with X present. The results are found in Table 50 in Appendix II. A uniform, lustrous plate deposit was obtained at 20 amp/sq ft, but the manganese content of the deposit dropped to 17 per cent. The manganese content increases rapidly with current density, rising to 78 per cent at 40 amp/sq ft, but, as was mentioned above, no plate forms on the edges of the panels. The deposits covered the entire specimen in previous tests run at 30 amp/sq ft (Table 49) with moderate linear agitation. With the same current density and no agitation, the edges remained unplated, and the manganese content was higher.

Addition agent X does not have sufficient advantage to make it worthwhile to seek its composition.

Hull-cell analyses were made of addition agents in the sulfate-borocitrate bath and the data are given in Table 51, Appendix II. The sulfate-borocitrate solution is just as susceptible to current-density changes as is the sulfate-citrate solution. The condition was not alleviated by any addition agent that was tried. Because composition of the deposit was so important in this work, single cathode panels had an advantage over the Hull-cell tests.

Activated-Carbon Treatment

The borocitrate solutions were also treated with activated carbon. A perusal of Table 52, Appendix II, reveals that no noticeable improvement was made. It should be noted that no deposit formed on the edges of the panels, regardless of whether or not they were treated with activated carbon. No explanation is known for the lack of deposit on the edges. Specimen 6429-44A (Table 42, Appendix II) was plated under the same conditions as Specimen 6429-72E (Table 52, Appendix II) and it was entirely covered, although edge effect was present. Specimen 44A had a coating containing 23.8 per cent manganese which was deposited at an efficiency of 12.8 per cent, and Specimen 72E had a coating with 17.7 per cent manganese, deposited at an efficiency of 23.4 per cent.

Agitation and Density Studies

Rotating cylindrical cathodes were used also in the sulfate-borocitrate solution. No microholes were observed, but the cathode had grooves visible at 20X. No significant difference in the plate was observed due to rotation. In this series of tests, both manganese and zinc in the deposit

were determined. Here the totals fall about 5 per cent (average value) short of 100 per cent. A deposit from a borocitrate solution was analyzed for oxygen and 0.11 per cent was found. This is too low to account for the discrepancy in metal analysis. (Table 53, Appendix II.)

The low density can be accounted for in the deposits from the sulfate-citrate solution by the presence of the microholes. However, this is not the case for deposits from the sulfate-borocitrate solutions, where no microholes are present. No explanation is apparent for the difference.

Fluoborate Solutions

Introduction

All the experiments performed with the fluoborate solutions were of an exploratory nature.

No promising leads were discovered which warranted going beyond the preliminary stage. Also, other baths appeared more profitable for study.

Simple Fluoborate Solutions

Simple fluoborate solutions produced deposits of low manganese content. Varying the mole ratio of manganese to zinc had little effect. The maximum manganese content was 3-1/4 per cent. The results are given in Table 54, Appendix II.

Addition-Agent Studies

When hide glue was present to the extent of 1 g/l, a deposit containing approximately 22 per cent manganese was obtained. (See Table 55, Appendix II.) The deposit was not so good as that obtained from the sulfate-citrate solution. The effect of various agents on the cathode polarization was studied, and the results are given in Figures 6 and 7. Up to 300 amp/sq ft, the polarization reaches a maximum of about -1.25 volts. This is insufficient to obtain 50 per cent manganese in the deposit.

Figure 8 shows the effect of two of the addition agents at a higher pH. With hide glue as the addition agent, a very large polarization was observed at approximately 100 amp/sq ft. An even larger polarization was observed with gelatin, but the magnitude was such as to be immeasurable quantitatively

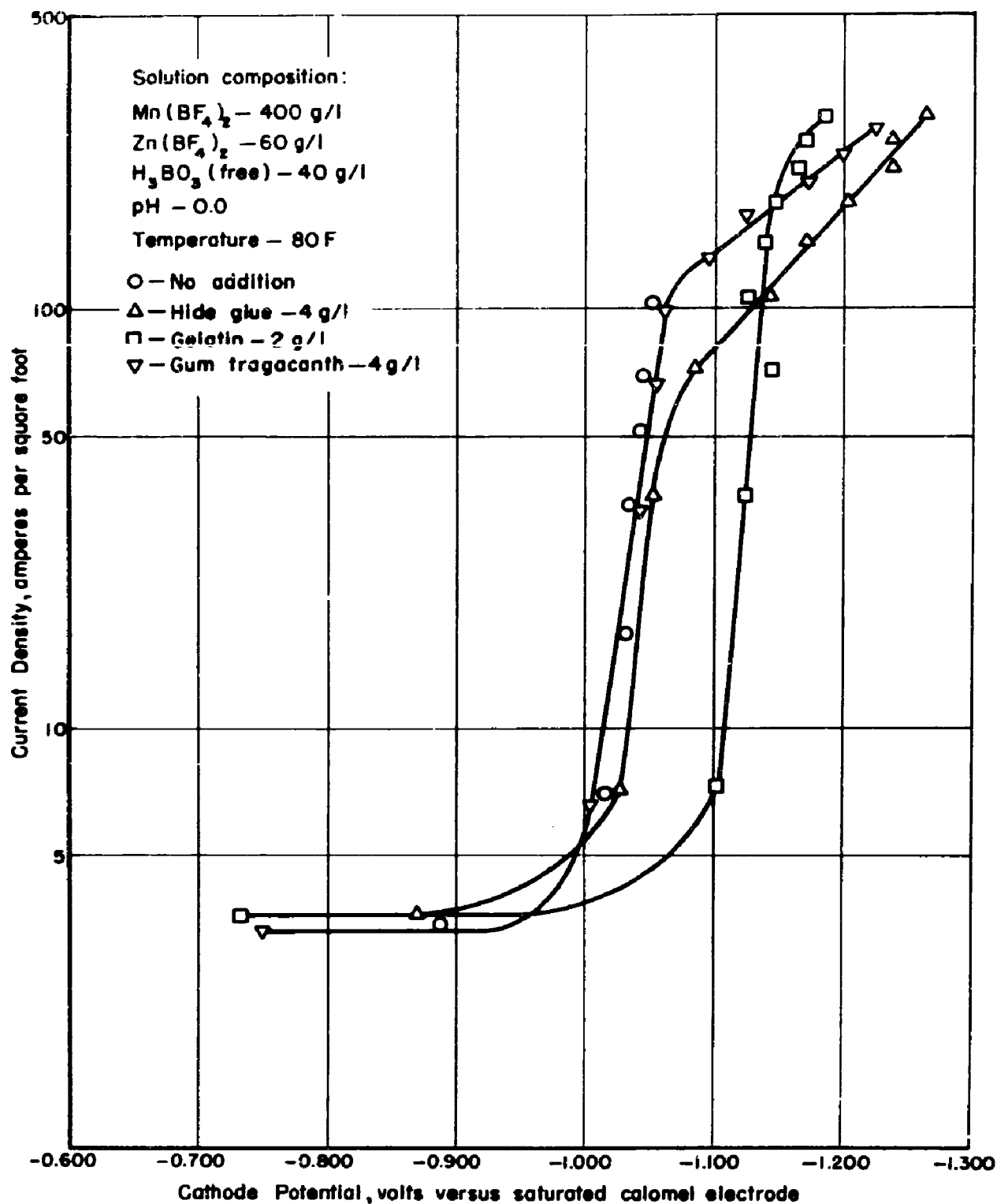


FIGURE 6. EFFECT OF ADDITION AGENTS ON THE CATHODE POTENTIAL IN THE LOW-pH MANGANESE-ZINC FLUOBORATE SOLUTION
A-499

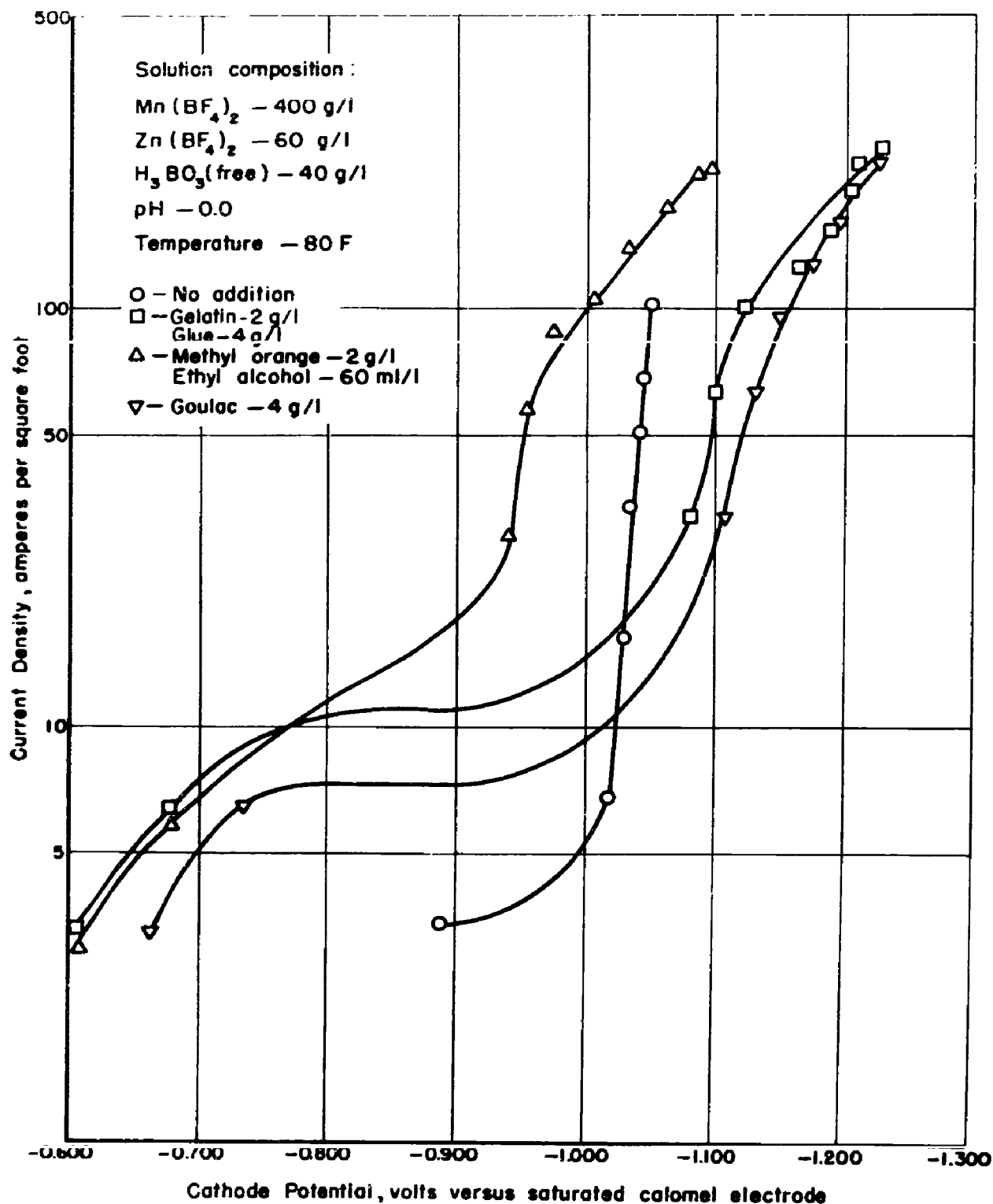


FIGURE 7. EFFECT OF ADDITION AGENTS ON THE CATHODE POTENTIAL IN THE LOW-pH MANGANESE-ZINC FLUOBORATE SOLUTION

A-500

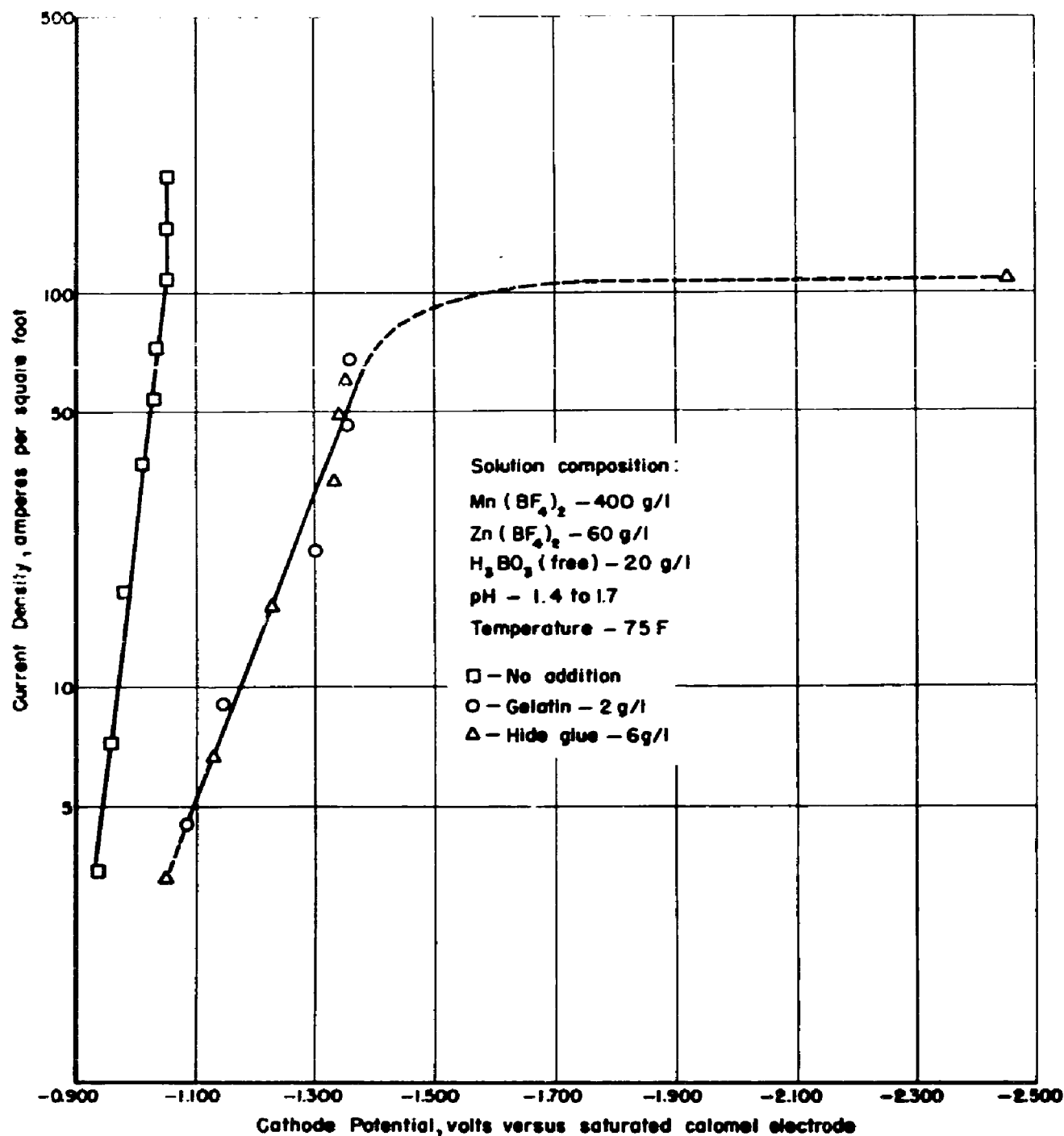


FIGURE 8. EFFECT OF ADDITION AGENTS ON CATHODE POTENTIAL IN MANGANESE-ZINC FLUOBORATE SOLUTION AT HIGHER pH
C-501

with the potentiometer in use. The deposit, however, was black and non-adherent. Table 56, Appendix II, describes some additional experiments at the higher pH values.

At 100 amp/sq ft and with gelatin or glue, the deposit either is poor or shows black edges. Table 57, Appendix II, contains the results of deposition experiments without addition agents, but either at higher current density, or at higher pH. Increase in pH has a more pronounced effect on increasing the manganese content of the deposit than does increase in the current density. This has been observed with other manganese-zinc solutions. Comparing Test Number 6429-20D (Table 56, Appendix II) with Test Number 6429-18C (Table 57, Appendix II) shows that the manganese content of the former is 22.4 per cent and that of the latter 21.6 per cent. The first one was plated from a solution containing gelatin. This checks with the polarization measurements. The efficiency and appearance were improved by the gelatin.

Effect of Superimposed Alternating Current

With superimposed alternating current, fairly high efficiencies were obtained, but the deposits were powdery. The results are listed in Table 58 in Appendix II. Various ratios of alternating current to direct current were tried, but no beneficial effects were observed.

Studies With Other Complex Ion Forming Solutions for Manganese-Zinc

In attempts to improve the properties and protective quality of manganese-zinc alloy plates, a number of other types of solutions were investigated. The essential data are described in the following sections.

Tetrasodium Ethylenediamine Tetraacetate Solutions

Tetrasodium ethylenediamine tetraacetate is one of a class of the so-called "sequestering agents". It is used in sequestering calcium or magnesium in hard waters, and has strong complexing action toward many other cations, including zinc and manganese. The compound is available in commercial form. The particular brand used in this work is marketed under the name Sequestrene NA4*. This commercial designation will be used for clarity of reference.

*Alrose Chemical Company, Providence, Rhode Island.

Extensive studies of Sequestrene have been made by Schwarzenbach and his students. They have determined equilibrium or instability constant for many of the complexes formed by Sequestrene and various cations. In a paper⁽⁵⁶⁾ where many of the heavy-metal complexes were discussed, the instability constant for the manganese complex is given as 4×10^{-14} , and that for the zinc complex is given as 8×10^{-17} . This would indicate that zinc is complexed more strongly than manganese. For manganese-zinc codeposition, this is desirable.

Experiments with various amounts of Sequestrene are described in Table 59 in Appendix II. The maximum amount of manganese obtained in the deposits was 2.4 per cent. This makes it appear either that Schwarzenbach's values are in error, or that they do not hold in the solutions used here.

The Hull cell was used in exploratory experiments and the results are shown in Table 60 in Appendix II. Additions such as boric acid and sodium citrate were made, to the detriment of the deposits. Because the composition of the plate must be known, the Hull cell was inconvenient in some phases of this research. It will disclose the current-density ranges in which good deposits will be obtained, and it can be useful for studies of addition agents, also. However, for this work, it was considered best to use single panels and determine the composition of each one.

Sequestrene baths were not believed to show sufficient promise to warrant further work.

Sulfate-Sulfamate Solutions

Piontelli has used sulfamate solutions extensively for both single-metal and alloy deposition. Addition of varying quantities of sulfamic acid to a manganese-zinc sulfate solution did not result in a high manganese content in the deposit, in spite of the fairly high polarization shown in Figure 9.

The deposits formed during the polarization measurements were analyzed, and these contained less than 1 per cent manganese. Data for these solutions are also recorded in Table 61, Appendix II.

Sulfate-Pyrophosphate Solutions

Table 61, Appendix II, also contains data on the manganese-zinc, sulfate-pyrophosphate solution. The efficiency of this bath was below 10 per cent and the deposit was powdery.

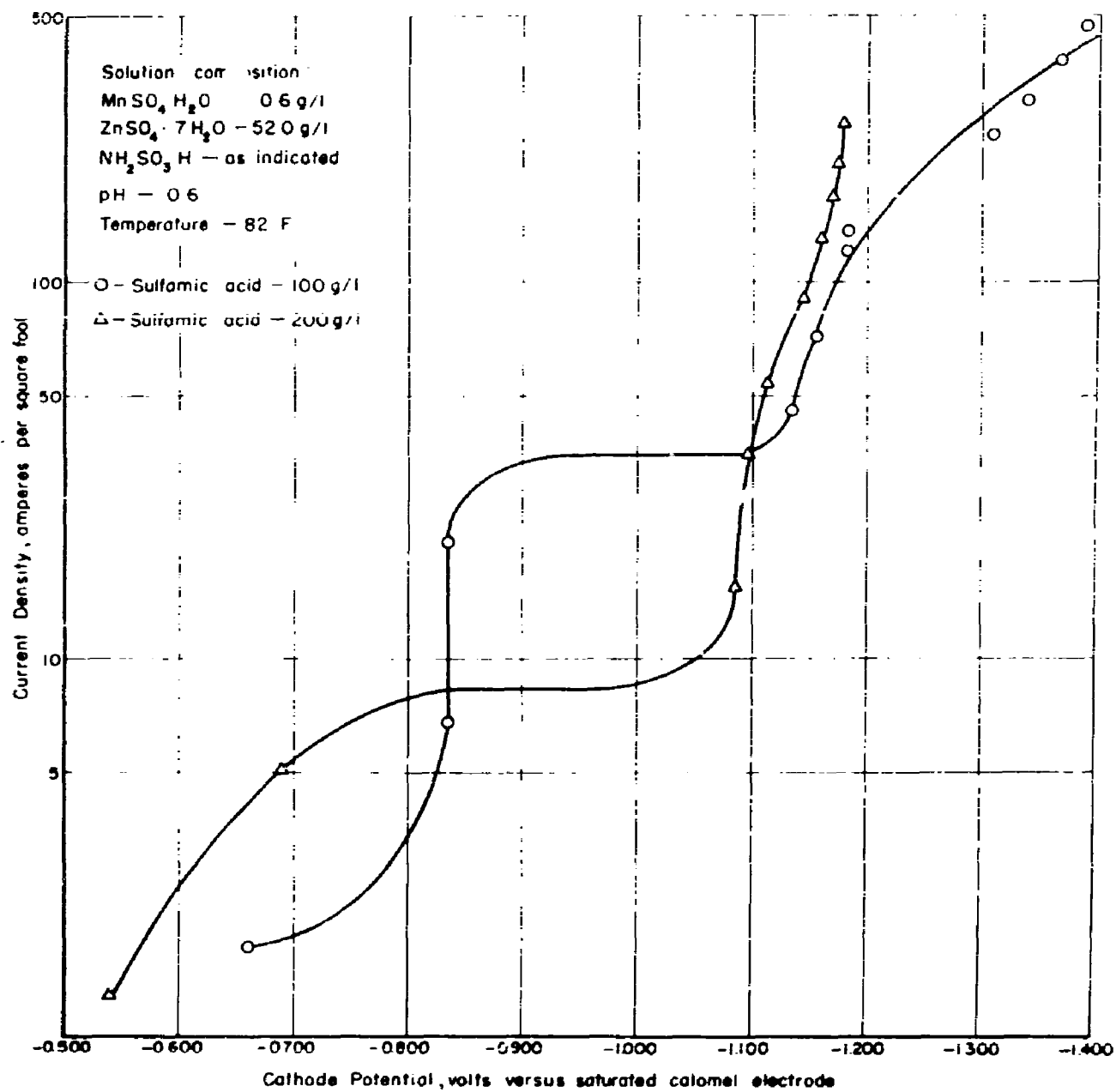


FIGURE 9. EFFECT OF SULFAMIC ACID ADDITIONS ON THE CATHODE POTENTIAL IN MANGANESE-ZINC SULFATE SOLUTION

C-502

Chloride-Citrate Solutions

A chloride-citrate bath was studied (Table 62, Appendix II). Poor plates containing approximately 30 per cent manganese were deposited at cathode efficiencies averaging 28 per cent. There was no plate on the edges of the panels. With 135 g/l $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in the catholyte, the manganese content of the deposit rose to 54 per cent. With the $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ content at 270 g/l, the deposit contained 80 per cent manganese. The efficiency dropped to 16 per cent. With 135 g/l of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, or greater, there was a deposit on the edges as well as on the centers, but the familiar edge-effect pattern was present.

Sulfate-Fluoride Solutions

The preliminary experiments for the deposition of manganese-zinc alloys from sulfate-fluoride solutions are given in Table 63, Appendix II. The manganese and zinc contents of the bath were the same as for the sulfate-citrate solutions. In addition to those two metals, 40 g/l sodium fluoride was present. The pH was 2.0. Temperature and current density were varied in this series of experiments with no improvement in the deposit, which was coarsely crystalline and had poor adhesion and coherence. The manganese content was below one per cent, except once, when it was three per cent. For the most part, efficiencies were high, but this it to be expected with low manganese.

No work was done beyond the experiments described here.

Concentrated Caustic Solutions

In a patent issued in 1918, Estelle⁽⁵⁷⁾ described a concentrated caustic solution for the electrolytic production of iron. The bath consisted of a slurry of ferric hydrate (hydroxide), and gave sound deposits. Actually, some of the iron was in solution, for even iron hydroxide is soluble to a very limited extent. This presented a novel type of bath, and one which appeared to have possibilities for alloy plating.

In alloy plating, it is sometimes desirable to have one element complexed and the other not complexed. In other cases, both elements may exist in different complexes. The concentrated caustic bath for manganese-zinc alloy deposition was akin to the latter. The zinc exists as the zincate and the manganese, due to the very low concentration of its ions, acts the same as if it were highly complexed.

Several experiments were performed using this type of bath. To a solution containing 300 g water and 300 g sodium hydroxide were added 100 g manganous sulfate monohydrate and 25 g zinc oxide. Table 64,

Appendix II, contains the data for the experiments. The manganese contents of the deposits were low (2 to 6 per cent), and, for this reason, the bath appeared to be of no further interest.

Sulfate-Borate Solutions

When iron rust is cathodically removed from steel corrosion-test panels, an organic inhibitor is usually added to the acid solution or protect the bare steel surfaces. One of these which has been used here is Reilly Acid Inhibitor No. 22.* Being a cathodically active material, it was thought that this material might make a good addition agent.

For these experiments (See Table 65 in Appendix II) a sulfate-borate solution was used. The boric acid was added because of its buffering action. Reilly No. 22 had an effect on the composition of the plate. At 50, 100, and 150 amp/sq ft, the manganese content of the deposit was 50 per cent or better, if the inhibitor concentration was one gram per liter or greater. The deposits were nodular and had a golden color. The golden color may be due to occluded inhibitor or reduction products of the inhibitor. In previous work with solutions designed to codeposit manganese and zinc, when the manganese content of the deposit rose, the cathode efficiency was lowered. In the sulfate-borate solution with Reilly No. 22 present, both factors increased simultaneously.

Raising the pH to 2.0 or 3.0 (Table 66, Appendix II) resulted in deposits inferior to those obtained at pH 1.0. No experiments were made with very strong acid solutions. The inhibitor is customarily used in strongly acid solutions and may be more active at the higher acid value.

Sulfate-Gluconic Acid Solutions

Table 61, Appendix II, gave the results of a single experiment on the codeposition of manganese and zinc from a sulfate-gluconic acid solution. Some promise was shown and further experiments were performed.

Table 67, Appendix II, details the experiments using a gluconic acid bath. The deposits from this type of bath were unsatisfactory. For the most part, the manganese contents of the deposits were low (less than ten per cent). Two deposits, containing 33 and 47 per cent manganese, respectively, were powdery.

Mixed Alkane Sulfonic Acid Solutions

Faust, et al. (58) have explored the possibility of using alkane sulfonic acids for plating copper and many other metals. The alkane sulfonic acids

*Reilly Tar and Chemical Company, Indianapolis, Indiana.

are a class of strong acids having the general formula



where R is a methyl, CH_3 , ethyl, C_2H_5 , or propyl, C_3H_7 , etc., group. For the work described herein, mixed alkane sulfonic acids were used. These are predominantly a mixture of methane, ethane, and propanesulfonic acids.

The first baths were prepared by dissolving granular zinc and electrolytic manganese in separate portions of concentrated acid.* Table 68, Appendix II, contains the bath compositions, plating conditions, and results. In most cases, no deposit or only a very slight deposit resulted. Manganese was found in but one of the deposits and then only to the extent of 1.3 per cent. The maximum efficiency was less than five per cent.

Sulfate-Sulfonic Acid Solutions

For the second group of experiments in which the mixed alkane sulfonic acids were used, the baths were prepared by dissolving the metal sulfates in water and adding various quantities of the mixed alkane sulfonic acids. Much better results were obtained with this type solution (See Table 69, Appendix II) as far as efficiencies and manganese content of the deposits were concerned. The deposits were poor, being nodular, or powdery or flaky.

Fluosilicate Solutions

The fluosilicate solutions were made up by dissolving granular zinc and electrolytic manganese in 30 per cent hydrofluosilicic (H_2SiF_6) acid solution. No deposit was formed when attempts were made to plate from solutions containing either zinc or manganese, but not both (see Table 70, Appendix II).

According to the Handbook of Chemistry and Physics⁽⁵⁸⁾, zinc forms a complex with fluosilicate and pyridine of the type $Zn(C_5H_5N)_4SiF_6$. No deposit was obtained from pyridine-fluosilicate solutions containing only zinc, or both manganese and zinc.

Sulfate-Thiocyanate Solutions

Only zinc was deposited in preliminary tests with sulfate-thiocyanate solutions (see Table 71, Appendix II).

DISCUSSION OF ESSENTIAL DATA — MANGANESE-TIN ELECTRODEPOSITION

Tests on Mn-Sn Alloy Plated Steel in "Wet-Dry" Exposure

Table 4 which is included in the discussion of manganese-zinc coatings also contains data on manganese-tin coatings in the "wet-dry" test. The

*Indust Chemical Company, 910 South Michigan Avenue, Chicago 80, Illinois.

coatings were of the Mn45-Sn55 type that were plated from the sulfate-tartrate solution during the factorial experiment. The preparation of these panels is described in Table 72, Appendix III.

The manganese-tin coatings appear to be slightly better than pure zinc coatings when tested in the wet-dry cabinet. They are not so good as the Mn75-Zn25 coatings, however.

X-Ray Diffraction Studies of Manganese-Tin Alloy Electrodeposits

The first panels to be X-rayed were Numbers 6530-22B and 6530-24C. These panels were plated on November 29, 1951, and were not X-rayed until January 3, 1952 (see Table 7 for X-ray results). The X-ray spectrometer showed tin only to be present. A second X-ray was made on Panel Number 6530-22B, several days later, using the powder method. This latter method has the advantage of being more sensitive than the spectrometer method. Nevertheless, the powder photograph showed only tin. These results were reminiscent of the results obtained with the manganese-tin coatings prepared by diffusion (see Final Report, dated February 23, 1951). It will be recalled that the diffused coatings showed MnSn_2 when X-rayed shortly after plating, but after a week or two only tin was detected in the same coatings. In addition, the diffused coatings, which were originally of a sound metallic nature, developed a powdery overlay after several days. It was definitely established that the powder was not gray tin.

Panels 6530-36A and 6530-36C were prepared on January 10, 1952, and were X-rayed immediately. In both bases, the spectrometer showed only a diffuse band. A powder picture of -36A run on the same day showed a trace of tin and a weak MnSn_2 line. The powder picture also had a diffuse band, indicating that the deposit is in part amorphous or extremely fine crystalline. A powder picture of -36A taken four days later revealed the tin pattern to be much stronger and the MnSn_2 pattern to be unchanged in intensity. Some three and a half months later, a powder picture of -36A disclosed no MnSn_2 and a strong tin pattern. An additional phase $\text{Mn}(\text{OH})_2$ had appeared. The latter is most likely a corrosion product which formed slowly on contact of the alloy with moist air. The X-ray results were qualitatively the same for -36C as for -36A, the differences being those of degree. Like the diffusion alloys, the electrodeposited alloys also develop powdery overlays within a week or two but are formed to a lesser degree with the latter.

The manganese-tin constitution diagram is given in Figure 10. MnSn_2 is the δ phase.

An X-ray spectrometer shot of a manganese-tin coating, deposited from a sulfate-fluoride bath, showed only tin. A powder picture of the same coating showed calcium stannate in addition to the tin. When an X-ray

TABLE 7. X-RAY DIFFRACTION STUDIES OF MANGANESE-TIN
AND MANGANESE-IRON ELECTROPLATES

Specimen Number	Type of Plate and Nominal Composition	Type Bath Used in Preparing Plate	Date Plated	Date X-Rayed	X-Ray Spectrometer Results (1)	X-Ray Powder Results (1)
6530-22B	Mn55-Sn45	Sulfate-Tartrate	November 29, 1951	January 3, 1952	S-Sn	---
-24C	Mn55-Sn45	Sulfate-Tartrate	November 29, 1951	January 9, 1952	---	S-Sn
-36A	Mn55-Sn45	Sulfate-Tartrate	January 10, 1952	January 3, 1952	S-Sn + VF-Fe	---
-36C	Mn55-Sn45	Sulfate-Tartrate	January 10, 1952	January 10, 1952	Diffuse Band + VF-Fe	VVF-Sn + VF-MnSn ₂ + Diffuse Band
				January 14, 1952	---	F-Sn + VF-MnSn ₂ + Diffuse Band
				April 28, 1952	---	S-Sn + F-Mn(OH) ₂
				January 10, 1952	M-Sn + F-MnSn ₂	---
				January 14, 1952	---	S-Sn + MS-MnSn ₂
				April 28, 1952	---	S-Sn + F-Mn(OH) ₂
6605-83C	Mn46-Sn54	Sulfate-Fluoride	March 13, 1952	March 20, 1952	S-Sn	---
				March 20, 1952	---	S-Sn + F CaSnO ₃
-86I	Mn10-Fe90	Sulfate-Fluoride	March 14, 1952	March 20, 1952	---	S-Fe + F CaSnO ₃

(1) The letters VVF, VF, F, M, MS, and S (Very, Very Faint, Faint, Medium, Medium Strong, and Strong) refer to the relative intensities of the lines for a particular phase.

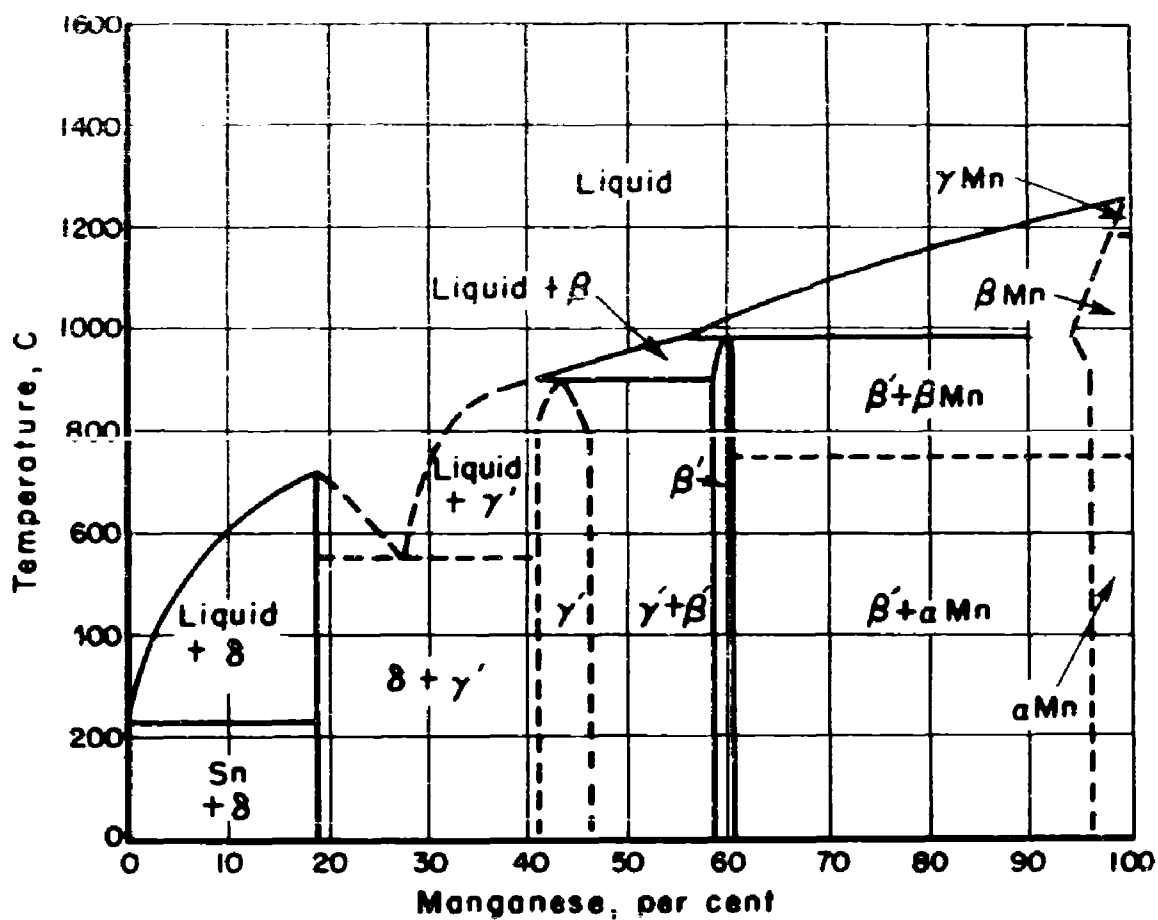


FIGURE 10. MANGANESE-TIN CONSTITUTION DIAGRAM
(Reference 46, Appendix I)

A-2577

powder picture was made of a manganese-iron coating which was deposited from a sulfate-fluoride solution, iron and calcium stannate patterns were observed. Sodium fluoride and manganous sulfate were present in both the manganese-tin and manganese-iron baths. Manganous sulfate was known to be free of calcium and tin, so that left the fluoride as a possible source of these contaminants. A spectrographic analysis of the sodium fluoride revealed it to contain up to 0.1 per cent calcium but no tin. This might explain the presence of calcium stannate in the manganese-tin deposits, but not in the manganese-iron plates. The only other explanation is that the X-ray pattern taken to represent calcium stannate had its origin in some unknown phase. If so, the resemblance is remarkable.

We are unable to explain the changes that take place in the manganese-tin coatings, both diffused and codeposited. To embark on an experimental program which would answer this question might result in an expenditure of time out of proportion to its value to the over-all problem. As long as the transformation does occur, the alloy probably will have little value as a protective coating.

Static Potential of the Manganese-Tin Electrodeposit

The potential values given in Table 8 show the Mn45-Sn55 alloy coating to be electronegative to steel. Cathodic protection would be provided by this coating which was plated from the sulfate-tartrate bath.

Statistical Study of the Sulfate-Tartrate Bath

Introduction

In the Final Report, dated February 23, 1951, experiments were described in which various manganese-tin alloy deposits were produced from sulfate-tartrate and sulfate-tartrate-oxalate solutions. The former solution produced deposits with tin contents above 10 per cent, while the latter solutions were used in obtaining plates with tin contents up to 10 per cent.

When the manganese-tin work was started, the objective was to make plates with the tin content in the range 0 to 10 per cent. Alloys in this composition range form solid solutions, which are generally preferable to two-phase alloys because of lower corrosion rates. "Wet-dry" tests with diffusion coatings, however, had shown the higher tin alloys to have fair-to-good corrosion resistance.

It was decided to investigate alloy electrodeposits with tin contents in the approximate range 40 to 60 per cent. For a more complete evaluation

TABLE 3. STATIC POTENTIAL MEASUREMENTS
OF AN ELECTRODEPOSITED
MANGANESE-TIN ALLOY IN THREE
PER CENT NaCl SOLUTION AT 90 F

Elapsed Time, minutes	Potentials ⁽¹⁾
	6530-22F Mn45-Sn55
1	-1.040
10	-1.158
20	-1.153
30	-1.157
40	-1.150
50	-1.150
60	-1.151
90	-1.152
120	-1.144
180	-1.134

(1) Potential versus saturated calomel electrode in
volts.

of the solution than was made previously, the statistical approach was chosen. For some time, this method was believed of value in the study of electroplating, and this was an opportunity to see what the method could do. The particular system of statistics which has been chosen is known as factorial experimentation. The techniques are described by Brownlee⁽⁶⁰⁾.

Factorial experimentation, a method well adapted to the study of chemical systems, is a fairly recent development. The techniques were originally developed for application to agricultural studies. A list of additional references pertaining to the method is given in Appendix I. (61,62, 63,64)

The method accomplishes four things:

1. It yields the maximum information from the fewest experiments.
2. It allows computation of error.
3. It allows computation of the significance of the conclusions.
4. It provides for minimization of systematic error.

A factorial experiment is one in which all or a properly chosen group of combinations of the levels of the independent variables under consideration are imposed successively on a system, and the response is observed. By the term "levels" is meant, for example, the two or three concentration of one of the solution constituents. One concentration would be a low level, and a second concentration would be an intermediate level. Such an experiment may be analyzed by a statistical procedure known as the analysis of variance. This gives us a quantitative estimate of the average response of the system to change in each variable considered, and furnishes a criterion as to whether the response is real or is the result of chance variations in the process. The interactions between variables can be estimated also.

Detailed Analysis of the Manganese-Tin Factorial Experiment

Proceeding exactly as for the hypothetical example given in Appendix III, the factorial experiment for the manganese-tin bath was set up. The only difference was in the larger number of variables in the actual experiment.

Table 9 contains a summary of the analyses of variance for the manganese-tin alloy plating experiments. This is a condensation of more detailed data which are found in Tables 73, 74, 75, and 76, Appendix III. The complete list of experiments is given in Table 77, Appendix III.

TABLE 8. SUMMARY OF ANALYSES OF VARIANCE OF EFFECTS
OF MANGANESE-TIN PLATING-BATH CONDITIONS

Source of Variance	Levels		Plating Voltage (Mean = 7.05)		Quality Rating of Plate (Mean = 32.6)		Per Cent Tin in Alloy (Mean = 56.2)		Cathode Current Efficiency (Mean = 4.10)	
	High	Low	Risk(2)	Deviation From Mean(1)	Risk	Deviation From Mean	Risk	Deviation From Mean	Risk	Deviation From Mean
Glue Content of Bath (A)	0.3 g/l	0.1 g/l	-	-	0.01	-5.5	<<< 0.001	-3.9	-	-
pH of Bath (B)	8.0	7.0	-	-	-	-	-	-	-	-
Bath Temperature (C)	140 F	100 F	0.001	-0.22	-	-	<<< 0.001	+1.5	0.01	-0.32
Current Density (D)	360 ASF	240 ASF	<<< 0.001	-1.05	0.05	+3.4	<< 0.001	+3.6	0.01	-0.28
Sodium Sulfate in Bath (E)	1.0 g/l	0.5 g/l	-	+1.56	0.05	+3.6	-	-	<< 0.001	-0.63
Tartaric Acid in Bath (F)	50 g/l	25 g/l	-	-	-	-	0.01	+1.4	-	-
Ammonium Sulfate in Bath (G)	250 g/l	200 g/l	-	-	0.05	-3.8	<< 0.001	+3.2	-	-
Manganese Sulfate in Bath (H)	150 g/l	100 g/l	0.01	+0.16	-	-	0.05	+1.0	0.001	-0.40
Tin Sulfate in Bath (I)	2.0 g/l	1.0 g/l	-	-	-	-	<<< 0.001	+2.9	<<< 0.001	+1.00
Interactions:										
AG	-	-	-	-	-	-	-	-	-	-
AI	-	-	-	-	-	-	-	-	-	-
BH	-	-	-	-	-	-	0.01	-1.5	-	-
CE	-	-	-	-	-	-	0.01	-1.6	-	-
CG	-	-	-	-	0.05	+3.9	0.001	+1.8	0.001	-0.38
CH	-	-	-	-	-	-	0.05	-1.0	-	-
CI	-	-	-	-	0.01	-4.4	-	-	-	-
DG	-	-	-	-	-	-	-	-	-	-
EG	-	-	0.05	-0.12	0.05	-3.5	-	-	0.05	-0.19
EH	-	-	-	-	-	-	0.05	-1.0	-	-
FG	-	-	-	-	-	-	0.05	+0.9	-	-
FI	-	-	-	-	0.05	-3.5	-	-	-	-
	-	-	-	-	-	-	0.05	-1.0	-	-
	-	-	-	-	-	-	0.05	-1.1	-	-

(1) The signs of the values shown under the headings "Deviation From Mean" were associated with the high levels of the independent variables. Negative values of the deviation for the quality rating indicate an improvement in the plate.

(2) Under the heading of "Risk" is the probability that such an effect would be observed in the absence of a real effect due to the source of variance.

The independent variables, solution composition, current density, temperature, etc., are listed vertically at the left side of the table. The four dependent variables, cell voltage, quality of plate, percentage of tin in the deposit, and cathode current efficiency, are listed across the top of the table.

Under each of the four dependent-factor headings are two columns, one headed "Risk", and the other headed "Deviation From Mean". Under "Risk" there is a number (or a dash) opposite each independent variable. This number signifies by its magnitude whether a change in the independent variable had a real effect on the dependent variable, or whether the effect was one of chance.

For example, to find the effect of the pH of the solution on the percentage of tin in the alloy, one enters Table 9 with these factors, and under "Risk" finds the value 0.01. This number tells us that the probability for this effect being due to chance is 0.01 or 1 in 100. One, therefore, is safe in believing that the effect is a real one. For risks greater than 0.05 (probability 1 in 20) one is not safe in drawing a conclusion.

In Table 9, a dash signifies that the risk is greater than 0.05. The "Deviation From Mean" values are preceded by a positive or negative sign. This gives the direction of the change in the dependent variable if the independent variable goes from the low to high level. The numerical value gives the magnitude of the change. Listed on the left of the table and below the independent variables is a series of two-letter symbols. These are the interactions between independent variables.

Table 10 lists the twelve best baths and sets of conditions for plating a sound manganese-tin alloy at maximum efficiency, and which contains 40 to 60 per cent tin. It is interesting to note that none of these baths was used experimentally in this work, rather they were deduced from the analysis of variance. The following is a more detailed discussion of the four dependent variables and how they are influenced by the plating conditions.

Quality of Plate. For good plate quality, the glue content of the bath should be 0.3 g/l and the cathode current density 240 amperes per square foot.

With those conditions, the bath operating temperature can be chosen at will. If 100 F is selected, the tin sulfate content of the bath should be 1.0 g/l; if 140 F, 2.0 g/l. Further, if 100 F is selected, the ammonium sulfate content of the bath can be chosen at will; if 140 F is selected, only 250 g/l of ammonium sulfate should be used. Regardless of which choices have been made so far, the manganese sulfate content of the bath can be chosen at will. If a manganese sulfate content of 100 g/l is selected, the

TABLE 10. MANGANESE-TIN ALLOY-PLATING BATHS SELECTED (ACCORDING TO STATISTICAL STUDY) TO DELIVER GOOD PLATES OF VARIOUS COMPOSITIONS

Factor	Factor Designator												
	Designator (1)												
Glue Content, g/l	a	b	c	d	e	f	g	h	i	ab	abf	aceghi	acefghi
pH	6.3	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	8.0	8.0	7.0	7.0
Temperature, F	100	100	100	100	100	100	100	100	100	100	100	140	140
Current Density, amp/sq ft	240	240	240	240	240	240	240	240	240	240	240	240	240
Sodium Sulfite, g/l	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.5	0.5	1.0	1.0
Tartaric Acid, g/l	25	25	25	25	25	25	25	25	25	50	50	25	50
Ammonium Sulfate, g/l	250	250	250	250	250	250	250	250	250	200	200	250	250
Manganese Sulfate, g/l	150	150	150	150	150	150	150	150	150	100	100	150	150
Stannous Sulfate, g/l	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	2.0	2.0
Per Cent Tin in Alloy	51.0	51.2	45.6	45.8	41.8	46.0	39.8	44.0	61.0	56.8	59.4	55.2	55.2
Quality of Plate	8.8	8.8	8.8	8.8	8.6	8.6	8.6	8.6	7.8	7.8	7.8	7.8	7.8
Plating Voltage	7.04	7.04	7.27	7.27	6.80	6.80	6.04	6.04	4.94	4.94	4.08	4.08	4.08
Efficiency	5.90	5.90	4.66	4.36	5.90	5.90	4.28	4.28	5.66	5.66	6.00	6.00	6.00

(1) The coded symbols contain only the designators of those factors which are at the high level.
The factors whose designators are absent from the coded symbols are at the low level.

pH of the bath should be 8.0 and the sodium sulfite 0.5 g/l. If 150 g/l manganese sulfate is selected, the pH of the bath should be 7.0 and the sodium sulfite 1.0 g/l.

Tin Content of the Alloy. The composition of the alloy from the bath is a complex function of the constitution of the bath. However, in general, the conditions that tend to produce a good plate at 140 F tend to raise the percentage of tin in the alloy, whereas those producing a good plate at 100 F tend to lower the percentage of tin in the alloy.

Cathode Current Efficiency. The average current efficiency of the baths tried was 4.10 per cent. The biggest improvement in the efficiency was with increased tin content, about 2.0 percentage points in going from 1.0 to 2.0 g/l of tin sulfate. Lowering the current density from 360 to 240 amperes per square foot brought an increase in current efficiency of about 1.2 percentage points. Under present conditions, not much can be done about raising the current efficiency of the bath because of the twin considerations of plate quality and percentage tin in the alloy.

Plating Voltage. As in the case of trying to raise current efficiency, not much can be done about lowering the plating voltage to save power, because of the necessity of obtaining a good plate and having some regulation of the tin content of the plate. It is of interest to note, however, that the voltage for plating at a pH of 8.0 was lower than that at 7.0. This agrees with the known fact that the conductivity of water goes through a minimum at a pH of 7.0. It is also of interest to note that increasing the glue content in the plating bath did not increase the plating voltage.

Experimental Verification of the Results of the Analysis of Variance

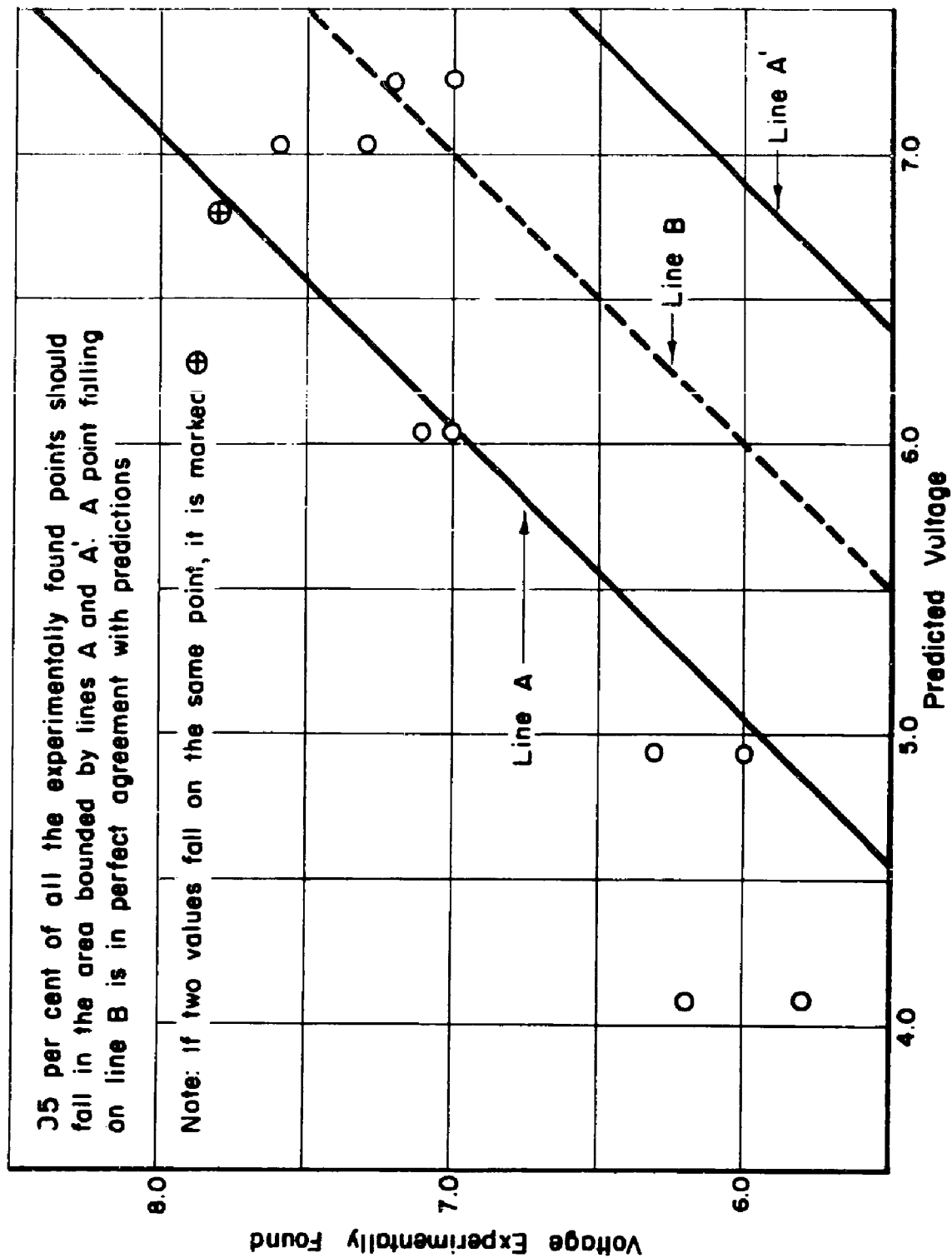
The "predicted" baths were tried and the experimental results were compared with the predictions. These values are given in Table 11. For easy reading, the same data are presented graphically. Complete details of the experimental work are found in Table 78, Appendix III.

Three graphs are presented - one each for agreement between expected and experimental cell voltage (Figure 11), per cent tin in the plate (Figure 12), and cathode current efficiency (Figure 13). On each graph, two parallel solid lines (Lines A and A') mark the 5 per cent limits of expected variation of the plotted points. Midway between the two solid lines is a dotted line (Line B) representing the exact predicted values. All points would fall on this line if there were perfect agreement between the expected and experimental values.

The cell voltages (Figure 11) averaged about 0.9 volt higher than, but otherwise agreed with, expectations. This rise in cell voltage was a block difference, depending on how specimens were grouped in terms of time for

TABLE 11. PREDICTED AND FOUND VALUES OF PLATING VARIABLES FOR "PREDICTED" BATHS

	Treatment											
	aegh	aefgh	abg	abfg	ach	aefh	ab	abf	acegh	acefghi	abegi	abcfigi
	Sample Number											
	6530-40I	6530-40A	6530-40C	6530-40E	6530-40H	6530-40B	6530-40D	6530-42A	6530-40G	6530-42D	6530-42B	6530-42C
Predicted:												
Per cent tin	51.0	51.2	45.6	45.8	41.8	46.0	39.8	44.0	61.0	56.8	59.4	55.2
Plate quality	8.8	8.8	8.8	8.8	8.6	8.6	8.6	8.6	7.8	7.8	7.8	7.8
Plating voltage	7.04	7.04	7.27	7.27	6.80	6.80	6.04	6.04	4.94	4.94	4.08	4.08
Cathode current efficiency	4.50	4.50	4.66	4.66	4.50	4.50	4.28	4.28	5.66	5.66	6.00	6.00
Found:												
Per cent tin	46.2	47.9	45.1	44.1	43.9	44.2	45.1	43.7	57.9	49.7	61.0	60.3
Plating voltage	7.6	7.3	7.0	7.2	7.8	7.8	7.0	7.1	6.3	6.0	6.2	5.8
Cathode current efficiency, %	3.74	2.72	4.02	3.74	4.14	3.24	4.63	3.93	6.57	5.95	6.20	6.40



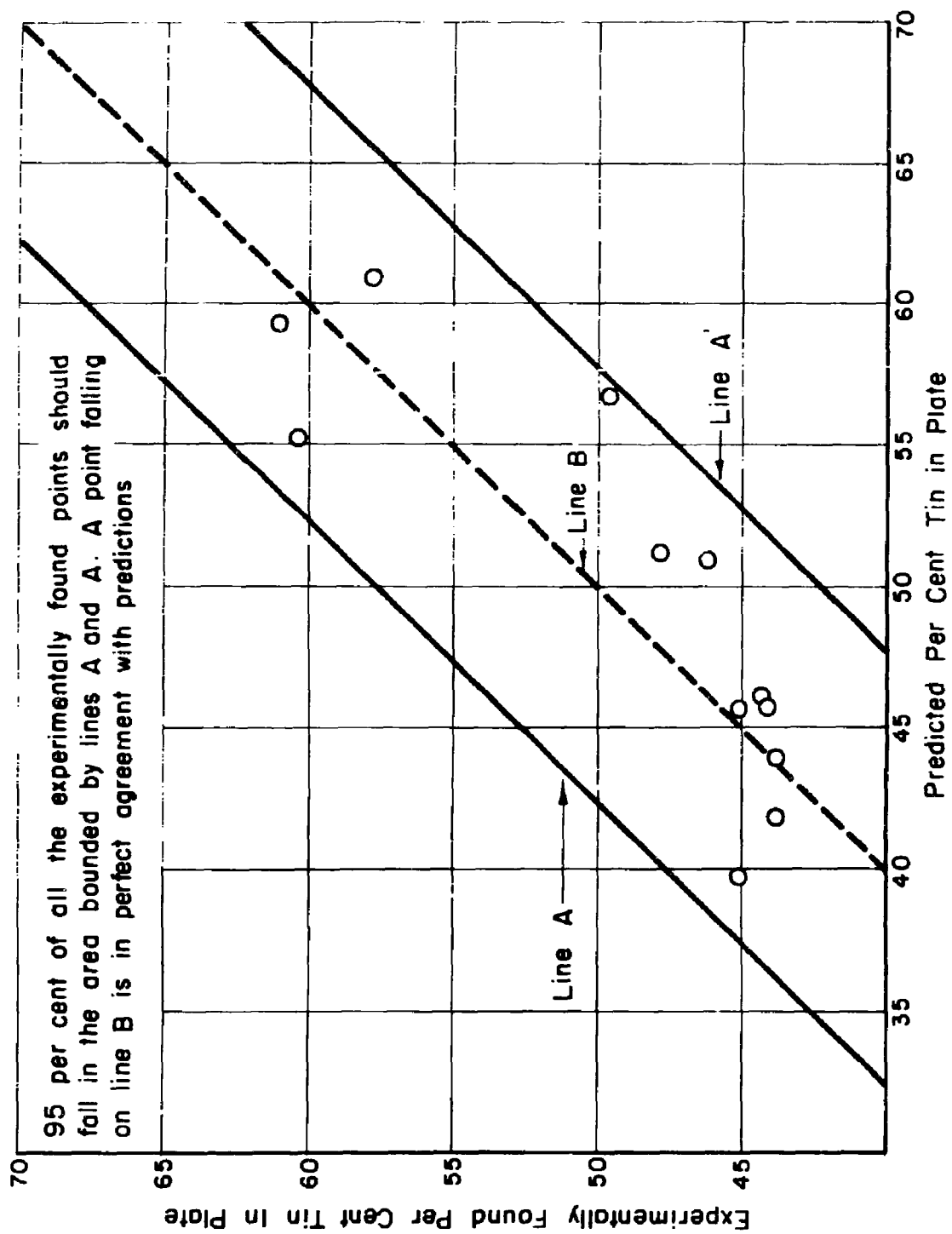


FIGURE 12. GRAPHICAL PLOT OF EXPERIMENTALLY FOUND PER CENT TIN IN PLATE AGAINST PREDICTED PER CENT TIN

A-2018

plating. The factorial experiment was in one randomized block and the verification in another. After the factorial experiment was run, slight changes were made in anode design and new porous cups were installed around the anodes. The changes, which are explained in Appendix II, are believed to have produced the voltage rise.

The graphs for both per cent tin in the plate (Figure 12) and current efficiency (Figure 13) show good agreement between expected and experimental values. Out of a total of 24 points in the two graphs, only one fell outside the 5 per cent limit lines. Since the graphs show such good agreement between expected and experimental values, the findings of the analyses of variance have been confirmed.

Over-All Results of the Factorial Experiment

One purpose in doing this work was to see if factorial experiments are usable to study alloy plating baths. Their value was demonstrated by the good agreement between the predictions of the analysis of variance and the experimental results.

The size and scope of the factorial experiment can be varied to suit the problem at hand. The one carried out here was quite comprehensive. For baths nearly ready for pilot-plant-scale work, such a comprehensive study would be profitable. For exploratory work, less comprehensive, smaller factorial experiments are usable. Graeco-Latin and Latin squares, as well as mere spot checks, are also valuable for exploratory work.

Another purpose in this work was to find out how the bath performed. The worst deficiency of the bath was the low cathode current efficiency. No means were uncovered by the factorial experiment for overcoming this deficiency.

Studies With Other Complex Ion Forming Solutions for Manganese-Tin

In attempts to improve the efficiency of manganese-tin codeposition and the properties of the plate, a number of other types of solutions were investigated. The essential data are described in the following sections.

Sulfate-Fluoride Solutions

Parkinson, in a study of tin-nickel alloy electrodeposition⁽³⁴⁾, used a fluoride-type solution with considerable success. Tin complexes with the

fluoride ion, according to his measurements, and the deposition potential of tin is made appreciably more negative. This factor appeared to be of promise for codeposition of manganese and tin, and an investigation was started.

The first experiments were performed using solutions containing manganous and stannous sulfates with sodium fluoride at a pH of 2. (See Table 79, Appendix III.) The deposits were muddy, nonadherent and contained only small amounts of manganese. With "Alrosol"*, a proprietary nonionic wetting agent of the fatty acid amide type, a more compact deposit was obtained at a cathode efficiency of 43 per cent. The deposit contained 20 per cent manganese. Hide-glue addition also improved the deposit and resulted in a relatively high efficiency (46 per cent) but the manganese content was only 4-1/2 per cent.

Table 80, Appendix III, records the results of experiments where the effects of agitation and higher temperature were studied with single addition agents and combinations of addition agents. At 150 F and moderate work-rod agitation, a deposit was obtained at 84 per cent cathode efficiency, and the alloy contained 51 per cent manganese. The deposit was coarsely crystalline and did not have the desired adhesion. The important fact was that a deposit containing 51 per cent manganese was obtained at such high current efficiency. It appeared that the only thing needed was some condition or addition agent that would refine the grain structure. The balance of the work was directed toward that goal.

Activated-carbon treatments, hydrofluoric acid additions, and ammonium bifluoride additions were tried (see Tables 81 and 82, Appendix III) without achieving a deposit that was satisfactory.

The effects of two types of agitation, each operating at several different speeds were then studied for the manganese-tin sulfate-fluoride bath. The first kind of agitation used was the regular work-rod type where the cathode moves linearly between, and equidistant from, the anodes (see Table 83, Appendix III). Paddle agitation was also used. Two flat, perforated paddles, one on each side of the stationary cathode, moved in a linear motion between the anodes and cathode. In general, the effect of increasing agitation was to lower the manganese content of the deposits.

Lack of reproducibility was observed in this series of tests. Tests 10D and 16A were run under the same conditions, yet there is considerable difference in the plate compositions and efficiencies. The difference in appearance was less marked.

Thus far, the sodium fluoride concentration had been held at 40 g/l. Lowering the concentration to 20 g/l or raising it to 80 g/l did not improve the deposits (see Table 84, Appendix III). The manganese content of the deposits was lower than when the sodium fluoride concentration was 40 g/l.

*Alrosc Chemical Company, Providence, Rhode Island.

Table 85, Appendix III, records the results of experiments utilizing various addition agents, and combinations of addition agents in the manganese-tin sulfate-fluoride bath. Sound deposits were not achieved by use of the addition agents listed in Table 85. Because the primary objective of these experiments was the production of satisfactory appearing deposits, plate analyses were not made.

Table 86, Appendix III, lists a few experiments where the pH of the sulfate-fluoride bath was lowered to 0.5. Even with Alrosol present, the manganese content of the deposits was below ten per cent. The deposits were not sound.

Safranek, Combs, and Faust⁽⁶⁵⁾ obtained ductile mirror-bright copper deposits from an acid-sulfate bath containing the sulfonated products of di-p-tolyl sulfoxide, di-p-tolyl disulfide, and the sodium salt of di-p-tolyl sulfide. These compounds functioned well in the strongly acid-type solution, and for this reason were tried in the sulfate-fluoride solution. Runs at pH 2.0 and 0.0 (see Table 87, Appendix III) using these agents alone and in combination resulted in poor deposits.

Because potassium fluoride is much more soluble than sodium fluoride, it was thought that a greater degree of complexing might result from its use. Table 88, Appendix II, records a series of experiments in which baths containing up to 200 g/l of the potassium salt were tested, with and without addition agents. Where the deposits were acceptable, the manganese content was very low. In general, the deposits were poor, and the manganese content did not exceed thirteen per cent.

Chloride-Fluoride Solutions

The substitution of chloride salts for sulfate salts in the fluoride-type manganese-tin baths did not result in an improvement. The deposits were generally coarsely crystalline, and frequently contained loose overlays (see Table 89, Appendix III).

Alrosol does not appear to have the same effect in a chloride-fluoride manganese-tin bath as it does in the sulfate-fluoride solution. When used in the latter solution, it tends to raise the manganese content of the deposit to 50 per cent or above. Table 90, Appendix III, contains the results of the experiments. The highest manganese content was 18-1/2 per cent. The deposits were rough and had only fair cohesion.

Sulfate-Fluoride-Tartrate Solutions

Tin forms a complex with tartrate as well as with fluoride. Additions of sodium tartrate to the sulfate-fluoride solution did not result in a

satisfactory plate. The manganese content of the deposits remained low, and the cathode efficiencies were generally of an intermediate order (see Table 91, Appendix III). The deposits were of poor quality.

Sulfate-Citrate Solutions

Preliminary tests for the deposition of manganese-tin alloys from sulfate-citrate solutions resulted in powdery deposits having relatively low manganese contents. The data are recorded in Table 92, Appendix III.

DISCUSSION OF ESSENTIAL DATA — MANGANESE-NICKEL ALLOY DEPOSITION

Introduction

The manganese-nickel system is one of the minor systems to be investigated on this project. Because of previous work with cast manganese-nickel alloys, however, it is thought to be of perhaps greater significance than the other minor systems (Mn-Cu, Mn-Cr, Mn-Mo, Mn-Fe).

Earlier, in the work with cast alloys (see Final Report, dated June 28, 1949), extreme polarization was observed with alloys containing about seven per cent nickel. The polarization was so great that insufficient current was available for protection of the steel portion of the couple. If the polarization can be controlled so as to allow a near-minimum protective current to flow, the alloy would protect steel for long periods.

Of the codeposited manganese-nickel alloys from solutions discussed briefly in this section, none was satisfactory.

Static Potentials of Electrodeposited Manganese-Nickel Alloys

The potential of a manganese-nickel coating which contained about ten per cent manganese is not sufficiently electronegative to protect steel sacrificially. (See Table 12.) This panel was plated from a sulfate bath.

TABLE 12. STATIC POTENTIALS OF ELECTRO-
DEPOSITED MANGANESE-NICKEL
ALLOYS IN THREE PER CENT NaCl
SOLUTION AT 90 F

Elapsed Time, minutes	Potentials ⁽¹⁾ Mn-Ni 6922-85H
1	-0.677
10	-0.713
20	-0.711
30	-0.710
40	-0.707
50	-0.705
60	-0.701
90	-0.698
120	-0.694
180	-0.686
240	-0.681
7 hr	-0.673

(1) Potentials versus saturated calomel electrode in
volts.

Types of Solution Investigated

Sulfate Solutions

Preliminary tests were made with regular manganese sulfate plating solutions to which were added small amounts of nickel sulfate. Details are found in Table 93, Appendix IV.

The high manganese content for this series was 11-1/2 per cent. The results were irregular; an increase in nickel content did not result in a regular change in composition or appearance.

Fluoborate Solutions

At a pH of 0.0, no deposit was obtained from a fluoborate solution. (Table 94, Appendix IV). At a pH of 2.1 to 2.5, a brown flaky deposit containing 20 per cent manganese was obtained at 28 per cent efficiency. Addition of hide glue did not improve the deposit.

Miscellaneous Solutions

A series of poor deposits was obtained from sulfate-citrate, sulfate-borocitrate, and sulfate-acetate solutions (Table 95, Appendix IV). No deposit was had from the sulfate-tartrate solution. The current efficiencies were all of the order of one per cent. The sulfate-citrate and sulfate-borocitrate solutions produced plates with 72 and 64 per cent manganese, respectively.

Effect of Ammonium Sulfate on the Sulfate-Citrate Solution at Various pH Values

The addition of ammonium sulfate to the manganese-nickel sulfate-citrate solution improved the appearance of the deposits (Table 96, Appendix IV) and the cathode efficiency. The content of manganese in the deposits did not exceed 20 per cent.

Sulfate-Fluoride Solutions

The experiments in which manganese and nickel were codeposited from a sulfate-fluoride bath are detailed in Table 97, Appendix IV.

The bath operated best at 150 F, and with a current density of 100 amp/sq ft, moderate work-rod agitation, and a pH of 2.0, deposits containing 20 per cent manganese were obtained. In appearance, the deposit was blue-black with gray spots. In a second experiment, using a fresh bath and run under apparently the same conditions, the manganese content of the deposit was less than one per cent.

Using the same bath from which the 20 per cent manganese deposit had been obtained, and increasing the rate of agitation, the deposits contained about one per cent manganese. The cell voltage dropped about 0.6 volt with the increased agitation. This indicated that the cathode potential was lower and this observation is supported by the lower manganese.

The last four experiments in Table 97 are interesting. The plating conditions for each were the same except for pH which started at 1.3 and was increased by 0.2 unit for each test. The same bath was used throughout. As the pH increased, both the efficiencies and manganese contents increased. At pH 1.9, the efficiency was 43 per cent and the manganese content was 37 per cent. The deposit was black mat with gray blots. The behavior of this bath is seen to be somewhat erratic.

Organic Amines Solutions

Organic amines have been used for electroplating, both with and without water. (66,67,68) A few experiments were made on the solubility of nickel and manganese compounds in several of the amines. Table 98, Appendix IV, contains the results.

Ethylenediamine and triethanolamine were not good solvents, although nickel carbonate was slightly soluble in the former. Addition of water increased the solubility of nickel salts, and where manganese salts were present a precipitate formed.

Manganese sulfate was soluble in ethanolamine, forming a pink solution. The solution became darker when heated. Nickel sulfate was insoluble, but the addition of water made it possible to keep both salts in solution. No plating tests were made with both salts present. A few electrolyses were run with only manganese in solution, and with no water present. No deposit was obtained. The resistance of the nonaqueous solution was high. At 8.4 volts, the current density was 0.014 amp/sq ft. Adding water (about 20 ml to 100 ml ethanolamine) permitted a current density of 0.05 amp/sq ft at 80 F, and 0.14 amp/sq ft at 140 F. No deposits were observed.

Sulfate-Gluconic Acid Solutions

The low efficiencies (below one per cent) obtained during preliminary experiments on the codeposition of manganese and nickel from

sulfate gluconic acid solutions indicate that these baths have little promise. Table 99, Appendix IV, lists the experiments and results.

DISCUSSION OF ESSENTIAL DATA — MANGANESE-CHROMIUM ELECTRODEPOSITION

Introduction

No satisfactory manganese chromium deposits were produced from any of the baths investigated. Hence no "wet-dry" tests and no potential tests were made.

Types of Baths Studied

Simple Sulfate Solution and Sulfate-Citrate Solution

Table 100, Appendix IV, contains the results of a few preliminary experiments on the codeposition of chromium and manganese from a simple solution, and from a sulfate-citrate solution. In all tests, manganese alone was detected in the cathode deposits.

Further tests were made on the sulfate-citrate solution (Table 101, Appendix IV) using higher concentrations for all components. The deposits were poor and consisted mostly of manganese.

Chloride-Citrate Solutions

The deposits from the chloride-citrate solutions showed no improvement over those from the sulfate-citrate solution. The data are given in Table 102, Appendix IV.

Chloride-Fluoride Solutions (Cr III)

The results from the chloride-fluoride solution were erratic. Where deposits were obtained, they were nonuniform and nonmetallic in appearance. Tables 103 and 104, Appendix IV, contain the details of these experiments. As an example of the inconsistent results, refer to Tests 80C and 80F in Table 103. They were both run under apparently identical conditions, yet the first test resulted in a deposit, and no deposit was obtained in the second. Variations in agitation and the use of addition agents caused no improvement.

Chloride-Fluoride (Cr VI) Solutions

Chloride-fluoride solutions, containing hexavalent chromium, produced deposits which were inferior to those from baths containing trivalent chromium (see Table 105, Appendix IV). The efficiencies were lower than those obtained in the trivalent bath. The deposits contained up to 44 per cent manganese.

Chloride-Fluosilicate and Sulfate-Fluoride Solutions (Cr III)

No deposits were obtained in attempting to plate manganese-chromium alloys from chloride-fluosilicate baths (Table 106, Appendix IV) or from sulfate-fluoride baths (Table 107, Appendix IV). Both baths contained chromium in the trivalent form.

DISCUSSION OF ESSENTIAL DATA — MANGANESE-IRON ELECTRODEPOSITION

Introduction

Only the sulfate-fluoride-type bath was investigated for the electrodeposition of manganese-iron alloys. The deposits were not sound enough for testing in the "wet-dry" cabinet. Static potential measurements were made.

Static Potential Measurements of Electrodeposited Manganese-Iron Alloys

The manganese-iron plates, for which potentials are given in Table 13, contained approximately nine or ten per cent manganese. It is apparent that this amount of manganese has a measurable effect on the potential in three per cent NaCl solution. The potential of steel is up to 100 millivolts more noble than the final values given in Table 13. This coating would be expected to provide some sacrificial protection for steel.

Sulfate-Fluoride Solutions

The codeposition of manganese and iron was achieved in a sulfate-fluoride bath (see Table 108, Appendix IV). The maximum manganese content was about 19 per cent, and was obtained at a current efficiency

TABLE 13. STATIC POTENTIALS OF ELECTRO-
DEPOSITED MANGANESE-IRON
ALLOYS IN THREE PER CENT NaCl
SOLUTION AT 90 F

Elapsed Time, minutes	Potentials ⁽¹⁾	
	Mn-Fe 6606-86F	Mn-Fe 6606-86G
1	-0.705	-0.698
10	-0.740	-0.726
20	-0.736	-0.726
30	-0.739	-0.736
60	-0.755	-0.750
120	-0.761	-0.756
210	-0.765	-0.763
5 hr 20 min	-0.767	-0.767
7 hr	-0.767	-0.767

(1) Potential versus saturated calomel electrode in
volts.

slightly above one hundred per cent. Raising the temperature increased the cathode efficiency, and an increase in the current density resulted in a higher manganese content. All the tests were made with the bath pH at about 1.8. Agitation decreased the manganese in the deposit to below one per cent. One plate which contained 13.7 per cent manganese had a uniform, fine-grained appearance.

The last three tests described in Table 108 were apparently run under identical conditions. Both manganese content and cathode efficiency increased. It would seem that there was an aging effect, since all three tests were made using the same solution. Small increases in the pH were thought to be responsible, as they were for the manganese-nickel bath (see above). Subsequent experiments from baths of the same composition did not reveal any aging effect, however.

The latter experiments are described in Table 109, Appendix IV. Plans were to use these specimens for potential measurements and X-ray diffraction studies. Cylindrical cathodes were used so that the alloys would be uniformly deposited.

As it developed, the anticipated aging effect did not appear to be at work in this second set of experiments. At 200 amp/sq ft, less manganese was found in the deposits than had formerly been obtained at 100 amp/sq ft. One specimen was X-rayed and this is described in Table 7. An iron pattern and a pattern for the mysterious calcium stannate was found. This was discussed in the section on manganese-tin from a fluoride bath.

DISCUSSION OF ESSENTIAL DATA — MANGANESE-MOLYBDENUM ELECTRODEPOSITION

Introduction

This alloy system was immediately recognized as one difficult for electrodeposition from aqueous solutions. Electrodeposition of binary and ternary alloys of molybdenum with other metals has been reported in the technical literature. So, for completeness in exploring prospects, a short study was made of manganese-molybdenum codeposition.

The results were much less encouraging than those of other manganese-alloy systems reported herein.

Sulfate-Fluoride Solutions

Ksycki and Yntema⁽⁶⁹⁾ have reported the successful electrodeposition of molybdenum from acid sulfate solutions containing potassium fluoride.

Several manganese-molybdenum baths were patterned after their bath. The experiments are described in Table 110, Appendix IV. Cathode efficiencies were all below one per cent. At 400 amp/sq ft, one of the deposits contained 29 per cent manganese. The deposits were not sound.

Sulfate-Citrate Solutions

McElwee and Holt⁽⁷⁰⁾ have deposited ternary cobalt-tungsten-molybdenum alloys from aqueous citrate solutions. We were unsuccessful in our attempts to plate manganese-molybdenum from a similar solution. Table 111, Appendix IV, records the results of the experiments. In only two of the sixteen tests was an appreciable deposit obtained. In both cases, the cathode was only partially covered, and the deposit was mostly manganese.

Wet-Dry Testing of Cadmium-Tin Alloy Plates

In 1951, Scott and Gray⁽⁷¹⁾ announced a cadmium-tin alloy coating deposited from a fluoborate bath which had phenomenal resistance to salt spray. The coating contained approximately 75 per cent cadmium, balance tin.

Under the sponsorship of Tin Research Institute, Incorporated, salt-spray tests were made at Battelle on the cadmium-tin alloy coating in comparison with pure cadmium plate on steel. While the results here were not so spectacular as those reported by Scott and Gray, they were impressive, nevertheless. The panels tested at Battelle had 0.3-mil coatings and rust first appeared after 1200 hours (this is an average figure for all tests). Pure cadmium-coated panels showed initial rust after 816 hours, although at least half of the surfaces were covered with bulky white corrosion products. The cadmium-coated panels rusted very rapidly following the initial appearance of rust. The cadmium-tin panels, on the other hand, showed relatively little advance of rust. The test was discontinued at 1872 hours (78 days), at which time the panels showed less than one per cent of their surfaces covered with rust. The pure cadmium-coated panels had rusted completely long before.

The above results made it appear advisable to test the cadmium-tin alloy electrocoatings in the "wet-dry" cabinet. Reference to Table 4 which appears earlier in this report reveals that the coatings had excellent resistance to corrosion in the "wet-dry" test. The reader is cautioned, however, not to accept these results as absolute. It will be recalled that pure cadmium coatings stand up abnormally long in the "wet-dry" test, and it is possible that some of the same characteristic may be inherent in the cadmium-tin coatings. They should be given further consideration, however.

EXPERIMENTAL APPARATUS AND METHODS*

Apparatus for Experimental Codeposition

For most of the work, Pyrex beakers served as plating tanks. The 250-ml, 400-ml, and 600-ml sizes were used for the majority of experiments, depending on the bath size. The beakers rested in a large rectangular water bath, equipped with thermostat-controlled electric immersion heaters. A copper coil was immersed in the water bath, and either steam or cold water could be passed through it. This enabled the operator to heat or cool the water to a given temperature with little delay. Air agitation in the water bath insured uniform temperature.

Two carbon anodes were used in each tank. The anodes were enclosed in porous Alundum cups to minimize diffusion of oxidation products to the catholyte. The sizes of anodes and cups varied with bath size. The Alundum cups were supported from the edges of the beakers by Chromel-wire clips.

Polyethylene containers were used exclusively for acid fluoride and fluoborate solutions. Beakers were made by cutting empty hydrofluoric acid bottles just below the shoulder. A maximum of about 400 ml could be contained in such a beaker.

Usually, relatively large (one to two liters) volumes of a given fluoride solution were made up at one time. Inexpensive polyethylene kitchen-ware**, having capacities up to two liters, was used. A polyethylene funnel*** and ordinary filter paper were used for filtering the fluoride and fluoborate solutions.

Carbon rods and Alundum cups were also used in the fluoride and fluoborate solutions.

Stainless steel was largely used as cathode material. Platinum, SAE 1010 steel, SAE 4130 steel, Monel, and yellow brass were also used. The cathodes were fastened in a screw clamp which was attached to the work rod. The work rod, which provided linear agitation, was located several inches above the beakers. The entire setup, water bath, beakers, work rod, etc., was located under a laboratory fume hood.

*The original experimental data for the work described herein are contained in the following Laboratory Record Books:

Number 5022, pp 68-100

Number 5561, pp 31-100

Number 5617, pp 23-54

Number 6245, pp 1-100

Number 6429, pp 1-100

Number 6530, pp 1-49

Number 6606, pp 1-100

Number 6922, pp 1-91

**Tupper Corporation, Farnumville, Massachusetts.

***American Agile Corporation, Plastics Division, Cleveland 3, Ohio.

The electric-current source for electrolysis was a d-c generator having a maximum capacity of 50 amperes at 15 volts.

The current for each bath was controlled by an individual circuit consisting of a variable rheostat, a switch, a fuse, and an ammeter. Four of these circuits were mounted on a panel fastened on the outside of the hood.

Circuit for Superimposing Alternating Current on Direct Current

The circuit which was used in this work where alternating current was superimposed on direct current is given in Figure 14. The direct current is controlled by a slide wire used as a potentiometer. The alternating current is controlled by a General Radio Type 200 CM Variac*, and a 6 to 1 step-down transformer. The alternating current was determined by use of a Ballantine Laboratories Model 300 vacuum tube Voltmeter**. The "Ballantine" was paralleled with a 0.01-ohm shunt, and the current was calculated from Ohm's law. The "Ballantine" is so constructed that it measures only the alternating currents.

The direct current was measured with a Weston, Model 280 d-c ammeter. This is a variable-range instrument and contains internal shunts. The d-c ammeter will give the true direct current as long as the wave form of the ac is purely sinusoidal. No attempt was made in the work described herein to determine the wave form of the ac. It can be measured with an oscilloscope and, if further work is done with superimposed ac, an oscilloscope will be used. Superimposing the ac does cause the needle of the d-c ammeter to vibrate somewhat, but this does not interfere with the reading.

There is danger of excess heating effect on the d-c ammeter coil due to the ac. This can be eliminated by use of an inductance in series with the ammeter coil but not with the shunt. A condenser in parallel with the coil can be used in addition to the inductance.

As shown in Figure 14, the d-c voltmeter measures the IR drop through the 0.01-ohm shunt and the ammeter, as well as that through the solution. The additional voltage recorded is not very high. In future work, the d-c voltmeter will be placed in the circuit as indicated by the dotted line.

*General Radio Company, Cambridge, Massachusetts.

**Ballantine Laboratories, Incorporated, Boonton, New Jersey.

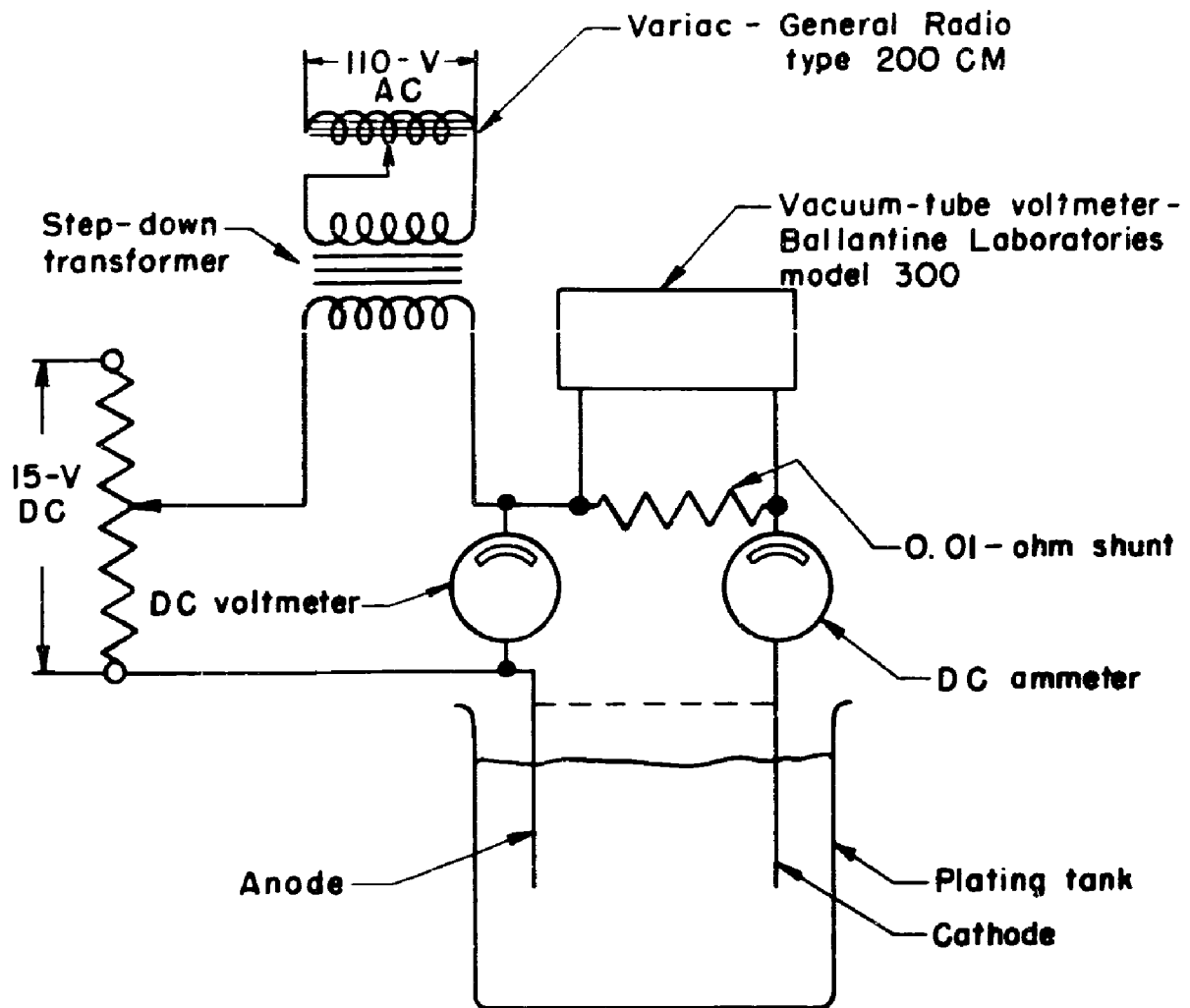


FIGURE 14. CIRCUIT USED FOR SUPERIMPOSING ALTERNATING CURRENT ON PLATING CELL

A - 1084

The Double Diaphragm Cell

The double diaphragm cell consisted of two rectangular Lucite cells with one wall missing from each. The two cells were clamped together so that a porous Alundum diaphragm formed a common fourth wall for each cell. Thus, a cell was formed with two compartments separated by a porous plate. The electrolyte was placed in both compartments. One compartment contained the cathode, and the other contained a carbon anode enclosed in a porous Alundum cup. In this way, there were two diaphragms between the anode and cathode.

Hull-Cell Tests

A 267-ml Lucite Hull cell* was used for this work. A 1/8-inch-thick carbon flat, which fitted snugly into the Hull cell, served as the anode. The anode was covered with a 1/8-inch-thick porous Alundum plate, the edges of which also fitted snugly against the walls of the Hull cell. The Alundum plate prevented most of the anodic oxidation products from mingling with the catholyte. A very small amount of the oxidized material did seep through at the edges.

The cathodes were 2-inch x 4-inch steel plates. Following each run, the plated cathodes were rinsed, dried, and sprayed with "Krylon"**, a clear and colorless plastic. This was done to preserve the deposits in their original condition, since manganese alloys are prone to surface oxidation. Actually, the deposits were darkened very slightly by the spray. This slight darkening did not interfere with the interpretation of the results.

Cell Used in Experiments Where Anode to Cathode Distance Was Varied

The rectangular cell used for varying anode to cathode distances was made from 1/4-inch Lucite sheets. They were glued together with a glue made by dissolving Lucite shavings in trichloroethylene.

The inside dimensions were 9 inches long x 2-3/8 inches wide x 2-7/8 inches deep.

*R. G. Hull and Company, Incorporated, Rocky River 16, Ohio.

**Krylon, Incorporated, Philadelphia 32, Pennsylvania.

Description of Paddles Used for Agitators

The paddles used to agitate the manganese-tin sulfate-fluoride solution were made of 1/4-inch-thick Lucite sheet. They measured 6 inches x 1-1/2 inches. Ten 1/4 inch holes were bored in each paddle and the top 2-1/2 inch section was hole-free. Two panels were used at the same time. They were fastened to the work rod, which moved them in a reciprocating motion, one on each side of the stationary cathode. The paddles were immersed 3-1/2 inches in the water, and the 1-1/2-inch dimension (width) was perpendicular to the cathode.

Preparation of Experimental Plating Solutions

General

No special techniques were necessary in preparing the solutions used in this work. With the exception of those mentioned below, the solutions were prepared by dissolving the reagents in distilled water, in the order given in the tables in the Appendixes. CP chemicals were used throughout.

Where gelatin was a bath component, the solution had to be heated to 120 F to effect dispersion of the gelatin. Subsequent cooling did not cause coagulation of the gelatin. The sulfate-citrate baths were best prepared by heating the solution containing both manganous and zinc sulfates to 120 F, and then adding the sodium citrate in the form of a solution.

The citric acid solution was made by dissolving electrolytic manganese and mossy zinc in separate portions of citric acid solution. The manganese was dissolved very rapidly, but the zinc solution was heated, since the rate of dissolution at room temperature was very slow. Precipitates occurred in both cases. The two mixtures were combined, and the sodium hydroxide solution was added until the pH was 5.2. The precipitates dissolved during the addition of the alkali, and a yellow solution resulted.

The manganese-zinc cyanide solution was prepared as follows: One mole of manganous sulfate monohydrate and two moles of sodium cyanide were dissolved in separate portions of distilled water. The solutions were combined, and the resultant precipitate was washed four times by decantation and then filtered on a Buchner funnel. The decantation and filtration were repeated. The precipitate was made into a slurry and a solution containing eight moles of sodium cyanide was added to it. The manganous cyanide dissolved rapidly, forming a complex manganese cyanide solution. The complex zinc solution was prepared by adding a solution containing 3.34 moles of sodium cyanide to a slurry containing one mole of zinc cyanide. The complex manganese solution and the complex zinc solution were then combined.

Preparation of Manganese-Zinc Pyrophosphate Solution

The preparation of the pyrophosphate solution required special care. The following procedure was followed here:

<u>Stock Solution A:</u>	
$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	100 g/l

<u>Stock Solution B:</u>	
$\text{K}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$	500 g/l

20 ml A was added to 60 ml B with rapid stirring. The resultant pH was 12.2, which was adjusted to 10.2 with dilute H_2SO_4 solution. (At higher pH, a brown precipitate formed.)

<u>Stock Solution C:</u>	
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	100 g/l

250 ml C were added to 200 ml . Then the manganese pyrophosphate solution was combined with zinc pyrophosphate solution.

Plating and Polishing Baths Used in Treating the Basis Steel Prior to Manganese-Zinc Plating

In the experiments recorded in Table 8, the basis metal was copper plated, zinc plated, or electropolished.

The SAE 4130 steel was electropolished by a proprietary process of the Battelle Development Corporation, Columbus 1, Ohio.

The flash copper plating was done in the following bath:

$\text{Cu}(\text{CN})_2$	26 g/l
NaCN	34 g/l
Rochelle Salt	30 g/l
Na_2CO_3	30 g/l
pH	12.6
Temperature	80 F
Time	3 minutes
Current Density	10 amp/sq ft
Agitation	None

The steel was given a thin zinc coating from the following bath:

Zn(CN) ₂	60 g/l
NaCN	23 g/l
NaOH	53 g/l
Temperature	114 F
Time	5 minutes
Current Density	10 amp/sq ft
Agitation	Work-rod type 33 cycles/min, 1-1/4" stroke

Preparation of Cadmium-Tin Alloy Deposits on Steel
for Testing in the "Wet-Dry" Cabinet

The directions given by Scott and Gray⁽⁷¹⁾ were followed, with one exception, in depositing a 75-25 cadmium-tin alloy on SAE 4130 steel. In the work here, Keystone Gelatin No. 431 was substituted for processed protein powder.

The bath make-up and plating conditions were as follows:

Cd(BF ₄) ₂ (50.82% solution)	254 ml/l
Sn(BF ₄) ₂ (46.1% solution)	68.5 ml/l
HF ₄ (42%)	61 ml/l
H ₃ BO ₃	20.2 g/l
NH ₄ BF ₄	5.0 g/l
Phenol Sulfonic Acid	1.5 ml/l
Keystone Gelatin No. 431	0.75 g/l
Current Density	48 amp/sq ft
Temperature	90 F
pH	2.5
Anodes	Individual anodes of Sn and Cd, which were bagged
Time	4-3/4 minutes for 0.3-mil plate

As made up, the pH of the solution was below 0.1. The pH was raised to 2.5 with NH₄OH.

The plates were made on 3 inch x 1 inch (plated area) SAE 4130 steel cathodes which had been cleaned in a hot alkaline cleaner, and given a dip in 3 N H₂SO₄ solution at 135 F.

Chemical analysis showed the deposit to contain 23 per cent cadmium.

Preparation of Cadmium-Plated Steel Specimens
for Use as Standards in the "Wet-Dry" Test

The cadmium-plating solution was made up from Cadolyte Single Salt*, a proprietary mixture. The bath composition and plating conditions were as follows:

Cadolyte Single Salt	120 g/l
Temperature	80 F
Current Density	30 amp/sq ft
Anodes	Steel

The cathodes were of the same material and size as those used for the cadmium-tin alloy deposition. The pretreatments were also identical.

Treatment of Baths With Activated Carbon

Activated carbon (grade S-51, Darco Corporation, 60 East 42nd Street, New York, New York) was used in certain cases to insure that the baths would be free of organic contaminants. The solutions were heated to 120 F, and 3 grams of activated carbon were added for each liter. The baths were held at 120 F for one hour and the solutions were stirred continuously. Then they were filtered.

Preparation of Manganese-Tin,
Sulfate-Tartrate Baths

To make the sulfate-tartrate baths for investigating the manganese-tin alloy-plating system, stock solutions were prepared and added to each other. The methods of preparation, compositions, and amounts of stock solutions corresponding to high and low levels of each bath ingredient were as follows:

- A.** Hide Glue Stock Solution, 6.6 g/l. Granulated hide glue was soaked overnight in water, and the resulting suspension was boiled for two hours. After cooling and diluting to the required volume, the solution was aged for a few days before use. High level 31.8 ml, low level 10.6 ml, each for a 700-ml bath.
- E. Na₂SO₃ Stock Solution, 30 g/l. The sodium sulfite was simply dissolved in the water. High level 23.4 ml, low level 11.7 ml, each for a 700-ml bath.

*The Udylyte Corporation, Detroit 11, Michigan.

**The symbols A, E, and F refer to the three independent variables connected with the solution itself and correspond to symbols in Tables 9, 10, 73, 74, 75, 76, and 77. The missing symbols B, C, and D refer to pH, temperature, and current density.

- F. Tartaric Acid Stock Solution, 400 g tartaric acid in 523 ml of water. The tartaric acid was simply dissolved in the water. High level 70 ml, low level 35 ml, each for a 700-ml bath.
- G. $(\text{NH}_4)_2\text{SO}_4$ Stock Solution, 1000 g in 1500 ml H_2O . The ammonium sulfate was dissolved in the water. High level 375 ml, low level 300 ml, each for a 700-ml bath.
- H. $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ Stock Solution, 1000 g in 1500 ml H_2O . The manganese sulfate was dissolved in the water. High level 184 ml, low level 123 ml, each for a 700-ml bath.
- I. SnSO_4 Stock Solution, 100 g in 1500 ml H_2O plus 100 ml H_2SO_4 (sp gr 1.84). The stannous sulfate was dissolved in the diluted sulfuric acid.

In making up a bath, the procedure was to pour E, G, and H into a beaker marked at the 700-cc level. F and I were poured into and mixed in another beaker and then poured into the first beaker. The glue was then added and the bath was brought to a pH of 7.0 or 8.0 as desired, according to a glass electrode, by means of ammonium hydroxide (sp gr 0.9015). The bath was then diluted with water to the 700-cc level.

The baths were electrolyzed in their 1000-cc beakers suspended in temperature-controlled baths. Anodes were round graphite rods, 1/2-inch diameter x 6 inches long, which were suspended in Alundum thimbles.* There were two anodes in each cell, one opposite each face of the 3-inch x 1-inch x 0.020-inch steel cathodes.

Each bath was used for one electrolysis (15 minutes) and was then discarded.

Description of Plating Methods Used for Other Than the Manganese-Tin Factorial Experiment

The cathodes were cleaned cathodically at 50 to 100 amp/sq. ft in a 180 F solution containing 75 g/l of Anodex**. The panels were rinsed with distilled water. No acid dip was used with the stainless steel or platinum cathodes.

The cathodes were immersed to the proper depth in the plating solution, and the current was turned on. At the same instant, the timer was

*Norton Company, Worcester 6, Massachusetts.

**MacDermid, Inc., Waterbury, Connecticut.

started. After a given time (usually 10 minutes), the current was turned off, and the plated panel was removed, rinsed with distilled water, and dried in a stream of filtered compressed air. Where the deposits were flaky or otherwise nonadherent, the deposits were dried by dipping in alcohol and, finally, in ether.

Description of Methods for Plating Specimens and Evaluating Results in the Factorial Experiment on Manganese-Tin

Plating Cycle

The specimens (steel, 4 inches x 1 inch x 0.020 inch) after thorough wiping with clean towels were treated cathodically in Anodex, 75 g/l, at 180 F for 45 seconds at 20 amperes per square foot; anodically for 15 seconds at the same current density. After rinsing, the specimens were dipped in 10 per cent sulfuric acid for 15 seconds. After again rinsing, the lower 3 inches of the specimens were plated.

Measurement of Plating Voltage

About 5 minutes after starting electrolysis, this measurement was made by means of a d-c voltmeter across the cell.

Measurement of Quality Rating of Plate

To make the observation of quality, three different observers, independently starting with the specimens in a random order, arranged them as well as they could in an order according to "quality" of the plate. The specimen quality rating was the number corresponding to the position of the specimen in the lineup. In Table 77 is recorded the average rating of each specimen. This was an intuitive rating based upon judging the relative severity of defects of different kinds. In spite of its being intuitive, the rating appears to have merit, since the analysis of variance shows pronounced effects due to the conditions imposed on the plating bath.

Calculation of Analysis of Variance

The first step in this calculation was to record the data in terms of punched holes on IBM* cards. There were 64 cards punched, one for each of the plates prepared. Next it was necessary to sort the cards in various ways according to the variables recorded on them. For each main effect, the deck of 64 cards was sorted into two decks of 32 cards each. In one of these decks, the variable of interest was always at its high level, and in the other deck, always at its low level.

*International Business Machines, Endicott, New York.

For each of the interactions, the deck was sorted into 4 decks of 16 cards each. In one of these decks, both variables of interest would be at their high level; in the second deck, both at their low level; in the third deck, one variable high and the other low; and in the fourth deck, the reverse of the third deck.

After each sorting, the data were recorded by typewriting in columns titled according to the classification of each deck.

For punching the data into the cards, a Type 026 IBM Printing Card Punch was used; for sorting the cards, a Type 101 IBM Electronic Statistical Machine; and for typing the sorted data, an IBM Cardtype. A Marchant machine was used to perform the calculations on the typed data. An IBM calculator and tabulator could have been used to advantage in place of the Marchant, but these machines were not available. They have since been installed at Battelle.

The calculations on the Marchant machine were performed as follows:

1. Obtain the grand total of the observations for the dependent variable of interest. Square this sum and divide by 64. The result is the correction factor which is used to correct the following squares for the fact that they are deviations from zero, not the mean.
2. Square the individual observations of the dependent variable of interest, sum the squares and subtract the correction factor. The result is the total sum of squares.
3. Obtain the totals corresponding to the columns typed by Cardtype. Square these totals, sum separately the squares corresponding to each source of variance, and divide by the number of observations in the columns summed. For the sums of squares of the main effects, subtract the correction factor from the figures found directly above. For the interactions, subtract not only the correction factor but also the sums of squares found for the main effects of the factors involved in the interaction under consideration.
4. To find the error sum of squares, subtract the sums of squares corresponding to each source of variance from the total sum of squares found in (2).
5. The mean squares for each source of variance is the sum of squares of each divided by the corresponding degrees of freedom. The degrees of freedom are the number of independent observations of the average deviation from the mean for each source of variance.

- b. The F for each source of variance is the quotient obtained by dividing each mean square by the error mean square. F (Snedecor's) is a measure of the likelihood of the observation being due to chance. Tables of F for different probability levels are available in most works on the subject. The usual interpretation is that when F corresponds to the 0.05 or lower probability level that a real effect due to the source of variance has been observed.

Methods Used for Analysis of Deposits

General

The composition of the alloy deposits, unless otherwise noted, was found by determining the manganese, and calculating the second element by difference. Manganese-tin deposits were the chief exceptions. It was easier to analyze for the tin.

The rapid, persulfate method for manganese was used. The coatings were removed from the stainless steel or platinum panels with 20 ml of dilute nitric acid (60 ml conc nitric acid in 1000 ml H_2O). The solution was transferred to a 500-ml Erlenmeyer flask. Twenty-five ml of the following acid mixture were then added to the nitric acid solution:

H_2SO_4 (conc)	100 ml
H_2O	525 ml
H_3PO_4 (85%)	125 ml
HNO_3 (conc)	250 ml

The mixture was brought to a boil, and 100 ml of hot distilled water, 10 ml of silver nitrate solution (10 g $AgNO_3$ in one liter H_2O), and 10 ml of persulfate solution (25 g $(NH_4)_2S_2O_8$ in 85 ml H_2O) were added. The solution was boiled for one minute, cooled to 15 to 20 C, and then titrated rapidly with a standard sodium arsenite solution to a yellow end point. The arsenite solution contained 1.52 g/l As_2O_3 and 1.0 g/l NaOH. It is standardized by running a standard manganese sample through the above procedure.

Method of Analysis for Tin in Manganese-Tin Alloy Plate

The SAE 1010 test panels were weighed before and after plating. They were then cut into small pieces, placed in a 250-ml Erlenmeyer flask, and 100 ml of hydrochloric acid solution (3 parts conc HCl + 1 part H_2O by volume) was added. A one-hole rubber stopper, containing an

inverted glass U-tube was placed firmly in the flask mouth, and the flask was placed on a medium-temperature hot plate. When the sample had dissolved, the flask was placed in a cooling trough with the free end of the inverted U-tube dipping into a saturated solution of sodium bicarbonate. As the solution in the flask cooled, the bicarbonate was sucked back into the acid, where it reacted to form CO_2 . The CO_2 kept the reduced tin from oxidizing. When the solution cooled to 70 F, it was titrated with a standard KI-KIO_3 solution, using starch as an indicator.

Gravimetric Determination of Zinc in Electro-deposited Manganese-Zinc Alloys

The following steps were followed in the quantitative determination of zinc in the manganese-zinc deposits:

1. The weighed deposit was dissolved in about 100 ml of dilute sulfuric acid solution (500 ml H_2O + 50 ml 1:1 H_2SO_4)
2. The solution containing the manganese and zinc was transferred to a 500-ml volumetric flask, and diluted to the mark with distilled water
3. An aliquot containing approximately 0.05 g zinc was taken
4. Five ml of a citric acid solution were added to the aliquot (100 ml H_2O + 100 g citric acid)
5. Two drops of methyl red indicator were added and the sample was neutralized to the yellow of the indicator with 1-1 NH_4OH solution
6. Thirty ml of a formic acid buffer were added (400 ml formic acid, 60 ml conc NH_4OH , and 1540 ml H_2O)
7. The solution was diluted to 200 ml with distilled water, ten ml Na_2S solution were added (100 ml H_2O + 10 g Na_2S), and the solution was stirred rapidly for 10 minutes, or until the precipitate coagulated
8. The solution was filtered on a Schleicher and Schuell* No. 589 Blue Ribbon paper, and the precipitate was washed thoroughly with a wash containing a small amount of buffer and some Na_2S
9. Paper and contents were dried and then ignited at 750 C
10. Weight of $\text{ZnO} \times 0.8034 = \text{g of Zn in sample}$

*Schleicher and Schuell, New York, New York.

Determination of Oxygen in Manganese-Zinc Alloy Electrodeposits

The manganese-zinc alloys which were to be analyzed for oxygen were deposited on passivated stainless steel cathodes. The deposits were stripped fairly easily, and broke into many small fragments in the process.

The fragmented coatings were analyzed for oxygen by the total-vacuum-fusion method, which consists of dissolving the tin-foil-wrapped sample in a carbon-saturated iron bath at 3000 F, extracting and collecting the gases for 30 minutes, and then analyzing the gases for oxygen, hydrogen, and nitrogen in a modified Orsat apparatus.

Cathode Current Efficiency Calculation

The cathode current efficiency for the sulfate-tartrate, manganese-tin solutions was calculated by means of the equation:

$$\text{Per Cent Efficiency} = [3.91 - 2.10 \text{ Sn}] \frac{W}{A} \times 100 ,$$

in which Sn = the percentage tin (expressed as a decimal) in the alloy, W is the weight of the deposit, and A is the amperage of the cell. It should be noted that this equation can be used only where the plating time is 15 minutes.

For all other solutions, a series of graphs was used. A graph was made for each alloy system by plotting the theoretical grams/amp-hr yield for one element as the left hand ordinate, and the theoretical grams/amp-hr yield for the second element as the right hand ordinate. The two points were then joined with a straight line. The per cent values for each binary alloy were plotted along the abscissae. After the deposit was analyzed, the theoretical yield for the specific alloy was obtained, and the actual yield was compared with it to obtain the cathode current efficiency.

Measurement of pH

A glass-electrode system was used to measure the pH of those solutions which did not attack glass. A battery-operated Beckman Model M glass-electrode pH meter was used at first. This was later replaced by an a-c operated Beckman Model H-2 glass-electrode pH meter. The latter meter was used for most of the work on this project. It has a built-in temperature compensator, and can be quickly changed over for potential measurements. The meters and electrode systems were checked frequently against standard buffer solutions.

The glass electrode cannot be used to measure the pH of fluoride or fluoborate solutions. For those solutions containing no oxidizing substances, a quinhydrone electrode was used. The electrode system comprises a gold electrode and a calomel electrode. These are specially constructed with plastic, so as to resist the fluoride solution. The electrodes* and meters were purchased from Beckman Instruments, Inc., South Pasadena, California.

In using the quinhydrone electrode system, the solution to be tested was saturated with quinhydrone, the electrodes were then immersed in the solution, and the pH reading was made in exactly the same way as with a glass electrode. Standardization is accomplished by using a standard buffer solution which has been saturated with quinhydrone.

For fluoride or fluoborate solutions containing oxidizing agents, colorimetric papers were used; a paper having the trade name Oxyphen, which is made in Switzerland, and distributed in the United States by the J. Einstein Company, Forest Hills, New York. These papers have the advantage of having the comparison colors on the paper strip. The comparison colors are wetted by the test solutions as well as the section of the strip which contains the indicator. This allows an easier and more accurate comparison.

Three sets of Oxyphen papers, each having a separate range of pH, were used. For rough measurements, there were available two sets covering the range 1.0 to 13.0 in 1.0 unit. For finer measurements, the set covering the range 1.2 to 2.7 in 0.3 unit, provided adequate control. Below pH 1.2, "Accutint" papers, accurate to about 0.2 units, were used. The latter were used only because the Oxyphen papers did not go below 1.2. "Accutint" papers are manufactured by Anachemia, Limitec, Montreal, Canada.

Measurement of Surface Tension

A Traube Stalagmometer was used to measure the surface tensions of several plating solutions.

The stalagmometer was a calibrated capillary tube, the lower end of which was flattened out to provide a larger dropping surface. The enlarged end was ground flat and polished. It was imperative that this polished surface be scrupulously clean, for proper drop formation. A bulb was blown near the center of the tube and calibration marks were etched on the tube above and below the bulb. A given volume of the unknown solution was allowed to drop slowly from the stalagmometer, and the drops were counted. This figure was compared then with that for pure water. The following equation was used to calculate the surface tension of the unknown liquid:

*Calomel Cell, Beckman No. 1170-14; Gold Electrode, Beckman No. 1190-14.

$$SE \text{ of } X = \frac{\text{Number of drops of H}_2\text{O} \times \text{Density of } X}{\text{Number of drops of } X} \times 70 \text{ .}$$

Measurement of Dynamic Cathode Potentials

The apparatus and methods used for measuring cathode potentials under dynamic conditions were described in detail in the Final Report, dated June 28, 1959. Essentially, the method comprised measuring the potential of the cathode in a plating cell while current was flowing. The cathode potential was measured against a saturated calomel cell fitted with a probing tip. Cylindrical cathodes were used because the current distribution is more uniform on them. In practice, we started with a very low current density and took measurements once every two or three minutes until the potential reached a steady state. Then the current density was increased by a small increment and the measurements repeated. This continued until relatively high current densities were reached.

The "Wet-Dry" Cabinet

A lead-lined, cork-insulated plywood box, measuring 34 inches x 25 inches x 25 inches, was the basis for the "wet-dry" cabinet pictured in Figure 15. This box was equipped with a 1/2-inch-thick Lucite door (A) (letters in parenthesis refer to Figure 15), on which the specimens were supported by being clamped between Lucite washers in such a way that the test pieces did not make contact with the 18-8 stainless steel machine screws which passed through the washers. Twenty-four specimens could be exposed at one time. To prevent gradual heat warping of the Lucite door, the edges were bound with angle iron.

The Lucite door was opened and closed in a predetermined cycle by a small motor (B), which, in turn, was actuated by a timing device (C), operating through relay (D). The motor (B) was a special type which has two field coils, one of which "shades" the other, causing reversal.

To provide high humidity when the door was closed, water in a copper pan was warmed by an electric immersion heater. The pan measured 16 inches x 16 inches x 5 inches deep. The heater (electrical leads at F) was regulated by a thermostatic control (hidden by Plate G), and the heater could function only when the Lucite door was closed. As a safety measure, two thermostatic controls were connected in series. If one failed to break the circuit, the other would do so. A constant level device (E) was connected to the copper pan and maintained the water at a depth of approximately four inches. The electric fan operated when the door opened, cooling and drying the specimens. When the door was

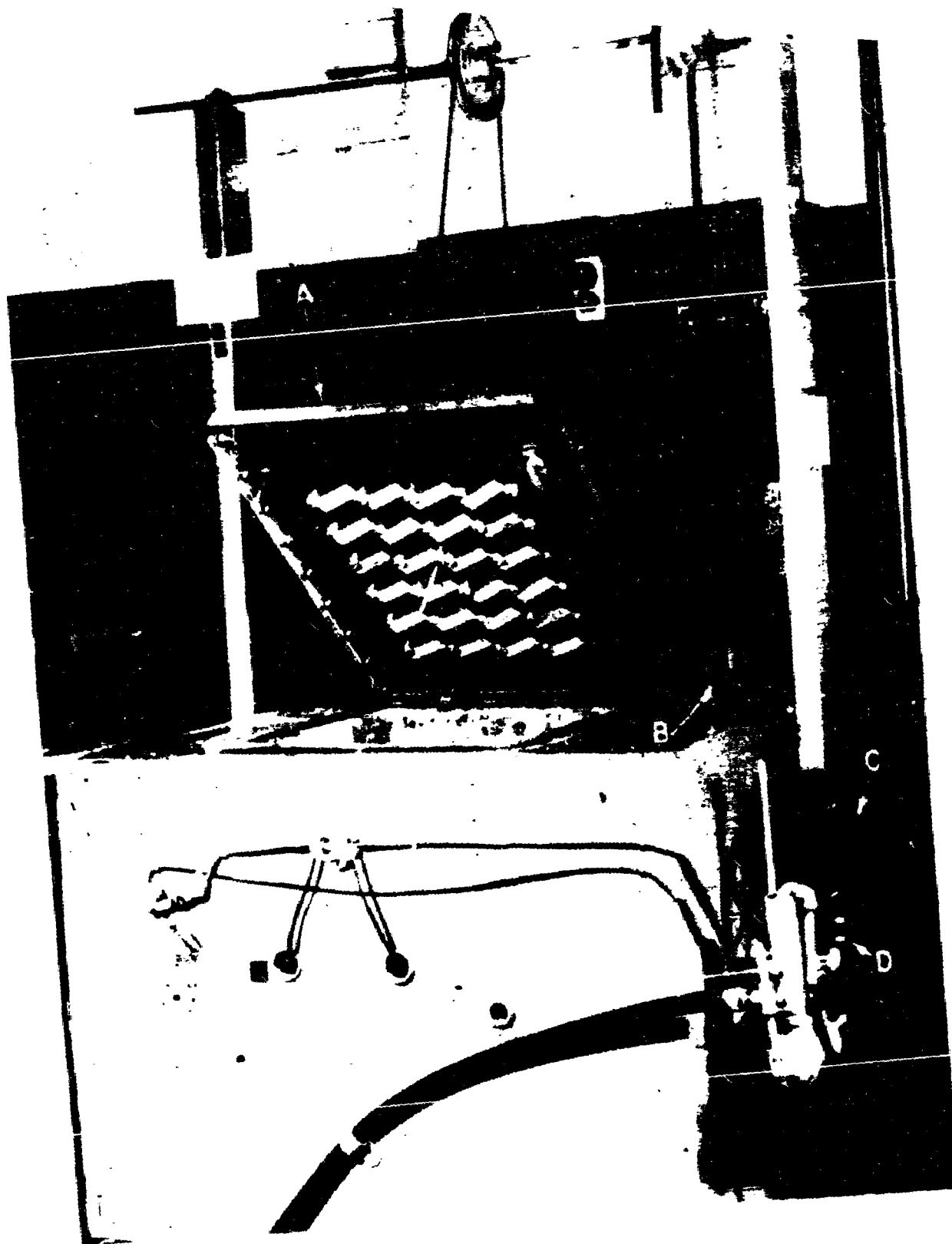


FIGURE 15. "WET-DRY" CABINET SHOWING DOOR OPEN AND CORRODING SPECIMENS IN PLACE

closed again, the fan stopped, and, in the humid atmosphere, moisture readily condensed on the chilled specimens. A schematic drawing of the electrical circuit is given in Figure 16.

The cabinet remained closed for eleven hours and open one hour. This constituted one cycle. There were two cycles per day. No correlation has been established between rate of corrosion in the cabinet, and rate of corrosion outdoors where dew occurs almost every night.

A minor change was made in the timing device after the photo in Figure 15 was made. Two timers connected in series and operating through a relay were substituted for the original timers. The latter could not handle the eleven-hour-closed - one-hour-open cycle. The two controls were necessary because the control tabs could not be set close enough to get the one-hour-open portion of the cycle.

Details of Electrical Circuit Components for "Wet-Dry" Cabinet

Motor - 110 volt ac Crise Electric Manufacturing Company, Columbus, Ohio.

Time Control - Two No. 303 controllers, Paragon Electric Company, Two Rivers, Wisconsin. The switches of these timers are connected in series. Both must be closed for current to pass through the circuit, but either one alone can break the circuit. Two controls were used because the tabs on the circular time-setting plate could not be set so close as to function for so small an interval as one hour.

Heater - Lo-Log, 2000-watt, 230-volt copper-clad immersion heater. American Instrument Company, Silver Spring, Maryland.

Relay - Double-pole, double-throw relay. Struthers-Dunn, Inc., Philadelphia, Pennsylvania. (Note: In Figure 16 the relay was not represented as being of the DPDT type for reasons of simplicity.)

Thermoregulators - Two, 110-volt, 10-amp thermostats connected in series. Fenwal, Inc., Ashland, Massachusetts.

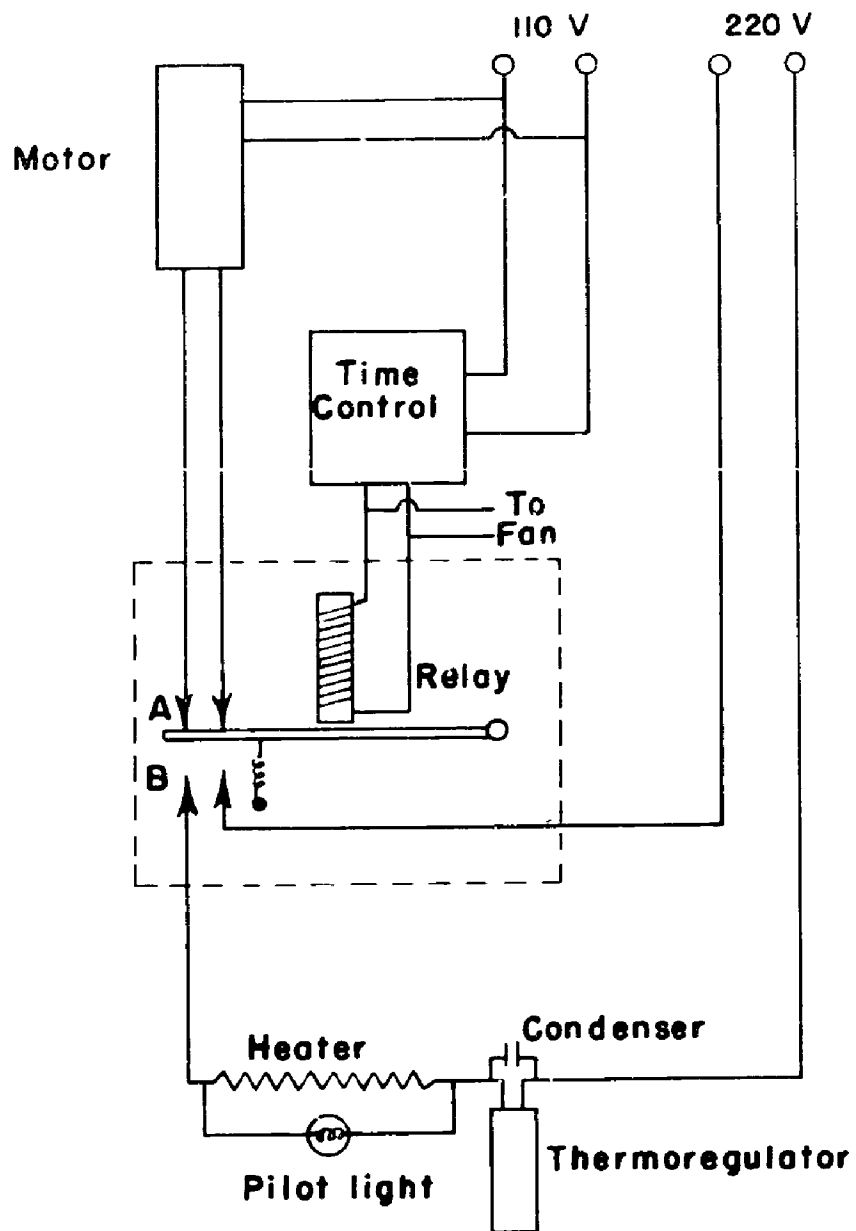


FIGURE 16. SCHEMATIC DIAGRAM OF ELECTRICAL
CIRCUIT FOR "WET-DRY" CABINET

A - 2578

APPENDIX I

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APPENDIX II

TABLE 14. CODEPOSITION OF MANGANESE AND ZINC FROM
SIMPLE SULFATE SOLUTIONS

Composition of Solution: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52 g/l

Test No.	pH	Temp. F	Current Density, amp/sq ft	Amount or Per Cent Manganese in Deposit ⁽¹⁾	Remarks
5561-46A	1.35	82	40	None	Light-gray deposit with crystalline edges
-46B	2.0	81	40	Less than 3%	Gray-black powdery deposit; pH changed to 2.8
-46C	5.9	82	40	Less than 3%	Black, rough deposit; pH changed to 3.7
-48A	1.4	82	60	Less than 3%	Crystalline edges; mat gray center
-48B	2.8	82	60	Less than 3%	Gray-black, treed deposit
-48C	6.1	82	60	Less than 3%	Black, treed deposit; pH changed to 3.2
-48D	1.3	81	100	Less than 3%	Crystalline edges; mat gray center
-48E	2.35	81	100	Less than 3%	Black, treed deposit
-50A	1.3	84	100	Less than 3%	Cathode agitated ⁽²⁾ ; crystalline edges, mat gray center
-50B	2.3	84	100	Less than 3%	Cathode agitated ⁽²⁾ ; black, treed deposit
-50C	1.45	116	40	Less than 1%	Mat gray deposit
-50D	2.8	116	40	Less than 1%	Mat gray deposit, but with trees
-50E	1.45	118	60	Less than 1%	Mat gray deposit with crystalline edges
-50F	2.4	116	60	Less than 1%	Mat gray, treed deposit
-52E	1.45	121	100	Less than 1%	Mat gray, treed deposit
-52F	2.5	118	100	Less than 1%	Mat gray, treed deposit
-52A	1.5	152	40	Less than 1%	Mat gray deposit; crystalline edges
-52B	2.4	150	40	Less than 1%	Mat gray deposit with dark edges
-52C	1.45	160	60	Less than 1%	Mat gray deposit; crystalline edges
-52D	2.7	160	60	Less than 1%	Mat gray, treed deposit
-54A	1.3	152	100	Less than 1%	Mat gray deposit; crystalline edges
-54B	2.4	152	100	Less than 1%	Mat gray, treed deposit
-54C	1.3	78	100	0.2%	Uniform, light-gray mat deposit; cathode efficiency 39.1%
-54D	1.3	78	100	0.2%	Uniform, light-gray mat deposit; cathode efficiency 40.7%
-54E	2.3	78	100	0.3%	Uniform, light-gray center, black edge; cathode efficiency 36.6%

(1) The amounts of manganese present were estimated by qualitative chemical tests.

(2) Work-rod agitation, 33 cycles/min, 1-1/4" stroke.

Note: Duration for all tests 10 minutes.

TABLE 15. CODEPOSITION OF MANGANESE AND ZINC FROM SULFATE SOLUTIONS CONTAINING EITHER SODIUM OR AMMONIUM ACETATE

Composition of Basic Solution: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ - 110.6 g/l (0.625 mole)
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ - 52 g/l (0.18 mole)

Test No.	Addition to Basic Solution	pH	Temp. F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Per Cent Manganese in Deposit	Remarks
5561-54G	NH_4Ac , 100 g/l	5.85	81	100	4.6	-	2.0	Dark-gray, porous plate having poor adhesion and treeing at edges
-58C	NH_4Ac , 200 g/l	5.85	80	100	3.8	31	0.2	Light-gray plate with treeing at edges
-60A	$\text{NaAc} \cdot 3\text{H}_2\text{O}$, 50 g/l	5.75	76	100	-	76.5	10.85	Black flaky deposit
-60B	$\text{NaAc} \cdot 3\text{H}_2\text{O}$, 100 g/l	6.05	76	100	-	49.4	19.7	Black flaky deposit
-60C	$\text{NaAc} \cdot 3\text{H}_2\text{O}$, 150 g/l	6.25	76	100	-	16.9	33.7	Black flaky deposit
-62D	$\text{NaAc} \cdot 3\text{H}_2\text{O}$, 150 g/l	6.25	78	100	-	12.5	35.7	Black flaky deposit
-60D	$\text{NaAc} \cdot 3\text{H}_2\text{O}$, 200 g/l	6.4	76	100	-	35.6	15.5	Black flaky deposit

Notes: Duration for all tests - 10 minutes.

Anodes - Carbon rods in Alundum cups.
 Cathodes - Stainless steel sheet - $1/2" \times 2"$ (immersed area).
 Where deposit was nonadherent, efficiency figures may be low.

TABLE 16. CODEPOSITION OF MANGANESE AND ZINC FROM SULFATE-ACETATE SOLUTIONS CONTAINING ADDITION AGENTS

Composition of Sol. in: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ - 110.6 g/l (0.625 mole)
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ - 52 g/l (0.18 mole)
 $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ - 150 g/l (1.1 mole)

Test No.	Addition Agent	pH	Temp, F	Time, min	Current Density, amp/sq ft	Cathode Efficiency, %	Per Cent Manganese in Deposit	Remarks
5561-62A	Hide Glue, 1 g/l	6.25	78	10	100	8.1	41.0	Gray and orange flaky deposit
-62B	$\text{Na}_2\text{S}_2\text{O}_3$, 0.05 g/l	6.3	78	10	100	13.8	33.2	Black flaky deposit
-62C	Hide Glue, 1 g/l	6.2	78	10	100	12.2	28.2	Black flaky deposit
-68B	None	6.3	76	40	6	104	0.7	Light-gray, slightly rough deposit; good adhesion
-68C	No. 431 Gelatin(1), 1 g/l	6.15	78	40	6	95.6	2.29	Smooth, dark gray to black deposit; good adhesion
-73A	None	6.25	80	15	20	93.5	0.55	Light-gray deposit; crystalline edges; good adhesion
-78B	No. 431 Gelatin(1), 1 g/l	6.2	80	15	25	103	14.1	Gray flaky deposit
-73C	RH-556(2), 1 g/l	6.2	80	15	20	72.5	1.9	Black powdery deposit
-78D	4-4' Diphenyl-Disulfonic Acid, 1 g/l	6.2	80	15	25	49.7	0.63	Light-gray, powdery deposit
-78E	Dextrose, 1 g/l	6.2	80	15	20	89	0.03	Light-gray deposit; crystalline edges; good adhesion
-80A	1-Amino-4-Nitro-Di-phenylamine-2 Sulfonic Acid, 1 g/l	6.1	80	15	25	86	11.5	Black powdery deposit
-80B	2, 4 Dimethyl-Sulfolane, 1 g/l	6.2	81	15	25	65.5	7.4	Black powdery deposit

(1) American Agricultural Chemical Company, Detroit, Michigan.

(2) E. I. duPont de Nemours and Company, Electroplating Division, Niagara Falls, New York.

Notes: Anodes - carbon rods in Alundum cups.

Cathodes - stainless steel sheets - 1/2" x 2" (immersed area).
 Where deposit was nonadherent, efficiency figures may be low.

TABLE 17. CODEPOSITION OF MANGANESE AND ZINC FROM
SULFATE-CITRATE SOLUTIONS

Test No.	pH	Temp, F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Per Cent Manganese in Deposit	Remarks
Bath Composition:							
			MnSO ₄ ·H ₂ O - 110.6 g/l				
			ZnSO ₄ ·7H ₂ O - 52 g/l				
			Na Citrate·2H ₂ O - 250 g/l				
6245-20D ⁽¹⁾	5.3	84	100	-	25.0	33.5	Light gray mat deposit, with bright edges; good adhesion
-20E	5.3	126	100	-	44.7	15.6	Light-gray mat deposit; fair adhesion
-20F	5.3	145	100	-	39.2	16.5	Medium-gray mat; poor adhesion
5531-90F	5.3	86	100	-	22.7	31.0	Blue-gray mat; good adhesion
Bath Composition:							
			MnSO ₄ ·H ₂ O - 110.6 g/l				
			ZnSO ₄ ·7H ₂ O - 52 g/l				
			Na Citrate·H ₂ O - 200 g/l				
6245-22D ⁽¹⁾	5.3	84	100	-	29.5	21.6	Gray to black deposit; no deposition on edges
-22E	5.3	125	100	-	45.8	16.7	Mat gray deposit
-22F	5.3	145	100	-	55.3	12.6	Mat gray deposit; coarsely crystalline
Bath Composition:							
			MnSO ₄ ·H ₂ O - 110.6 g/l				
			ZnSO ₄ ·7H ₂ O - 52 g/l				
			Na Citrate·2H ₂ O - 100 g/l				
6245-22A ⁽¹⁾	5.3	84	100	-	21.6	16.6	Dark, mat center; no deposit on edges
-22B	5.3	125	100	-	57.0	12.7	Mat gray; poor adhesion
-22C	5.3	145	100	-	48.0	5.1	Dark, mat center; no deposit on edges

TABLE 17. (Continued)

Test No.	pH	Temp, F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Per Cent Manganese in Deposit	Remarks
Bath Composition:							
			MnSO ₄ ·H ₂ O - 110.6 g/l				
			ZnSO ₄ ·7H ₂ O - 52 g/l				
			Na Citrate·2H ₂ O - 50 g/l				
6245-30A	5.3	80	25	4.0	90	14.3	Powdery, gray, black deposit
-32A	5.3	83	40	5.2	57.5	11.1	Burned edges, dark powdery center
-32E ⁽²⁾	5.3	82	40	5.2	19.4	40.5	Nonuniform, brown-gray deposit
-34C ^(1,2)	5.3	84	40	-	28.0	32.4	Flaky, brown-black deposit
Bath Composition:							
			MnSO ₄ ·H ₂ O - 110.6 g/l				
			ZnSO ₄ ·7H ₂ O - 52 g/l				
			Na Citrate·2H ₂ O - 250 g/l				
			Methyl Alcohol - 200 ml/l				
6245-26A	5.3	84	72	8.0	36.5	35.8	Nonuniform, dark to light deposit
-26E ⁽¹⁾	5.3	84	100	-	19.05	58.6	Nonuniform, dark to light deposit
-28B ⁽³⁾	5.3	84	100	-	21.8	48.5	Light to medium gray mat
Bath Composition:							
			MnSO ₄ ·H ₂ O - 110.6 g/l				
			ZnSO ₄ ·7H ₂ O - 52 g/l				
			K Citrate·H ₂ O - 250 g/l				
5561-90D	5.3	84	25	-	50.1	3.1	Smooth, blue-gray deposit
-90F	5.3	86	40	-	41.5	17.5	Smooth, blue-gray deposit
-90F	5.3	86	100	-	22.7	31.0	Smooth, blue-gray deposit
6245-9A	5.3	87	245	-	16.2	84.6	Light-gray, mat deposit; good adhesion

(1) Work-rod agitation, 33 cycles/min, 1-1/4" stroke.

(2) 2 g/l Hide Glue.

(3) Work-rod agitation, 86 cycles/min, 1-1/4" stroke.

Notes: Duration of all tests - 10 minutes.

Anodes - Carbon rods in porous Alundum cups.

Cathodes - Stainless steel sheet - 1/2" x 2" (immersion area). Cathode for 6245-9A was a round rod, 1/4" in diameter, with 1-1/2" immersed.

TABLE 1. PREPARATION OF MANGANESE-ZINC-ALLOY-COATED SPECIMENS FOR "WET-DRY" TEST AND FOR X-RAY DIFFRACTION TEST. SULFATE-CITRATE PLATING SOLUTION

Bath Composition: $MnSO_4 \cdot H_2O$ 110.6 g/l
 $ZnSO_4 \cdot 7H_2O$ 52.0 g/l
 $Na citrate \cdot 2H_2O$ 250.0 g/l

Test No.	Cathode Material	pH	Temp, F	Time, min	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, per cent	Manganese in Deposit, per cent	Thickness, one side, mil(1)	Weight of Deposit, grams	Remarks
8245-44A ⁽²⁾	Stainless ⁽²⁾	5.3	88	15	125	-	-	87.0	0.8	-	Light gray. Poor adherence in center.
8245-44C	SAE 4130 ⁽³⁾	5.3	88	15	125	-	-	-	0.8	-	Light gray on edges, dark center, good adherence. X-rayed. See Table 6.
9245-44D	SAE 4130	5.3	88	12	100	-	-	-	0.6	-	Same as -44 C. Exposed in "Wet-Dry". See Table 4.
-44E	Stainless	5.3	88	10	100	6.0	29.8	49.2	0.3	0.2060	Very light edges, light-gray center.
-46A	Stainless	5.3	88	11	75	5.0	21.0	60.5	0.3	0.1489	Very light edges, light-gray center.
-46B ⁽⁴⁾	Stainless	5.3	95	9	125	7.5	25.8	73.2	0.7	0.2462	Very light edges, light-gray center.
-46C	Stainless	5.3	89	6	150	9.0	-	-	0.3	-	Very light edges, light-gray center.
-46D	SAE 4130	5.3	88	10	100	6.0	-	-	0.4	-	Very light edges, light-gray center. X-rayed. See Table 6.
-46E	SAE 4130	5.3	92	10	100	6.0	-	-	0.4	-	Light-gray center, lighter edges. Exposed in "Wet-Dry". See Table 4.
-46F	Stainless	5.3	94	10	100	6.0	25.4	50.9	0.5	0.2225	Light-gray center, lighter edges.
-48A ⁽⁴⁾	Stainless	5.3	85	7	100	7.5	-	-	0.5	-	Light-gray center, lighter edges.
-48B	Stainless	5.3	82	7	100	9.0	-	-	0.4	-	Light-gray center, lighter edges.
-48C	Stainless	5.3	84	4	100	8.5	-	-	0.2	-	Light-gray center, lighter edges.
-48D	Stainless	5.3	83	5.5	100	8.5	23.4	86.6	0.3	0.1038	Gray center, metallic-gray edges. pH 5.5 at end of run.
-48E	Stainless	5.3	84	5.5	100	8.0	31.2	68.8	0.3	0.1472	Like -46F.
-18F	SAE 4130	5.3	84	5.5	100	9.0	-	-	0.25	-	Gray center, light-gray edges. X-rayed. See Table 6.
-56A ⁽⁴⁾	Stainless	5.3	89	5.5	100	6.2	25.8	46.2	0.3	0.1422	Gray center, light-gray edges.

TABLE 18. (Continued)

Test No.	Cathode Material	pH	Temp, F	Time, min	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, per cent	Manganese in Deposit, per cent	Thickness, mil(1)	Weight of Deposit, grams	Remarks
6245-56B	SAE 4130	5.3	80	5.5	100	6.6	-	-	0.3	-	Bright metallic edges. Gray-mat center. Exposed in "Wet-Dry". See Table 4.
-56C	SAE 4130	5.3	82	5.5	100	6.8	-	-	0.3	-	Same as -56B. Also exposed in "Wet-Dry". See Table 4.
-56D	Stainless	5.3	82	5.5	100	7.2	28.2	43.0	0.3	0.1432	Light edges, dark center.
-56E	Stainless	5.3	82	5.5	100	7.0	29.0	45.5	0.3	0.1537	Light edges, dark center.
-56F	SAE 4130	5.3	84	5.5	100	6.4	-	-	0.3	-	Light edges, dark center.
-56G	SAE 4130	5.3	84	5.5	100	6.4	-	-	0.3	-	Light edges, dark center. X-rayed. See Table 3.
-56H	Stainless	5.3	84	5.5	100	6.6	31.1	45.2	0.3	0.1648	Light edges, dark center.
-58A	SAE 4130	5.3	88	5.5	100	6.2	-	-	0.3	-	Light edges, dark center. Exposed in "Wet-Dry". See Table 4.
-58B	SAE 4130	5.3	88	5.5	100	6.0	-	-	0.25	-	Light edges, dark center. Exposed in "Wet-Dry". See Table 4.
-58C	Stainless	5.3	88	5.5	100	6.2	29.8	45.4	0.3	0.1578	Light edges, dark center.
6429-8A ⁽⁴⁾	Stainless	5.3	82	18.5	100	-	25.4	50	0.6	0.4098	Gray center, bright edges.
-8C	SAE 4130	5.3	82	25	100	6.0	-	-	1.6	-	Gray center, bright edges. Nickel plated over Mn-Zn and specimen examined metallographically.
-8D	Stainless	5.3	82	20	100	-	20.4	39.0	-	0.3688	Gray center, bright edges.
-12A ⁽⁴⁾	Stainless	5.3	82	15	100	-	33.2	53.5	-	0.4351	Gray center, bright edges.
-12B	SAE 4130	5.3	82	24	100	-	-	-	1.5	-	Gray center, bright edges. Nickel plated over Mn-Zn and specimen examined metallographically.

(1) Thickness measured with a micrometer mounted on a jig so that the panels could be measured at the same spot before and after plating.

(2) 18-8 stainless steel cathodes measuring 3 inches x 1-1/8-inches (immersed area).

(3) SAE 4130 steel cathodes measuring 3 inches x 1 inch (immersed area).

(4) Fresh bath.

Notes. Solution volume in all cases was one liter.

Anodes: Two carbon flats, 4 inches x 2 inches x 1/4-inch in rectangular porous Alundum cups, 3-1/2-inches x 2-1/2-inches x 3/4-inch.

Agitation: Work rod, 33 cycles per minute, 1-1/4-inch stroke.

TABLE 13. CODEPOSITION OF MANGANESE AND ZINC FROM A SULFATE-CITRATE SOLUTION; EFFECT OF AMMONIUM ION

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250.0 g/l
pH 5.3

Test No.	Addition	Cell Volts	Cathode Efficiency, %	Manganese In Deposit, %	Remarks
6425-7C	$(\text{NH}_4)_2\text{SO}_4$ 135 g/l	5.6	-	-	Dark gray, mat center; black, powdery, nodular edges; pH of cathode layer by drainage method 6-7
-70D	$(\text{NH}_4)_2\text{SO}_4$ 135 g/l	5.6	-	-	Dark gray, mat center; black, powdery, nodular edges; more nodules than 70C
-70E(1)	$(\text{NH}_4)_2\text{SO}_4$ 135 g/l	5.6	24.8	1.5	Same as 70C
-70F	$(\text{NH}_4)_2\text{SO}_4$ 135 g/l	5.6	12.6	0.47	Same as 70D
-72A(1)	$(\text{NH}_4)_2\text{SO}_4$ 50 g/l	5.2	25.2	9.5	One side was uniform gray mat, other side had nonuniform gray-black center with powdery edges; cathode layer pH 6-8
-72B	$(\text{NH}_4)_2\text{SO}_4$ 50 g/l	5.2	17.8	5.8	Nonuniform gray-black deposit; cathode layer pH 6-8

(1) No agitation.

Notes: Duration of all tests - 10 minutes.

Temperature - 79 F.

Current density - 1.00 amp/sq ft.

Anodes - Carbon sheets 4" x 2" x 1/4" in porous Alundum cups.

Anolyte - $(\text{NH}_4)_2\text{SO}_4$ (135 g/l).

Cathodes - Stainless 3" x 1-1/8" (immersed area).

Work rod - Agitation, 33 cycles/minute, 1-1/4" stroke.

TABLE 20. CODEPOSITION OF MANGANESE AND ZINC FROM SULFATE-CITRATE AND SULFATE-BOROCITRATE SOLUTIONS: TOTAL ANALYSIS OF DEPOSITS

No. 1 Bath Composition:		No. 2 Bath Composition:	
MnSO ₄ ·H ₂ O		MnSO ₄ ·H ₂ O	
110.6 g/l		110.6 g/l	
ZnSO ₄ ·7H ₂ O		ZnSO ₄ ·7H ₂ O	
52.0 g/l		52.0 g/l	
Na Citrate·2H ₂ O		Na Citrate·2H ₂ O	
250.0 g/l		250.0 g/l	
pH		H ₃ BO ₃	
5.3		pH	
		5.3	

Test No.	Bath No.	Addition Agent	Time, min	Cell Volts	Current Density, amp/sq ft	Cathode Efficiency, %	Manganese		Zinc		Percentage Error	Weight of Deposit, gram	Microappearance of Surface	Macroappearance of Surface
							in Deposit(1), %	in Deposit(1), %	in Deposit(1), %	in Deposit(1), %				
6606-38A(4) -38B(2)(4)	1	None	10	6.4	90	17.1	27.9	73.2	+1.1	0.171	-	Uniform, gray mat		
	1	None	30	7.2	90	-	-	-	-	-	-	Ditto		
-40A	1	None	20	-	100	36.2	40.6	59.5	+0.1	0.579	Microholes distributed uniformly over entire surface	Uniform, mat gray center; bright edges		
-40B(5)	1	None	20	5.8	100	30.8	35.0	68.1	+3.1	0.4972	Ditto	Ditto		
-48C	1	X(3) 10 g/l	20	5.8	100	15.9	54.2	47.0	+1.2	0.2476	-	Uniform, mat gray center; rough, dark-gray edges		
-38C	2	X(3) 10 g/l	60	-	30	4.4	45.0	62.7	+7.7	0.0628	-	Gray mat to lustrous center; brown edges		
-38D(2)	2	X(3) 10 g/l	60	4.6	30	-	-	-	-	-	-	Flaky nonadherent coating. Reserved for O ₂ analysis(6)		

Footnotes appear on the following page.

Footnotes for Table 20

- (1) In these experiments, both manganese and zinc were determined by analysis.
- (2) Plated on electropolished and passivated stainless steel panels, so that deposit could be stripped easily.
- (3) X is a proprietary material, still under development, whose composition has not been revealed.
- (4) Rubber used on cathode.
- (5) Solution heated to boiling prior to electrolysis.
- (6) 6606-38B, 0.14% O₂.
6606-38D, 0.11% O₂.

Notes: Work-rod agitation - 33 cycles/min, 1-1/4" stroke
Anodes - Carbon flats, 4" x 2" x 1/4", in porous Alundum cups
Analyte - Na₂SO₄, 142 g/l
Cathodes - Stainless steel, 3" x 1" (immersed area)

TABLE 21. CODEPOSITION OF MANGANESE AND ZINC FROM
RELATIVELY DILUTE SULFATE-CITRATE SOLUTIONS

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ - 55.3 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ - 26.0 g/l
 $\text{Na citrate} \cdot 2\text{H}_2\text{O}$ - 125.0 g/l

Test No.	pH	Temp, F	Current Density, amp/sq ft	Cathode Efficiency, per cent	Manganese in Deposit, per cent	Remarks
6245-38E(2)	5.3	86	40	34.6	16.3	Blue-gray, metallic appearance. Deposit adhered well.
-38A(1)(2)	5.3	86	100	46.6	33.2	Blue-gray, metallic appearance. Deposit adhered well.
-38D(2)	5.3	86	100	36.4	24.4	Blue-gray, metallic appearance. Deposit adhered well.
-38G(2)	5.3	86	210	30.8	57.4	Blue-gray center, powdery edges.

(1) Anolyte 50 g Na Citrate $\cdot 2\text{H}_2\text{O}$ in 250 ml H_2O .
 (2) Bath contained a small amount of precipitated salts which were white and crystalline.

Notes: Duration of all tests - 10 minutes.
 Anodes - Carbon rods in Alundum cups.
 Cathode - Stainless steel sheet - 2 inches x 1 1/2 inch (immersed area).

TABLE 22. CODEPOSITION OF MANGANESE AND ZINC FROM CITRATE SOLUTIONS; EFFECT OF ACTIVATED-CARBON TREATMENT AND DOUBLE DIAPHRAGM CELL

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 410.0 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250.0 g/l

Test No.	Cathode Material	pH	Temp. F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Remarks
6429-28A	SAE 4130	5.3	84	100	-	-	-	-	Front(1) of specimen had gray mat center; lighter edges Back(1) of specimen had light-gray mat center; darker edges
-28B	SAE 4130	5.3	89	100	-	-	-	-	See Table 5 for X-ray results
-28C	SAE 4130	5.3	94	100	-	-	-	-	Same as 28A; see Table 5 for X-ray results
-28D	Stainless	5.5	102	100	10.4	27.3	29	0.1358	Same as 28A; see Table 5 for X-ray results Same as 28A

(1) A single anode was used in the double diaphragm cell. The surface of the cathode which faced the anode is the "front", while the opposite surface is the "back". See section on "Experimental Work" for description of cell.

Notes: Duration of all tests - 5.5 minutes.
 Agitation - Work rod, 1-1/4" stroke, 33 cycles/minute.
 Anode - One carbon flat 4" x 2" x 1/2" in a rectangular porous aluminum cup.
 Cathodes - Stainless steel 3" x 1-1/8" (immersed area); SAE 4130 3" x 1" (immersed area).
 Anolyte - 500 ml $(\text{NH}_4)_2\text{SO}_4$ solution (135 g/l).
 Catholyte - 500 ml.

TABLE 23. CODEPOSITION OF MANGANESE AND ZINC FROM SULFATE-CITRATE SOLUTIONS; INFLUENCE OF ANODE TO CATHODE DISTANCE ON PLATE DISTRIBUTION(1)

Bath Composition: $MnSO_4 \cdot H_2O$ 110.6 g/l
 $ZnSO_4 \cdot 7H_2O$ 52.0 g/l
 Na Citrate $\cdot 2H_2O$ 250.0 g/l
 pH 5.3

Test No.	Anode to Cathode Distance, inches	Dimensions of Cathode, (depth x width) inches		Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, per cent	Manganese in Deposit, per cent	Weight of Deposit, gram	Microappearance of Deposit	Macroappearance of Deposit
605A-5A	4.5 on both sides	2 x 1		100	10.3	21.6	47.0	0.1100	Uniformly distributed microholes	Uniform gray mat center, edges and top lustrous
-58C	4.25 on side A	2 x 2-3/8		100	20	37.0	76.2	0.1230	Uniformly distributed microholes; less on side B than side A	Side A - uniform dark-gray mat
	4.75 on side B									Side B - uniform light-gray mat
-60B	9 (anodes on one side only)	1 x 2-3/8		28	15.0	45.0	24.4	0.0403	Nonuniform high and low areas	Uniform gray mat; edge effect at liquid-air interface
-60A(2)	9 (anodes on one side only)	2 x 2-3/8		100	35 → 30	35.1	51.4	0.2100	Uniformly distributed microholes	Ditto
	9 (anodes on one side only)	2-1/8 x 2-3/8		95	35 → 26	31.0	43.5	0.1932	Ditto	"
-66C	9 (anodes on one side only)	2 x 1/2		100	12	34.6	35.6	0.0165	"	"
-66D	6-1/4 (anodes on one side only)	2 x 1/2		100	9.0	34.0	27.8	0.0400	"	Gray to dark-gray mat center, lustrous edges
-66E	3-1/2 (anodes on one side only)	2 x 1/2		100	6.4	31.1	24.5	0.0425	"	Gray mat center, lustrous edges
									"	Uniform gray mat

Footnotes appear on the following page.

Footnotes for Table 23

- (1) See section on experimental work for description of cell.
- (2) Temperature increased during run from 80 F to 102 F.

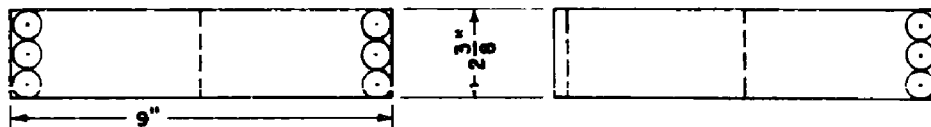
Notes: No agitation

Anodes - three or six carbon rods, each enclosed in a 3/4 inch diam porous Alundum cup

Anolyte - Na_2SO_4 142 g/l

Time - 10 minutes

Temperature - 80 F



Schematic top view of anode and cathode arrangements in the cell

TABLE 21. CODEPOSITION OF MANGANESE AND ZINC FROM SULFATE-CITRATE SOLUTIONS; EFFECT OF ANODE ARRANGEMENT

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250.0 g/l pH 5.3							
Test No.	Anode Arrangement	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Remarks
6429-32A (1)	Standard(3)	150	-	-	-	-	Edge effect
-82B(1,2)	Four flat carbon anodes arranged in a square	150	-	-	-	-	Uniform, powdery, black deposit
-82C	Standard(3)	150	-	-	-	-	Edge effect
-82D	One round carbon rod, 1/2" diam x 4" long on each side of cathode	150	-	-	-	-	Edge effect
-82E(1)	Two flat carbon anodes on each side of cathode	115	7.4	26.6	29.6	0.2295	Very marked edge effect
-82F(4)	Two flat carbon anodes on each side of cathode	115	7.1	24.1	32.1	0.2295	slight edge effect
-82G(6)	Two flat carbon anodes on each side of cathode	150	8.4	23.5	45.0	0.2791	Greater edge effect than 82E
							Very marked edge effect

Footnotes appear on the following page.

Footnotes appear on the following page.

Footnotes for Table 24

- (1) Work rod agitation - 33 cycles/minute, 1-1/4" stroke.
- (2) Solution diluted so that concentrations are halved.
- (3) One flat carbon anode on each side of the cathode; anodes measured 4" x 2" x 1/2", and were enclosed in porous Alundum cups.
- (4) SAE 4130 cathodes.

Notes: Duration of all tests - 10 minutes

Anolyte - $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (322 g/l).

Agitation - Work rod, 33 cycles/minute, 1-1/4" stroke.

Cathodes - Stainless 3" x 1-1/8"; SAE 4130 3" x 1" (Immersed area).

Robbers used on all tests.

TABLE 25. CODEPOSITION OF MANGANESE AND ZINC FROM SULFATE CITRATE SOLUTIONS; EFFECT OF ROBBER

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250.0 g/l
 pH 5.3

Test No.	Anode Arrangement, etc	Time, min	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Thickness of Deposit, One Side, mil	Weight of Deposit, gram	Remarks
6429-74B ⁽¹⁾	Standard	5.5	100	7.8	30.0	34.8	-	0.1329	Mat gray center; edge effect
-74C ⁽¹⁾	Standard with cathode at an angle to anodes	5.0	100	-	-	-	-	0.0819	Mat gray center; edge effect
-74D ⁽¹⁾	Standard; robber around cathode	5.0	100	-	-	-	-	0.2029	Uniform mat gray deposit; no edge effect
-78A ⁽¹⁾	Standard; robber around cathode	5.5	90	5.8	-	-	-	0.1181	Uniform mat gray deposit; no edge effect
-78B ⁽¹⁾	Standard; robber around cathode	5.5	90	5.8	25.6	25.6	0.15	0.1114	Uniform mat gray deposit; no edge effect
-78C ⁽¹⁾	Standard; robber around cathode	10.0	90	5.8	-	-	0.3	0.1963	Uniform mat gray deposit; no edge effect
-78D ^(1,2)	Standard; robber around cathode	5.5	90	-	26.9	25.6	-	0.1202	Uniform mat gray deposit; no edge effect
-78F ⁽³⁾	Standard; robber around cathode	10.0	90	6.0	27.4	23.3	0.3	0.2216	Mat gray deposit with slight edge effect
-78G ⁽³⁾	Standard; robber around cathode	5.0	90	6.0	23.6	21.8	0.15	-	Mat gray deposit with slight edge effect
-78I ^(2,3)	Standard; robber around cathode	10.0	90	6.8	24.9	23.4	-	0.2024	Uniform mat gray deposit

Footnotes appear on the following page.

(1) Anolyte - $(\text{NH}_4)_2\text{SO}_4$ (135 g/l).

(2) Stainless steel cathodes - 3" x 1-1/8" (immersed area).

(3) Anolyte - $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (322 g/l).

Notes: Bath temperature for all tests - 80 F.

Work rod agitation - 33 cycles/minute, 1-1/4" stroke.

Cathodes - Stainless 3" x 1-1/8"; SAE 4130 3" x 1" (immersed area).

TABLE 26. CODEPOSITION OF MANGANESE AND ZINC FROM A SULFATE-CITRATE SOLUTION, USING A "ROBBER" ON THE CATHODE

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l
 Citric Acid(1) 178.0 g/l
 pH 5.3

Test No.	Cathode Material	Cell Volts	Thickness One Side, mil	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Remarks
6C06-2A	Stainless	7.0	-	22.7	27.4	0.2040	Uniform, mat gray deposit
-2B	SAE 4130	6.4	0.3	-	-	0.1945	Uniform, mat gray deposit
-2C	SAE 4130	6.2	0.35	-	-	0.1940	Uniform, mat gray deposit
-2D	Stainless	6.4	-	23.3	26.4	0.2100	Uniform, mat gray deposit
-2E	SAE 4130	6.4	0.35	-	-	0.1897	Uniform, mat gray deposit
-2F	SAE 4130	6.4	0.35	-	-	0.1913	Uniform, mat gray deposit
-2G	Stainless	6.5	-	22.2	26.3	0.1995	Uniform, mat gray deposit
-2H	SAE 4130	6.9	0.3	-	-	0.1910	Mat gray bottom, semibright top
-2I	SAE 4130	6.6	0.35	-	-	0.1736	Uniform mat gray
-2J	SAE 4130	6.5	0.35	-	-	0.1600	Uniform mat gray
-2K	Stainless	6.2	-	14.8	30.3	0.1729	Uniform mat gray, but with slight edge effect

(1) No Na citrate - $2\text{H}_2\text{O}$ was available at the time of this experiment so an equivalent amount of citric acid was used. The pH was then raised, using NaOH .
 Notes: Agitation - Work rod, 33 cycles/minute, 1-1/4" stroke.
 pH - 5.3
 Temperature - 80 F.
 Current Density - 90 amp/sq ft.
 Time - 10 minutes.
 Anodes - Carbon flats 4" x 2" x 1/4" in rectangular porous Aluminum cups.
 Anolyte - Na_2SO_4 (anhyd.) (142 g/l).
 Cathodes - Stainless 3-1/8" x 1" (immersed area); SAE 4130 3" x 1" (immersed area).

TABLE 27. CODEPOSITION OF MANGANESE AND ZINC FROM SULFATE-CITRATE SOLUTIONS; EFFECT OF ACTIVATED-CARBON TREATMENT

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250 g/l
pH 5.3

Test No.	Cathode Material	Temp, F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese In Deposit, %	Thickness One Side, mil	Weight of Deposit, grams	Remarks
6249-30A ⁽¹⁾	Stainless	89	100	8.0	32	43	0.4	0.1559	Gray mat deposit with slight edge effect
-30B ⁽²⁾	Stainless	86	100	7.0	38.5	31.3	0.5	0.1917	Same as 6249-30A
-30C ⁽¹⁾	SAE 4130	86	100	6.4	-	-	0.3	-	Same as 6249-30A
-30D ⁽²⁾	SAE 4130	82	100	6.4	-	-	0.3	-	Gray mat deposit; less edge effect than 30A, 30B, and 30C
-30E ⁽²⁾	SAE 4130	89	100	6.8	-	-	0.3	-	Same as 6249-30D
-30F ⁽²⁾	SAE 4130	84	100	6.0	-	-	0.3	-	Gray mat deposit; less edge effect than 30D
-30G ⁽²⁾	Stainless	84	100	6.8	33.3	42.6	-	0.1560	Same as 30A
-30H ⁽²⁾	Stainless	84	100	6.8	37.5	27.8	-	0.1872	Same as 30A

(1) Not treated with activated carbon.

(2) Treated with activated carbon.

Notes: Duration of all tests - 5.5 minutes.

Agitation - Work rod, 1-1/4" stroke, 33 cycles per minute.

Anodes - Two carbon flats 4" x 2" x 1/4" in rectangular porous Alundum cups.

Cathodes - Stainless steel 3" x 1-1/8" (immersed area); SAE 4130 3" x 1" (immersed area).

Bath size - One liter.

TABLE 28 CODEPOSITION OF MANGANESE AND ZINC FROM A SULFATE-CITRATE SOLUTION;
EFFECT OF "AGING" THE SOLUTION

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250.0 g/l
pH 5.3

Test No.	Date and Time	Cathode Material	Treatment of Bath Prior to Electrolysis	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Thickness, One Side, mil	Weight of Deposit, gram	Appearance of Deposit(1)
6603-42A	1/30/52 11:30 a. m.	Stainless	None	6.8	23.5	1.2	0.35	0.1857	Uniform, gray mat center; bright gray edges
-42B	1/30/52 4:30 p. m.	SAE 4130	None	6.8	25.1	-	-	0.1971	Same as 42A but larger edge area
-42C	1/31/52 11:00 a. m.	Stainless	Solution boiled; precipitate redissolved	6.0	24.2	41.8	0.35	0.1910	Same as 42A but less edge area
-42D	1/31/52 4:00 p. m.	SAE 4130	None	7.0	35.5	-	0.5	0.2579	Uniform, gray mat center; edge area greater than 42A, less than 42B
-42E	2/1/52 3:00 p. m.	Stainless	Solution boiled; precipitate redissolved	-	31.0	26.1	0.4	0.2574	Same as 42A but less edge area
-42F	2/1/52 3:30 p. m.	SAE 4130	None	6.4	30.1	-	0.5	0.2377	Same as 42D
-50A	2/4/52 3:30 p. m.	SAE 4130	Solution boiled; precipitate redissolved.	6.8	31.2	-	0.5	0.2451	Same as 42B
-50B	2/7/52 10:00 a. m.	Stainless	Solution boiled; precipitate redissolved.	6.4	30.2	40.5	0.5	0.2385	Same as 42A

TABLE 28. (Continued)

Test No.	Date and Time	Cathode Material	Treatment of Bath Prior to Electrolysis	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Thickness, One Side, mil	Weight of Deposit, gram	Appearance of Deposit ⁽¹⁾
6606-50C	2/7/52 1:00 p.m.	SAE 4130	None	6.6	28.4	-	0.65	0.2232	Same as 42A
-50D	2/8/52 4:00 p.m.	SAE 4130	Solution boiled; precipitate redissolved	7.2	36.9	56.0	0.65	0.2892	Same as 42D

(1) The appearance of the deposits given in this column refers to "macro" appearance. When viewed under a low-power microscope, all the deposits showed very small holes uniformly distributed over the plate.

Notes: Work-rod agitation - 33 cycles/min, 1-1/4" stroke
 Temperature - 80 F
 Time - 10 minutes
 Current density - 100 amp/sq ft

Anodes - Carbon flats, 4" x 2" x 1/4", in porous Aluminum cups
 Cathodes - 3" x 1" (immersed area)
 Same bath used for all tests

TABLE 29. (Continued)

Test No.	Appearance of Hull Cell Cathodes	Addition Agent or Treatment	Cell Current, amps	Descriptive Code for Appearance of Hull Cell Cathodes																		
66C6-35C	<table><tr><td>G</td><td>M</td><td>D</td><td></td><td>L</td><td></td><td>B</td><td></td><td>G</td></tr><tr><td></td><td>G</td><td>G</td><td></td><td>G</td><td></td><td></td><td></td><td></td></tr></table>	G	M	D		L		B		G		G	G		G					X ⁽³⁾ 10 g/l H ₂ O ₂ treatment ⁽²⁾	3	See p AII-23 for descriptive code
G	M	D		L		B		G														
	G	G		G																		
-37A	<table><tr><td>G</td><td>M</td><td>LB</td><td>Lb</td><td>G</td><td>nd</td><td>B</td><td>D</td><td>G</td></tr><tr><td></td><td>G</td><td>G</td><td>G</td><td>G</td><td></td><td>G</td><td>G</td><td></td></tr></table>	G	M	LB	Lb	G	nd	B	D	G		G	G	G	G		G	G		X ⁽³⁾ 10 g/l H ₂ O ₂ treatment ⁽²⁾	3	
G	M	LB	Lb	G	nd	B	D	G														
	G	G	G	G		G	G															
-37B	<table><tr><td></td><td>M</td><td>L</td><td>B</td><td>G</td><td>G</td><td>B</td><td>D</td><td>G</td></tr><tr><td></td><td>G</td><td>G</td><td>G</td><td></td><td></td><td></td><td></td><td></td></tr></table>		M	L	B	G	G	B	D	G		G	G	G						X ⁽³⁾ 10 g/l Solution first heated to boiling	3	
	M	L	B	G	G	B	D	G														
	G	G	G																			
-37C	<table><tr><td></td><td>D</td><td>M</td><td>b</td><td>B</td><td>D</td><td></td><td></td><td></td></tr><tr><td></td><td>G</td><td>G</td><td>G</td><td>G</td><td>G</td><td></td><td></td><td></td></tr></table>		D	M	b	B	D					G	G	G	G	G				No addition agent Solution first heated to boiling	3	
	D	M	b	B	D																	
	G	G	G	G	G																	

(1) The Hull Cell used in this work was purchased from the R. O. Hull and Company, Incorporated, Rocky River 16, Ohio.

(2) The treatment consisted of adding 4 ml/1 H₂O₂ (30%) and boiling.

(3) X is a proprietary compound still under development. Its composition has not been disclosed.

TABLE 30. CODEPOSITION OF MANGANESE AND ZINC ON VARIOUS SURFACES FROM A SULFATE-CITRATE SOLUTION FOLLOWING TREATMENT WITH ACTIVATED CARBON

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250.0 g/l
pH 5.3

Test No.	Cathode Material	Surface Treatment of Cathode	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Thickness One Side, mil	Weight of Deposit, gram	Remarks
6429-40A	Stainless	None	100	-	25.2	21.6	-	0.1275	Mat gray center; lighter edges
-40B(1)	SAE 1010	Cyanide Zn 0.05 mil	100	7.2	-	-	0.3	-	Uniform mat gray center; slight edge effect
-40D(2)	SAE 1010	Cyanide Zn 0.04 mil	100	7.2	-	-	0.3	-	Nonuniform, gray-black center; more edge effect than 40B
-40F(1,3)	SAE 1010	Cyanide Zn 0.04 mil	100	7.2	-	-	0.3	-	Nonuniform, gray-black center; very slight edge effect
-42A(4)	SAE 1010	Cyanide Cu 0.035 mil	100	7.2	-	-	0.3	-	Uniform, gray mat deposit; less edge effect than 40F
-42C(4)	SAE 1010	Cyanide Cu 0.035 mil	100	7.2	-	-	0.3	-	Uniform, gray mat deposit; slight black edge effect
-42E(5)	SAE 1010	Cyanide Cu 0.035 mil	100	7.2	-	-	0.3	-	Nonuniform, gray-black deposit; no edge effect
-42G	Stainless	None	100	-	23.8	31.0	-	0.1184	Nonuniform, gray black deposit
-52A(6)	Stainless	None	100	-	29.8	41.0	-	0.1430	Mat gray center; lighter edges
-52B	SAE 4130	Electropolished	100	5.8	-	-	0.3	-	Nonuniform gray mat center; slight edge effect
-52C	SAE 4130	Electropolished	100	5.8	-	-	0.3	-	Nonuniform gray mat center; black spots along edge

Footnotes appear on the following page.

Footnotes for Table 30

- (1) The zinc deposit was rinsed and dried after zinc plating. Immediately before immersion in the manganese-zinc solution the zinc-plated specimens were wetted with distilled water, and placed in bath with current on.
- (2) The zinc-coated panel was rinsed and placed immediately in the manganese-zinc solution.
- (3) Zinc deposit was not uniform.
- (4) Same as Procedure (1), except panels were copper plated.
- (5) Copper deposit dried after plating, dipped in 20% H_2SO_4 solution (80 F) for 20 seconds, rinsed, and placed in manganese-zinc solution with current on.
- (6) Fresh bath.

Notes: All panels agitated by work rod, 33 cycles/minute, 1-1/4" stroke.

Anodes - Two carbon flats 4" x 2" x 1/4" in rectangular porous Alundum cups.

Cathodes - Stainless steel 1-1/8" x 3" (immersed area); SAE 4130 1" x 3" (immersed area).

Solution temperature for all tests was 80 F.

TABLE 31. CODEPOSITION OF MANGANESE AND ZINC ON VARIOUS SURFACES FROM A SULFATE-CITRATE SOLUTION

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250 g/l
pH 5.3

Test No.	Cathode Material	Surface Treatment of Cathode	Temp, F	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Thickness One Side, mil	Weight of Deposit, gram	Remarks
-56A	Stainless	None	89	7.0	40.9	38.4	-	0.1812	Gray, mat center; slight edge effect
-56C(1)	SAE 1010	Cyanide Zn 0.04 mil	83	-	-	-	-	-	Gray, mat center; slight edge effect
-56D(1)	SAE 1010	Cyanide Zn 0.04 mil	83	-	-	-	-	-	Gray, mat center; slight edge effect
-56E(1)	SAE 1010	Cyanide Zn 0.04 mil	83	-	-	-	-	-	Gray, mat center; slight edge effect
-56G	SAE 4130	Electropolished	80	-	-	-	-	-	Nonuniform gray mat with black areas
-58A(2)	SAE 4130	Electropolished	80	-	-	-	0.3	-	Nonuniform gray mat with black areas
-58B(2)	SAE 4130	Electropolished	80	-	-	-	0.3	-	Nonuniform gray mat with black areas
-58D	SAE 1010	Cyanide Cu 0.035 mil	80	-	-	-	-	-	Nonuniform gray mat with black areas
-58E	SAE 1010	Cyanide Cu 0.035 mil	80	-	-	-	0.3	-	Nonuniform gray mat with black areas
-58F	SAE 1010	Cyanide Cu 0.035 mil	80	-	-	-	-	-	Nonuniform gray mat with black areas
-58G	Stainless	None	80	6.2	30.7	20.7	-	0.1401	Nonuniform gray mat with black areas

Footnotes appear on the following page.

Footnotes for Table 31

- (1) After plating these panels with zinc, the deposit was dried. Before plating with Mn-Zn the zinc surface was wetted with distilled water. The panel was immersed in Mn-Zn bath with current on.
- (2) Dipped in dilute H_2SO_4 , rinsed, and into the Mn-Zn bath with current on.
- (3) Same procedure as for zinc-coated panels.

Notes: Work rod agitation - 33 cycles/minute, 1-1/4" stroke.

Time for all tests - 5.5 minutes.

Current density for all tests - 100 amp/sq ft.

Anodes - Carbon sheets 4" x 2" x 1/4" in porous Alundum cups.

Anolyte - $(NH_4)_2SO_4$ (135 g/l).

Cathodes - Stainless 3" x 1-1/8"; SAE 4130 3" x 1" (immersed area).

TABLE 32. CODEPOSITION OF MANGANESE AND ZINC FROM SULFATE-CITRATE SOLUTIONS; EFFECT OF DILUTION ON CATHODE EFFICIENCY

Test No.	Time, min	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Remarks
Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l Na Citrate $\cdot 2\text{H}_2\text{O}$ 250.0 g/l Hide glue 2.0 g/l pH 5.3							
6429-32A (1)	10	40	4.6	3.7	53.0	0.0129	Lustrous, lightly milky center; black edges
-32B	10	40	4.6	2.55	78.0	0.0086	Lustrous, lightly milky center; black edges
Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 55.3 g/l $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 26.0 g/l Na Citrate $\cdot 2\text{H}_2\text{O}$ 125.0 g/l Hide glue 2.0 g/l pH 5.3							
6429-32C (1)	10	40	5.0	-	-	-	Lustrous center; black edges
-32D (1,2)	34	40	4.0	3.4	46.5	0.0365	Blue-gray center, surrounded by a lustrous area

(1) Work rod agitation - 33 cycles/minute, 1-1/4" stroke.

(2) SAE 4130 Cathode.

Notes: Both baths treated with activated carbon.

Anodes - Carbon sheets 4" x 2" x 1/8" in porous Alundum cups.

Cathodes - Stainless 3" x 1-1/8"; SAE 4130 3" x 1" (immersed area).

Anolyte - $(\text{NH}_4)_2\text{SO}_4$ (135 g/l).

Hide: Glue - One month old.

TABLE 33. CODEPOSITION OF MANGANESE AND ZINC FROM A SULFATE-CITRATE SOLUTION CONTAINING HIDE GLUE

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 55.3 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 26.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 125.0 g/l
 Hide glue 2 g/l
 pH 5.3

Test No.	Time, min	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Remarks
6429-94A (1,4)	20	50	5.6	16.0	12.4	0.1468	Uniform, lustrous center; black edges
-94B (1,4)	10	75	6.6	-	-	-	Nonuniform, black powdery deposit
-94C (1)	10	60	-	15.1	20.2	0.0835	Uniform, lustrous center; broad black edges
-94D (1)	10	40	5.0	19.7	7.0	0.0748	Uniform, lustrous center; narrow black edge
-94E (1,6)	40	40	-	19.0	11.8	0.2530	Uniform, lustrous center; narrow black edge; thickness 0.4 mil (one side)
-94F (1,4,6)	40	40	-	16.8	10.3	0.2252	Uniform lustrous center; narrow black edge; thickness 0.3 mil (one side)
-94G (1,5)	10	40-50	4.8	-	18.2	0.0999	Uniform lustrous center; narrow black edge;
-94H (1,3)	10	40	-	23.6	17.9	0.0860	Uniform lustrous center; narrow black edge;
-94I (2,3,5)	10	40	-	< 1.0	-	-	Black, streaked center; brown, powdery edges
-94J (2,3,5)	10	40	5.2	5.3	35.6	0.0191	Black, streaked center; brown, powdery edges

Footnotes appear on the following page.

Footnotes for Table 33

- (1) Two-month-old hide glue.
- (2) Two-day-old hide glue.
- (3) Bath treated with activated carbon.
- (4) Robber used.
- (5) Bath worked for 20 minutes before test.
- (6) SAE 4130 panels.

Notes: Temperature for all tests - 80 F.

Work rod agitation - 33 cycles/minute, 1-1/4" stroke.

Anodes - Carbon sheets 4" x 2" x 1/4" in Alundum cups.

Cathodes - Stainless 3" x 1-1/8"; SAE 4130 3" x 1" (immersed area).

TABLE 34. CODEPOSITION OF MANGANESE AND ZINC FROM RELATIVELY DILUTE SULFATE-CITRATE SOLUTIONS CONTAINING ADDITION AGENTS

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 55.3 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 26.0 g/l
 $\text{Na citrate} \cdot 2\text{H}_2\text{O}$ 125.0 g/l

Test No.	Addition Agent	pH	Temp, F	Current Density, amp/sq ft	Cathode Efficiency, per cent	Manganese in Deposit, per cent	Remarks
6245-40B ⁽¹⁾	Hide Glue	5.3	85	40	19.3	67.5	Metallic center, dark edges.
-40A ⁽¹⁾	Hide Glue	5.3	85	100	-	-	Gray powdery center, black edges.
-40H ⁽¹⁾	Glycerol	5.3	85	40	31.3	23.8	Mat gray center, light-gray edges.
-40D ⁽¹⁾	Glycerol	5.3	85	100	-	-	Uniform light-gray, powdery deposit.
-40F ⁽¹⁾	Glycol	5.3	85	40	-	-	Nonuniform mat-gray deposit.
-40G ⁽¹⁾	Glycol	5.3	85	100	-	-	Powdery, gray deposit.

(1) White, crystalline precipitate formed in bath after two days.

Notes: Duration of all tests - 10 minutes.

Anodes - Carbon rods in Alundum cups.

Cathodes - Stainless steel sheets - 2 inches x 1/2-inch (immersed area).

TABLE 35. CODEPOSITION OF MANGANESE AND ZINC FROM SULFATE-CITRATE SOLUTION: EFFECT OF WETTING AGENTS

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250.0 g/l
pH 5.3

Test No.	Addition Agent	Surface Tension, dynes/cm	Cell Voltage	Cathode Efficiency, %	Manganese in Deposit, %	Thickness of Deposit, mil	Weight of Deposit, gram	Microappearance of Deposit	Macroappearance of Deposit
6506-46B	None	78	7.5	21.2	43.1	0.4	0.1692	Uniform distribution of microholes	Gray mat center; brighter edges
-46C	Alroso ⁽¹⁾	22	9.5	24.2	42.1	0.3	0.1936	Ditto	Gray to black, nonuniform center; black edges
-46D	Duponol ⁽²⁾ ME dry	46	7.0	12.7	76.8	0.4	0.0951	Ditto	Ditto

(1) Alroso Chemical Company, Providence, Rhode Island.

(2) E. I. du Pont de Nemours and Company, Wilmington, Delaware.

Notes: Work-rod agitation - 33 cycles/min, 1-1/4" stroke

Temperature - 80 F

Time - 10 minutes

Current density - 100 amp/sq ft

Anodes - Carbon flats, 4" x 2" x 1/4", in porous Aluminum cups

Anolyte - Na_2SO_4 , 142 g/l

Cathodes - Stainless, 3" x 1"

TABLE 36. CODEPOSITION OF MANGANESE AND ZINC FROM SULFATE-CITRATE SOLUTIONS;
STUDIES WITH STILL AND ROTATING CYLINDRICAL CATHODES

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250.0 g/l pH 5.3											
Test No.	Agitation	Time, min	Cell Volts	Cathode Efficiency, %	Manganese in Deposit(1), %	Zinc in Deposit(1), %	Percentage Error	Thickness of Deposit, mil	Weight of Deposit, gram	Microappearance of Deposit	Macroappearance of Deposit
6506-43A	None	10	4.4	24.8	32.2	70.5	+2.7	0.5	0.0787	Microholes distributed uniformly over surface	Uniform, gray mat
-43B	None	20	4.3	27.1	25.7	76.1	+2.1	1.4	0.1739	Ditto	Upper portion, gray mat; lower portion, rough gray
-43C	None	30	5.0	30.5	26.6	75.1	+2.0	2.2	0.2922	"	Uniform, gray mat
-43D	50 rpm	10	4.4	28.4	33.1	68.0	+1.1	0.6	0.0900	"	Ditto
-43E	50 rpm	20	4.6	31.6	24.4	82.2	+6.6	1.4	0.2036	"	"
-43F	50 rpm	30	4.6	34.5	22.5	77.3	-0.2	2.2	0.3309	"	"

(1) Both manganese and zinc determined by analysis.

Notes: Anodes - Carbon flats, 4" x 2" x 1/4", in porous Alundum cups

Anolyte - Na_2SO_4 , 142 g/l

Cathodes - Round stainless steel rods, 1/4" diameter x 3" long (immersed area); lower end of rod "stopped off" with closed rubber tube

Current density - 100 amp/sq ft

TABLE 37. CODEPOSITION OF MANGANESE AND ZINC FROM SULFATE-CITRATE SOLUTIONS;
DEVELOPMENT OF MICROHOLES WITH TIME

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.0 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250.0 g/l
pH 5.3

Test No.	Bath No. (1)	Time, min	Cell Volts (1)	Microappearance of Deposit	Macroappearance of Deposit
9006-91A	1	1	--	No microholes visible at 40X	Slightly heavier deposit in center, deposit just dulls the buffed base metal.
91B	2	2	--	Microholes just visible in center of panel	Same as 91A, except center now has gray mat appearance
91C	1	3	13.0	Microholes now visible over entire panel	Ditto
91D	2	4	7.8	Ditto	"
91E	1	5	10.0	"	Gray mat center, lustrous edges
91F	2	6	8.0	"	Ditto
91G	1	7	9.4	"	"
91H	2	10	8.0	"	"

(1) Two baths of exactly the same composition were used. The differences in voltages are due to different IR drops through the Alundum cups.

Notes: Work-rod agitation - 33 cycles/min, 1-1/4" stroke

Anodes - carbon flats 4" x 2" x 1/4" in porous Alundum cups

Anolyte - Na_2SO_4 142 g/l

Cathodes - SAE 4130 steel 3" x 1-1/16", polished with 320-grit belt and buffed

Current density - 100 amp/sq ft

Temperature - 80 F

TABLE 38 CODEPOSITION OF MANGANESE AND ZINC
FROM CITRATE SOLUTIONS

Bath Composition⁽¹⁾: Citric acid (monohydrate) - 212 g/l
Electrolytic manganese - 17.7 g/l
Mossy zinc - 3.9 g/l

Test No.	pH	Temp, F	Current Density, amp/sq ft	Cathode Efficiency, %	Per Cent Manganese in Deposit	Remarks
-25A	5.3	84	40	-	-	No deposit
-25B	5.3	84	100	1.04	64	No deposit in center; black deposit on edges
-25C	5.3	84	150	1.04	67.5	Dark gray mat deposit
-25D	5.3	84	215	1.03	57.5	Black mat deposit; slightly powdery

(1) The solution was prepared by dissolving electrolytic manganese in one portion of citric acid, and dissolving the zinc in a second portion of citric acid. The two solutions were then combined, and the pH and volume adjusted.

Notes: Duration of all tests - 10 minutes.

Anodes - Carbon rods in Alundum cups.

Cathodes - Stainless steel sheet - 1/2" x 2" (immersed area).

TABLE 39. CODEPOSITION OF MANGANESE AND ZINC FROM A SULFATE-CITRATE SOLUTION;
EFFECT OF SUPERIMPOSED ALTERNATING CURRENT

Bath Composition: $MnSO_4 \cdot H_2O$ 110.6 g/l
 $ZnSO_4 \cdot 7H_2O$ 52.0 g/l
 Citric Acid 176.0 g/l
 pH 5.3

Test No.	Direct-Current			DC Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Remarks
	Density, amp/sq ft	AC, amperes	DC, amperes					
-0300-05	100	4.0	4.6	0.87	24.5	48.5	0.2117	Nonuniform gray to dark-gray center; edge effect
-06C	100	20.0	4.6	4.35	25.2	44.5	0.2165	Nonuniform gray to dark-gray center; edge effect
-06A	100	40.0	4.6	8.7	31.8	87.0	0.2616	Semibright center; slight edge effect
-06D	100	None	4.6	-	25.6	42.0	0.2215	Nonuniform gray to dark-gray center; edge effect
-06E	50	20.0	2.3	8.7	17.5	38.5	0.1502	Nonuniform gray to dark-gray center; but less edge effect
-06F	75	30.0	3.45	8.7	21.6	48.0	0.1870	Nonuniform gray to dark-gray center; edge effect
-06G	100	40.0	4.6	8.7	27.6	47.8	0.2380	Nonuniform gray to dark-gray center; edge effect
-06H(1)	70	40.0	4.6	8.7	29.4	24.6	0.2610	Nonuniform gray to dark-gray center; edge effect
-06I	115	40.0	5.3	7.5	27.5	38.0	0.2369	Nonuniform gray to dark-gray center; edge effect
-06J	100	52.0	4.6	11.3	23.4	67.0	0.1950	Semibright center; slight edge effect

TABLE 39. (Continued)

Test No.	Direct-Current Density, amp/sq ft	AC, amperes	DC, amperes	Ratio, ac amp/dc amp	DC Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Remarks
6606-6K	75	40.0	3.45	11.5	-	21.8	39.7	0.1865	Nonuniform gray to dark-gray center; edge effect
-6L(1)	70	50.0	4.6	10.9	7.8	22.5	36.5	0.1945	Nonuniform gray to dark-gray center; edge effect
-6M(2,3)	100	20.0	4.2	4.75	-	-	51.8	0.3370	Nonuniform gray to dark-gray center; edge effect
-9A(3)	100	4.0	4.2	0.95	7.5	29.0	68.0	0.2400	Blue-gray center, surrounded by semi-bright area; edge effect
-9B(1,3)	70	4.0	4.2	0.95	7.2	21.8	41.5	0.1875	Nearly uniform, mat gray deposit; slight edge effect

(1) Robber was used for these tests.

(2) Time unknown.

(3) SAE 4130 cathodes 3" x 1" (immersed area).

Notes: Duration of all tests - 10 minutes.

Agitation - Work rod, 33 cycles/minute, 1-1/4" stroke.

Anodes - Carbon sheets 4" x 2" x 1/4" in rectangular porous Alundum cups.

Cathodes - Stainless steel 3" x 1-1/8" (immersed area).

Temperature - 80 F.

TABLE 40. CODEPOSITION OF MANGANESE AND ZINC FROM A SULFATE-CITRATE SOLUTION: PREPARATION OF 75% MANGANESE ALLOY PLATES FOR WET-DRY TEST BY USE OF SUPERIMPOSED ALTERNATING CURRENT

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250.0 g/l
pH 5.3

Test No.	Cathode Material	Temp, F	Time, min	Alternating Current, amperes	Direct Current, amperes	Ratio, A-C amp/ D-C amp	D-C Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Thickness of One Side, mil	Weight of Deposit, gram	Remarks
660E-10A	Stainless	80	10	52.0	4.6	11.3	6.5	27.6	53.0	-	0.2380	Gray mat center; lighter edges
-10B	Stainless	87	10	52.0	4.6	11.3	6.9	28.0	45.0	-	0.2420	Ditto
-10C	SAE 4130	83	10	48.0	4.2	11.4	7.5	31.0	73.0	0.4	0.2335	Light gray, mat center; lighter edges
-10D	SAE 4130	83	10	48.0	4.2	11.4	7.5	31.4	71.5	0.4	0.2370	Ditto
-10E	SAE 4130	83	8	48.0	4.2	11.4	7.5	-	-	0.3	0.1905	Used for "wet-dry" test; see Table 4
-10F	SAE 4130	80	8	48.0	4.2	11.4	7.5	-	-	0.3	0.1902	Ditto
-10G	SAE 4130	80	8	48.0	4.2	11.4	-	-	-	0.3	0.1890	"
-10H	SAE 4130	80	8	48.0	4.2	11.4	7.0	29.8	79.0	-	0.1800	Light-gray, mat center; lighter edges

Notes: Work-rod agitation - 33 cycles/min, 1-1/4" stroke
Cathodes - Stainless steel, 1-1/8" x 3" (immersed area)
SAE 4130, 1" x 3" (immersed area)
Anodes - Carbon flaps, 4" x 2" x 1/4", in porous Aluminum cups
Anolyte - Na_2SO_3 , 142 g/l

TABLE 41. CODEPOSITION OF MANGANESE AND SULFATE-BOROCITRATE SOLUTIONS;

No. 1 Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250.0 g/l
pH 5.3

Test No.	Bath No.	Addition Agent	Time, min	Temp, F	Agitation	Current Density, amp/sq ft	Volts	Cathode Efficiency, %
6606-63A ⁽²⁾	1	None	10	52	None	50	5.0	27.0
6606-97A ⁽³⁾	1	Gelatin 1 g/l	10	80	33 - 1-1/4 ⁽¹⁾	100	--	7.8
-97B ⁽³⁾	1	Urea 2 g/l	10	80	33 - 1-1/4	100	--	32.0
6022-5A ⁽⁴⁾	1	None	10	80	33 - 1-1/4	100	7.5	--
-5B ⁽⁴⁾	1	None	10	80	33 - 1-1/4	100	7.2	--
-5C ⁽⁵⁾	1	None	10	80	33 - 1-1/4	100	7.0	--
-5D ⁽⁵⁾	1	None	10	80	33 - 1-1/4	100	7.4	--
6606-24C ⁽⁶⁾	2	X ⁽⁷⁾ 10 g/l	60	80	None	20	4.2	11.2
-24D ⁽⁶⁾	2	X ⁽⁷⁾ 10 g/l	60	80	None	20	--	26.7

(1) Work-rod agitation 33 cycles/min, 1-1/4" stroke.

(2) Anodes - carbon rods in Alundum cups.
Cathodes - stainless steel 1" x 1/2" (immersed area).
Anolyte - Na_2SO_4 142 g/l.
Bath became mushy at 60 F and crystalline below 50 F.

(3) Anodes - round carbon rods in porous Alundum cups.
Anolyte - Na_2SO_4 142 g/l.
Cathodes - stainless steel 3" x 1-1/16" (plated area).
Keystone Gelatin No. 431 was used for 6606-97A.

(4) One alloy anode (99% lead, 1% silver) used; enclosed in porous Alundum cup.
Anolyte - Na_2SO_4 142 g/l.
Cathodes - SAE 4130 steel 3" x 1" (plated area).

ZINC FROM SULFATE-CITRATE SOLUTIONS AND
MISCELLANEOUS EXPERIMENTS

No. 2 Bath Composition:	MnSO ₄ ·H ₂ O	110.6 g/l
	ZnSO ₄ ·7H ₂ O	52.0 g/l
	Na Citrate·2H ₂ O	250.0 g/l
	H ₃ BO ₃	99.0 g/l
	pH	5.3

Manganese in Deposit, %	Weight of Deposit, gram	Microappearance of Deposit	Macroappearance of Deposit
31.2	0.0369	Uniformly distributed microholes	Nonuniform gray to dark-gray mat
83.5	0.0639	Pebbled surface	Powdery, nonuniform gray to black
43.5	0.2783	Uniformly distributed microholes	Gray mat with edge effect
--	0.1830	Ditto	Gray mat center, slightly darker edges
--	0.1727	"	Ditto
--	0.1819	"	"
--	0.1629	"	"
--	0.1811	Mat deposit with no microholes	One side light-gray to brown-gray mat center with lustrous edges; other side light-gray mat with brown-gray edges
--	0.4646	Ditto	Medium-gray mat center to brown-gray edges

- (5) One round carbon anode used; enclosed in porous Alundum cup.
Anolyte - Na₂SO₄ 142 g/l.
Cathodes - SAE 4130 steel 3" x 1" (plated area).
- (6) Anodes - two carbon flats 4" x 2" x 1/4" in porous Alundum cups.
Anolyte - Na₂SO₄ 142 g/l.
Cathodes - SAE 1010 steel 4" x 2" x 2-3/4". A 1/2" band around the edges, on both sides was
stopped off with lacquer. The plated area on each side was 3" x 1-3/4".
- (7) These panels were exposed in the "wet-dry" cabinet. X is a proprietary compound still under
development. Its chemical nature has not been disclosed.

TABLE 42. CODEPOSITION OF MANGANESE AND ZINC FROM SULFATE-BROCKHAUSE SOLUTIONS; ATTEMPTS TO RAISE THE CURRENT EFFICIENCY

Test No.	Addition Agent	pH	Temp, F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Remarks
-43H	None	5.3	80	40	5.5	11.5	29.4	0.0110	Uniform mat gray deposit
Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l									
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l									
Na Citrate $\cdot 2\text{H}_2\text{O}$ 250.0 g/l									
H_3BO_3 99.0 g/l									
-43A	None	5.3	70	40	4.0	12.8	23.8	0.0138	Uniform, mat gray center; darker edges
Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 55.3 g/l									
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 20.0 g/l									
Na Citrate $\cdot 2\text{H}_2\text{O}$ 125.0 g/l									
H_3BO_3 49.5 g/l									
-44B	Hide glue 2 g/l	5.3	70	40	4.0	6.7	25.2	0.0072	Milky, metallic center; brown lower edge
-44F	None	3.5	72	40	1.0	36.2	11.0	0.0392	Mat gray with dark lower edge
-46B	None	3.5	66	40	4.0	30.8	10.6	0.0330	Mat gray with dark lower edge
-46D	Hide glue 2 g/l	3.5	66	40	4.0	20.8	8.6	0.0232	Uniform, bright deposit; no edge effect
-46E	None	3.5	66	60	4.6	21.4	10.5	0.0403	Uniform, bright center; black lower edge
-44C	None	5.3	70	40	4.2	11.4	27.0	0.0124	Uniform, gray, mat center; dark edges
Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 27.6 g/l									
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 13.0 g/l									
Na Citrate $\cdot 2\text{H}_2\text{O}$ 62.5 g/l									
H_3BO_3 24.7 g/l									
-44D	Hide glue 2 g/l	5.3	70	40	4.2	4.6	58.5	0.0048	Milky, metallic center; dark edges

Notes appear on the following page.

Notes for Table 42

Notes: Duration of all tests - 10 minutes.

Agitation - Work rod, 33 cycles/minute, 1-1/4" stroke.

Anodes - Carbon rods 1/4" x 4" in porous Alundum cups.

Cathodes - Stainless steel 2" x 1/2" (immersed area).

TABLE 43. CODEPOSITION OF MANGANESE AND ZINC FROM SULFATE-BOROCITRATE SOLUTIONS; EFFECT OF SULFITE

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 55.6 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 26.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 125.0 g/l
 H_3BO_3 49.5 g/l

Test No.	Additions of Na_2SO_3 , g/l	pH	Temp, F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Remarks
-6429-65A	None	5.3	80	40	4.2	26.7	20.2	0.0286	Uniform mat gray deposit
-65B	0.05	5.3	80	40	-	20.6	20.6	0.0222	Uniform mat gray deposit
-66C	0.10	5.3	80	40	4.6	24.2	20.4	0.0259	Uniform mat gray deposit
-66D	0.25	5.3	80	40	6.2	23.1	21.8	0.0248	Uniform mat gray deposit
-66E	0.50	5.3	80	40	4.8	25.0	21.2	0.0267	Uniform mat gray deposit
-68A	0.05	6.2	79	40	4.4	1.3	48.3	0.0018	Light brown center; brown edges
-68B	0.10	6.2	79	40	4.4	1.5	38.2	0.0020	Dark brown to blue center on one side; other side gray mat center; edges on both sides were brown
-68C	0.25	6.2	79	40	5.2	-	-	-	Dark brown to blue center on one side; other side gray mat center; edges on both sides were brown
-68D	0.50	6.2	79	40	5.2	5.6	76.0	0.0054	Gray mat center; dark edges
-68E	5.0	6.2	79	40	5.8	7.0	85.5	0.0069	One side bright; other side dark metallic center with dark edges
-70A (1)	5.0	6.2	79	100	-	<1.0	-	-	Very slight deposit; cathode layer pH = 8-9 (paper)

(1) No agitation.

Notes: Time for all tests - 10 minutes.

Agitation - Work rod type, 33 cycles/minute, 1-1/4" stroke.

Anodes - Round carbon rods 1/4" diam x 4-1/2" long enclosed in porous Alundum cups.

Cathodes - Stainless steel 1/2" x 2" (immersed area).
 Bath size - 500 ml.

Baths treated with activated carbon.

Anolyte - $(\text{NH}_4)_2\text{SO}_4$ (135 g/l).

TABLE 44. THE CODEPOSITION OF MANGANESE AND ZINC FROM SULFATE-BOROCITRATE SOLUTIONS; EFFECT OF VARYING AMOUNTS OF THIOSULFATE AT DIFFERENT pH VALUES

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 55.3 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 26.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 125.0 g/l
 H_3BO_3 49.5 g/l

Test No.	Additions of $\text{Na}_2\text{S}_2\text{O}_3$, g/l	pH	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Remarks
-62A	0.02	5.3	5.2	25.2	10.6	0.0272	Gray mat center; dark edges
-62C	0.04	5.3	5.2	22.2	22.0	0.0234	Gray mat center; dark edges
-62E	0.24	5.3	4.8	25.4	12.8	0.0274	Nonuniform, gray-black powdery deposit
-64A	0.44	5.3	4.6	22.0	20.0	0.0210	Black powdery deposit
-64C	0.64	5.3	4.4	26.4	11.5	0.0287	Black powdery deposit
-64E	1.04	5.3	4.6	23.0	15.0	0.0249	Black, powdery deposit
-62B	0.02	6.2	4.4	6.1	73.5	0.0059	Gray metallic center; brown edges
-62D	0.04	6.2	5.2	2.7	32.0	0.0028	Gray metallic center; brown edges
-62F	0.24	6.2	4.8	12.0	86.0	0.0115	Gray metallic center; no deposit on edge
-64B	0.44	6.2	4.4	15.4	85.5	0.0146	Gray metallic center; no deposit on edge
-64D	0.64	6.2	-	20.0	88.0	0.0191	Gray metallic center; no deposit on edge
-64F	1.04	6.2	4.8	18.0	81.0	0.0172	Gray metallic center; no deposit on edge

Notes: Time for all tests - 10 minutes.

Temperature for all tests - 80 F.

Current density for all tests - 40 amp/sq ft.

Agitation work rod - 33 cycles/min, 1-1/4" stroke.

Anodes - Round carbon rods 1/4" diam x 4-1/2" long enclosed in porous Alundum cups.

Cathodes - Stainless steel 1/2" x 2" (immersed area).

Bath size - 500 ml.

Baths treated with activated carbon.

Anolyte $(\text{NH}_4)_2\text{SO}_4$ (135 g/l).

TABLE 45. CODEPOSITION OF MANGANESE AND ZINC FROM A SULFATE-BOROCITRATE SOLUTION; EFFECT OF THIOSULFATE

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 55.3 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 26.0 g/l
 $\text{Na Citrate} \cdot \text{H}_2\text{O}$ 125.0 g/l
 H_3BO_3 49.5 g/l
 $\text{Na}_2\text{S}_2\text{O}_3$ 0.5 g/l (except as noted)
 pH 6.2

Test No.	Temp, F	Time, min	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Remarks
6429-54A ⁽¹⁾	76	20	10	2.8	10	28	0.0053	Mat gray deposit
-54B ⁽¹⁾	76	10	40	4.2	1	12	0.0010	Gray, metallic center; brown edges
-54C	70	10	40	5.2	6.2	44.5	0.0065	Gray, metallic center; wide brown edges
-54D	76	20	10	2.8	15.2	9.7	0.0087	Uniform black deposit
-54E	70	15	40	-	27.4	86	0.0391	One side mat gray; other side brown
-54F	70	10	40	6.4	18.3	87.5	0.0175	Brown-gray metallic deposit
-60A ⁽²⁾	80	10	40	4.8	21.5	84.0	0.0200	Gray mat center; small edge effect
-60B	80	10	40	4.6	18.7	85.0	0.0171	Gray mat center; small edge effect
-60C	80	10	40	4.2	23.6	86.5	0.0220	Gray mat center; small edge effect
-60D	80	20	10	3.0	12.5	7.8	0.0070	Nonuniform black deposit
-60E	80	20	20	4.2	18.8	68.5	0.0194	Blue-gray metallic deposit
-60F	80	15	30	4.2	33.2	85.0	0.0363	Nonuniform brown-gray deposit

(1) No thiosulfate. (2) Bath stood two days without use, and then the tests starting with 60A were run. Bath size - 500 ml

Notes: Agitation - Work rod type, 33 cycles/minute, 1-1/4" stroke. Bath treated with activated carbon.

Anodes - Round carbon rods 1/4" diam x 4-1/2" long enclosed in porous Alundum cups. Anolyte - $(\text{NH}_4)_2\text{SO}_4$ (135 g/l).

Cathodes - Stainless steel 1/2" x 2" (immersed area).

TABLE 46. CODEPOSITION OF MANGANESE AND ZINC FROM A SULFATE-BOROCITRATE SOLUTION; EFFECT OF A "ROBBER"

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 55.3 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 26.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 125.0 g/l
 H_3BO_3 49.5 g/l
pH 6.2

Test No.	Time, min	Current Density, amp/sq ft	Cell Volts	Thickness One Side, mil	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Remarks
6429-80A(1)	20	17	4.0	-	8.0	52.0	0.0236	Metallic gray - sample center; black edges
-80B(1)	60	17	3.8	0.5	-	-	0.0904	Metallic gray - black center; black edges
-80C(1)	60	17	3.5	0.4	-	-	-	Metallic gray - black center; black edges
-80D	20	20	3.6	-	17.0	86.5	0.0577	Gray to light-brown mat; no edge effect
-80E	60	20	3.8	-	17.0	87.0	0.1680	Gray to light-brown mat; no edge effect

(1) Wire "robber" around cathode.

(2) Cathodes were SAE 4130 steel 1" x 3" (immersed area).

Notes: Agitation - Work rod, 33 cycles/minute, 1-1/4" stroke.

Anodes - Carbon flats 2" x 4" x 1/4" in rectangular porous Alundum cups.

Cathodes - Stainless steel 1" x 3-1/8" (immersed area).

Anolyte - $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (322 g/l).

Bath - 1000 π^1 , treated with activated carbon.

TABLE 47. CODEPOSITION OF MANGANESE AND ZINC FROM A SULFATE-BOROCITRATE SOLUTION; EFFECT OF "AGING" THE SOLUTION

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250.0 g/l
 H_3BO_3 99.0 g/l
pH 5.3

Test No.	Date and Time	Cathode Material	Treatment of Bath Prior to Electrolysis	Cell Volts	Cathode Efficiency(1), %	Manganese in Deposit, %	Thickness of One Side, mil	Weight of Deposit, gram	Macroappearance of Deposit	Microappearance of Deposit
6606-44A	1/31/52	4:00 p.m.	Stainless	None	4.4	3.5	66.0	0.0317	One side light-gray mat center, powdery brown edges. Other side brown, powdery deposit	Center portion composed of fairly coarse, irregular crystals. No holes visible
-44B	1/31/52	4:30 p.m.	SAE 4130	None	4.4	5.4	-	0.0499	Ditto	Fine, uniform crystals. No holes visible
-44C	2/1/52	3:00 p.m.	Stainless	None	4.4	2.3	55.5	0.0216	Light-gray mat center; brown, powdery edges	Ditto
-44D	2/1/52	4:00 p.m.	SAE 4130	None	4.4	6.1	-	0.0569	Ditto	-
-44E(2)	2/4/52	3:00 p.m.	SAE 4130	Solution boiled. 9.0(2)	-	-	-	-	Brown, powdery deposit	-
-44F	2/4/52	3:30 p.m.	SAE 4130	Precipitate redissolved	4.8	2.4	-	0.0225	No deposit in center; brown, powdery deposit on edges	-

TABLE 47. (Continued)

Test No.	Date and Time	Cathode Material	Treatment of Bath Prior to Electrolysis	Cell Volts	Cathode Efficiency(1), %	Manganese in Deposit, %	Thickness of One Side, mil	Weight of Deposit, gram	Macroappearance of Deposit	Microappearance of Deposit	
6000-52A	2/7/52	4:00 p. m.	Stainless	Solution boiled. Precipitate redissolved. Solution filtered	4.4	2.6	70.1	-	0.0235	Same as -44C	Same as -44C
-52B	2/7/52	4:30 p. m.	SAE 4130	None	4.4	3.0	-	-	0.0285	Same as -44C	Same as -44C
-52C	2/8/52	4:00 p. m.	Stainless	Solution treated with activated carbon. Qualitative test for zinc positive	4.2	4.3	75.3	-	0.0385	Ditto	Same as -44C
-52D	2/8/52	4:30 p. m.	SAE 4130	None	4.5	3.3	-	-	0.0302	"	Same as -44B
-52E	2/8/52	-	Stainless	A new bath of the same composition was used here(3).	5.0	8.8	84.2	-	0.0581	"	Same as -44A
										But less brown edge	

(1) Where manganese was not determined, the cathode efficiencies were calculated on the basis of 60% Mn in the deposits.

(2) 100 amp/sq ft cathode current density.

(3) Used to check results of previous tests.

Notes: Work-rod agitation - 33 cycles/min, 1-1/4" stroke

Temperature - 80 F

Current Density - 40 amp/sq ft

Time - 30 minutes

Cathodes - 3" x 1" (immersed area)

Anodes - Carbon flats, 4" x 2" x 1/4", in porous Alundum cups

TABLE 48. CODEPOSITION OF MANGANESE AND ZINC FROM A SULFATE-BOROCITRATE SOLUTION; EFFECTS OF ADDITION AGENTS AT DIFFERENT pH VALUES

Path Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250.0 g/l
 H_3BO_3 99.0 g/l

Test No.	Addition Agent	pH	Time, min	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Remarks
6606-14H	None	5.3	20	5.5	11.5	29.4	0.0220	Uniform, gray mat deposit
-14E	X(1)	5 g/l	20	4.2	6.3	77.0	0.0110	Lustrous, gray mat center; no deposit on edges
-14D	Na salt of X(1)	5 g/l	10	4.6	3.5	58.3	0.0035	Ditto
-14A	X(1)	10 g/l	10	4.4	5.8	78.0	0.0052	"
-14B	Sulfonated cresol	10 g/l	10	4.2	12.9	31.4	0.0138	Gray, mat center; no deposit on edges
-14C	Glycine	2 g/l	10	6.2	4.8	26.0	0.0052	Black, powdery deposit
-14G	Urea	2 g/l	20	4.2	5.8	46.0	0.0108	Lustrous, gray mat center; no deposit on edges
-14L	X(1)	10 g/l	20	4.6	2.2	47.0	0.0045	Brown, powdery deposit
-14J	Na salt of X(1)	5 g/l	20	4.8	3.0	46.0	0.0062	Ditto
-14I	Sulfonated cresol	10 g/l	20	4.8	8.7	39.5	0.0180	"
-14K	Urea	2 g/l	20	4.6	2.1	46.5	0.0043	"
14M	None	7.5	20	-	1.3	73.0	0.0026	Gray, mat center; brown edges

Footnotes for Table 48

(1) X is a proprietary material, still under development, whose composition has not been revealed.

Notes: Work-rod agitation - 33 cycles/min, 1-1/4" stroke

Current density - 40 amp/sq ft

Temperature - 80 F

Cathodes - Stainless steel, 1" x 1/2" (immersed area)

Anodes - Carbon rods, 1/4" diameter x 4-1/2" long, in porous Alundum cups

Anolyte - Na_2SO_4 , 142 g/l

TABLE 49. CODEPOSITION OF MANGANESE AND ZINC FROM A SULFATE-BOROCITRATE SOLUTION;
PLATE-DENSITY STUDIES FOR SOLUTION CONTAINING ADDITION AGENT X(1)

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250.0 g/l
 H_3BO_3 98.0 g/l
 $\text{X}(1)$ 10 g/l
pH 5.3

Test No.	Cathode Material	Time, min	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Thickness of One Side, mil	Weight of Deposit, gram	Remarks
660C-18A	Stainless	30	30	3.8	11.2	37.0	0.15	0.0875	Four areas in center, varying from bright to mat gray; bright-gray edges
-18B	Stainless	70	30	4.0	10.5	38.0	0.7	0.1920	Ditto
-18D	SAE 4130	60	30	4.3	-	-	0.6	0.1685	"
-18E	SAE 4130	30	30	4.3	-	-	0.15	0.1037	"
-18F(2)	SAE 4130	30	30	4.3	-	-	0.2	0.1040	"
		30	30	4.3	-	-	0.2	0.0760	"
-18C	Stainless with robber	60	40	4.4	14.4	18.8	1.0	0.3180	Uniform, light-gray mat deposit

(1) X is a proprietary material, still under development, whose composition has not been revealed.

(2) Specimen plated 30 minutes, removed, dried, and weighed, and thickness measured; panel then plated for an additional 30 minutes.

Notes: Work-Rod Agitation - 33 cycles/min. 1-1/4" stroke

Anodes - Carbon flats, 4" x 2" x 1/4", in porous Alundum cups
Anolyte - Na_2SO_4 , 142 g/l

Cathodes - 3" x 1" (immersed area)

TABLE 50. CODEPOSITION OF MANGANESE AND ZINC FROM SULFATE-BOROCITRATE SOLUTIONS;
EFFECT OF ADDITION AGENT X⁽¹⁾ UNDER VARYING CONDITIONS

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250.0 g/l
 H_3BO_3 99.0 g/l
 $\text{X}^{(1)}$ 10.0 g/l (except as noted)
pH 5.3

Test No.	Treatment of Bath Prior to Electrolysis	Agitation	Time, min	Curr. Den., amp/sq. cm	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Remarks
-14B	None	Yes ⁽²⁾	20	20	3.6	30.0	17.1	0.0330	Uniform, lustrous, light-gray deposit
-14N	None	Yes ⁽²⁾	20	30	4.0	15.5	47.5	0.0185	Light-gray mat center; black edges
-14A	None	Yes ⁽²⁾	10	40	4.4	5.8	78.0	0.0052	Lustrous, light-gray center; no deposit on edges
-22A	None	No	15	30	4.0	7.6	75.5	0.0255	Lustrous to mat gray center; no deposit on edges
-22B	H_2O_2 (30%) 10 ml/l, boiled	No	30	30	-	5.2	64.6	0.0360	Iditto
-22C	None	No	30	30	-	6.8	68.2	0.0465	"
-22D	H_2O_2 (30%) 10 ml/l, boiled	No	30	30	-	6.7	64.2	0.0455	Lustrous to mat gray center; no deposit on edges
-22E ⁽³⁾	None	No	30	30	-	8.9	58.5	0.0629	One side lustrous to bright gray, other side gray mat; bright edges
-22F	None	No	30	20	-	14.3	48.3	0.0675	Lustrous to mat gray center; bright edges
-22G	H_2O_2 (30%) 10 ml/l, boiled	No	30	20	-	12.3	53.0	0.0580	Light-gray, mat center; bright edges

⁽¹⁾Notations appear on the following page.

Footnotes for Table 50

- (1) X is a proprietary material, still under development, whose composition has not been revealed.
- (2) Work-rod agitation is 33 cycles/min with a 1-1/4" stroke.
- (3) This bath had 20 g/l of X.

Notes: Temperature - 80 F

Cathodes - Stainless steel, 1" x 3" (immersed area) for tests -22A through -22G, 1/2" x 1" (immersed area) for tests -14E, -14N, and -14A

Anodes - Carbon rods, 1/4" x 4-1/2", in porous Alundum cups for tests -14E, -14N, and -14A; carbon flats, 4" x 2" x 1/4", in porous Alundum cups for tests -22A through -22G

Electrolyte - Na₂SO₄, 142 g/l

TABLE 51. HULL CELL⁽¹⁾ ANALYSES OF ADDITION AGENTS IN THE SULFATE-BOROCITRATE SOLUTION

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250.0 g/l
 H_3BO_3 99.0 g/l
 pH 5.0

Test No.	Appearance of Hull Cell Cathodes	Addition Agent or Treatment	Cell Current, amps	Descriptive Code for Appearance of Hull Cell Cathodes
	84 38 17 2			
	Current densities for cell current of 2 amperes			
	42 19 8 1			
	Current densities for cell current of 1 amp			
CC-16-20A	P G M D G G G MD G G G G b g G	None	1.0	G B b g D L M V I P nc
-21A	P B G M D MD G b g G	None	2.0	
-20B	P B MD G M G 8 G b G	H_2O_2 Treatment ⁽²⁾	1.0	
-20C	P B MD G D G b G 3 G D G	X 10 g/l	1.0	

In assigning colors to the various sections of the panels, it was found best not to use all the shades necessary to describe the panels in complete detail, because the charts would be so complicated as to be useless. Accordingly, certain basic colors were chosen, and used somewhat loosely. For example, all "medium grays" are not exactly the same. Furthermore, all the minor bands are not included, as this, too, would tend to make the charts complicated.

TABLE 51. (Continued)

Test No.	Appearance of Hull Cell Cathodes	Addition Agent or Treatment	Cell Current, amps	Descriptive Code for Appearance of Hull Cell Cathodes
3626-20D	P B I G M G B G MD G b G g G D G	X 10 g/l H ₂ O ₂ 4 ml/l	1.0	See p AII-55 for descriptive code
-20E	P B M D M G B G MD G I G g G D G	X 10 g/l H ₂ O ₂ Treatment(2)	1.0	
Current densities for cell current of 1 amp				
-21C	P B D G M G D to b G D to b G	Aniline 2 g/l	1.0	
-21D	P B VD G D G M G D to b G D to b G	Phenol 2 g/l	1.0	
-21E	B nd M IG b G	Pyridine 2 g/l	1.0	
-21F	P B M G VD G D G D to b G D to b G	Catechol 2 g/l	1.0	

TABLE 51. (Continued)

Test No.	Appearance of Hull Cell Cathodes	Addition Agent or Treatment	Cell Current, amps	Descriptive Code for Appearance of Hull Cell Cathodes
6608-21G	nd	Quinoline 2 g/l	1.0	See p AII-55 for descriptive code
-21H	P M G M G D G	Gelatin 2 g/l	1.0	
-21B	P 1 G B G G G M G M G L8 G 8 G b G	X 2 g/l H ₂ O ₂ Treatment ⁽²⁾	1.0	

(1) The Hull cell used in this work was purchased from R. O. Hull and Company, Incorporated, Rocky River 16, Ohio.

(2) The treatment consisted of adding 4 ml/l H₂O₂ (30%) and then boiling the solution.

TABLE 52. CODEPOSITION OF MANGANESE AND ZINC FROM SULFATE-BOROCITRATE SOLUTIONS; EFFECT OF TREATMENT WITH ACTIVATED CARBON

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 55.3 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 26.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 125 g/l
 H_3BO_3 49.5 g/l
 pH 5.3

Test No.	Temp, °F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Remarks
6429-72E(1)	79	40	5.2	23.4	17.7	0.0255	Mat, gray center; no deposit on edges
-72C(2)	79	40	4.2	25.4	(3)	0.0278	Mat, gray center; no deposit on edges
-76A(1)	80	60	5.6	13.5	24.0	0.0218	Mat, gray center; no deposit on edges
-76B(2)	80	60	6.0	8.1	18.2	0.0131	Mat, gray center; no deposit on edges
-76C(1)	80	70	6.0	5.0	22.2	0.0093	Mat, gray center; no deposit on edges
-76D(2)	80	70	7.0	7.1	23.5	0.0087	Mat, gray center; no deposit on edges
-72D(2)	79	100	6.8	1.4	31.4	0.0039	Mat, gray center; no deposit on edges

- (1) Bath not treated with activated carbon.
 (2) Bath treated with activated carbon.
 (3) Analytical sample was lost.

Notes: Time for all tests - 10 minutes.
 Anodes - Carbon rods 1/4" x 4" in porous Alundum cups.
 Cathodes - Stainless steel 1/2" x 2" (immersed area).
 Agitation - Work rod type, 33 cycles/minute, 1-1/4" stroke.

TABLE 53. CODEPOSITION OF MANGANESE AND ZINC FROM SULFATE-BOROCITRATE SOLUTIONS:
STUDIES WITH STILL AND ROTATING CYLINDRICAL CATHODES

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52.0 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250.0 g/l
 H_3BO_3 99.0 g/l
pH 5.3

Test No.	Agitation	Time, min	Cell Volts	Cathode Efficiency, %	Manganese in Deposit ⁽¹⁾ , %	Zinc in Deposit ⁽²⁾ , %	Percentage Error	Thickness of Deposit, mil	Weight of Deposit, gram	Microappearance of Deposit	Macroappearance of Deposit
-54C	None	30	3.3	10.7	20.7	75.3	-4.3	0.1	0.0207	No microholes; grooves visible at 20X	Uniform gray mat deposit
-54B	None	60	3.2	8.8	29.5	60.2	-11.3	0.25	0.0224	No microholes; grooves and nodules	Uniform gray mat; slightly nodular
-54D	None	90	3.3	8.8	16.9	5.5	5.4	0.5	0.0572	Nodular powdery surface with grooves	Uniform, blue-gray mat
-54G	50 rpm	30	3.2	7.5	40.4	52.5	-7.1	0.1	0.0141	No microholes; grooves visible at 20X	Uniform gray mat deposit
-54E	50 rpm	60	3.2	8.1	23.4	78.2	+1.6	0.3	0.0313	Nodular powdery surface with grooves	Uniform gray mat; slightly nodular
-54F	50 rpm	120	3.2	6.2	22.9	77.3	+0.2	0.5	0.0397	Ditto	Ditto

(1) Where the deposits were powdery, the efficiency figures are probably low due to loss of deposit in the drying operation.

(2) Both manganese and zinc were determined by chemical analysis.

Notes: Anodes - Carbon flats, 4" x 2" x 1/4", in porous Aluminum cups
Cathodes - Round stainless steel rods, 3" long x 1/4" diam; lower end of cathode stopped off

Temperature - 80 F
Current Density - 20 amp/sq ft
Anolyte - Na_2SO_4 , 1-2 g/l

TABLE 54. CODEPOSITION OF MANGANESE AND ZINC
FROM SIMPLE FLUORIDE SOLUTIONS

Test No.	pH ⁽¹⁾	Temp, F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Per Cent Manganese in Deposit	Remarks
Bath Composition:							
		Mn(BF ₄) ₂ - 230 g/l	mole ratio $\frac{\text{Mn}}{\text{Zn}} = 1$				
		Zn(BF ₄) ₂ - 240 g/l					
		H ₃ BO ₃ (Free) - 40 g/l					
5561-88D	0.0	86	25	-	74	faint trace	Blue-gray mat deposit; crystalline edges
-88E	0.0	86	40	-	55.5	faint trace	Blue-gray mat deposit; crystalline edges
-88F	0.0	86	100	-	73	0.11	Blue-gray mat deposit; crystalline edges
Bath Composition:							
		Mn(BF ₄) ₂ - 400 g/l	mole ratio $\frac{\text{Mn}}{\text{Zn}} = 3.5$				
		Zn(BF ₄) ₂ - 120 g/l					
		H ₃ BO ₃ (Free) - 12 g/l					
5561-88A	0.0	86	25	-	74.5	none	Blue-gray mat deposit
-88B	0.0	86	40	-	66.5	0.13	Blue-gray mat deposit; crystalline edges
-88C	0.0	86	100	-	38.3	0.4	Blue-gray mat deposit crystalline edges
Bath Composition:							
		Mn(BF ₄) ₂ - 400 g/l	mole ratio $\frac{\text{Mn}}{\text{Zn}} = 7.0$				
		Zn(BF ₄) ₂ - 60 g/l					
		H ₃ BO ₃ (Free) - 8 g/l					
5561-90A	0.0	84	25	-	54.1	0.52	Blue-gray mat deposit; crystalline edges
-90B	0.0	86	40	-	46.8	0.64	Deposit blue-gray mat at top; bottom is coarsely crystalline
-90C	0.0	86	100	-	35.6	0.69	Deposit blue-gray mat at top; bottom is coarsely crystalline

TABLE 54. (Continued)

Test No.	pH ⁽¹⁾	Temp, F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Per Cent Manganese in Deposit	Remarks
Bath Composition:							
		Mn(BF ₄) ₂ - 400 g/l	mole ratio $\frac{\text{Mn}}{\text{Zn}} = 7.0$				
		Zn(BF ₄) ₂ - 60 g/l					
		H ₃ BO ₃ (Free) - 8 g/l					
6245-20A ⁽²⁾	0.0	84	100	-	20.6	3.26	Dark, gray mat deposit; poor adhesion
-20B	0.0	126	100	4.8	32.4	0.97	Gray mat deposit
-20C	0.0	145	100	2.8	40.5	0.48	Dark gray deposit

(1) pH measured with papers.

(2) Cathode agitated, 33 cycles per minute, 1-1/4" stroke.

TABLE 55. CODEPOSITION OF MANGANESE AND ZINC FROM FLUOBORATE SOLUTIONS CONTAINING ADDITION AGENTS

Solution Composition: $Mn(BF_4)_2$ - 400 g/l
 $Zn(BF_4)_2$ - 60 g/l
 H_3BO_3 (Free) - 8 g/l

Test No.	Addition Agent	pH(1)	Temp, F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency %	Per Cent Manganese in Deposit	Remarks
6245-26D	4 Amino-4 Nitro-Diphenylamine-2							
	Sulfonic Acid, 2 g/l	0.0	84	50	7.2	80	1.06	Mat gray, coarsely crystalline deposit
-26C	Hide Glue, 2 g/l	0.0	84	100	4.0	42.5	3.87	Gray-blue mat deposit
-28D	Hide Glue, 2 g/l	0.0	84	71.5	-	57	4.85	Bright, metallic deposit one side. Upper portion of other side was blue-gray mat
-23A(2)	Hide Glue, 2 g/l	0.0	84	100	-	57.2	4.8	Rough edges; metallic; blue-gray center
-30D	Hide Glue, 2 g/l	0.0	80	143	-	68	17.8	Bright edges; dark center
-32D	Hide Glue, 4 g/l	0.0	83	143	-	64	21.8	Nonuniform gray-black deposit
-34B	Hide Glue, 4 g/l	0.0	82	71.5	4.0	35	3.2	Bright in spots; streaked
-34F(3)	Hide Glue, 4 g/l	0.0	84	71.5	-	40.5	7.2	Bright in spots

(1) pH measured by paper.

(2) 20-minute run. Note difference between this test and 26-C. Only difference in conditions was in time, yet manganese content is different, as is efficiency.

(3) Work-rod agitation, 33 cycles per minute, 1-1/4" stroke.

TABLE 56. CODEPOSITION OF MANGANESE AND ZINC FROM FLUOBORATE SOLUTION.
EFFECTS OF ADDITION AGENTS AT HIGHER pH

Bath Composition: Mn(BF ₄) ₂ 400 g/l Zn(BF ₄) ₂ 60 g/l H ₃ BO ₃ (Free) 20 g/l									
Test No.	Addition Agent	pH ⁽¹⁾	Temp, F	Current Density, amp/sq ft	Cathode Efficiency, in Deposit, per cent		Manganese in Deposit, per cent	Remarks	
					Cell Volts	per cent			
6429-20A ⁽²⁾	None	1.4 to 1.7	80	100	4.2	34.6	2.55	Crystalline gray deposit.	
-20B ⁽²⁾	Gelatin	2 g/l	1.4 to 1.7	80	100	5.2	71.0	13.0	Gray-mat deposit, bottom edge black.
-20D	Gelatin	2 g/l	1.4 to 1.7	78	100	4.2	57.0	22.4	Black, powdery upper portion, gray-mat bottom.
-20E	None	1.7 to 1.9	78	100	4.2	24.2	20.0	Blue-gray, powdery deposit.	
-20F	Hide Glue	6 g/l	1.7 to 1.9	78	100	4.8	67.5	12.8	Gray-mat center, black edges.
-18B ⁽³⁾	Na cit·2H ₂ O	100 g/l	1.7 to 1.9	76	100	6.0	7.8	35.4	Slightly powdery, brown deposit.

(1) pH measured with paper. The values are given over a range of pH because of uncertainty of reading the papers.
 (2) Work-rod agitation, 33 cycles per minute, 1-1/4-inch stroke.
 (3) Precipitate formed after electrolysis.

Notes: Duration of all tests - 10 minutes.
 Anodes - Carbor. rods in Alundum cups.
 Cathodes - Stainless steel sheet - 2 inches x 1/2-inch (immersed area).

TABLE 57. CODEPOSITION OF MANGANESE AND ZINC FROM FLUOBORATE SOLUTION AT (1) HIGHER CURRENT DENSITY AND (2) HIGHER pH

Bath Composition: $Mn(BF_4)_2$ 400 g/l
 $Zn(BF_4)_2$ 60 g/l
 H_3BO_3 (Free) 22 g/l

Test No.	pH ⁽¹⁾	Temp, F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, per cent	Manganese in Deposit, per cent	Remarks
6245-70A	0.0	83	145	4.5	31.4	6.75	Metallic and bright, bottom edge black.
-70C ⁽²⁾	0.0	88	145	4.2	24.0	3.88	Metallic and bright, bottom edge black.
-70D ⁽³⁾	0.0	86	145	4.0	24.2	2.45	Same as -70C but with less black area.
6429-18C	1.4 to 1.7	76	100	5.0	30.0	21.6	Gray, powdery deposit.
-18D	2.7 to 3.1	76	100	4.2	29.8	22.8	Gray, powdery deposit. Precipitate formed on solution following electrolysis.

(1) pH measured with paper. The higher values are given over a range of pH because of uncertainty of reading the papers.
 (2) Added 21 g/l H_3BO_3 .
 (3) Work-rod agitation, 33 cycles per minute, 1-1/4-inch stroke.

Notes: Duration of all tests - 10 minutes.
 Anodes - Carbon rods in Alundum cups.
 Cathodes - Stainless steel sheets - 2 inches x 1/2-inch (immersed area).

TABLE 58. CODEPOSITION OF MANGANESE AND ZINC FROM A FLUOBORATE SOLUTION;
EFFECT OF SUPERIMPOSED ALTERNATING CURRENT

Bath Composition:					95.4 g/l				
Min (90% Electrolytic)					700 g/l				
HBF ₄ (44.5% Solution)					118 g/l				
Zn(BF ₄) ₂ (50.5% Solution)					30 g/l ⁽¹⁾				
H ₃ BO ₃ (Free)					1.4 to 1.7				
pH (Paper)									
Test No.	Temp, F	AC, amperes	DC, amperes	Ratio, a-c amp/d-c amp	D-C Cell Volts	Cathode Efficiency ⁽²⁾ , %	Manganese in Deposit, %	Weight of Deposit, gram	Remarks
-12A	80	None	4.2	-	4.5	22.0	11.4	0.1846	Dark gray, powdery center; lighter gray edges
-12B	80	48	4.2	11.4	5.5	55.0	16.8	0.4603	Ditto
-12C ⁽³⁾	72	None	4.2	-	5.5	41.3	23.5	0.3395	"
-12D	72	2.0	4.2	0.48	6.0	69.5	21.5	0.5730	"
-12E	76	4.0	4.2	0.95	5.8	38.0	25.5	0.3130	"
-12F	76	48	4.2	11.4	5.9	43.5	27.0	0.3580	"
-12G	78	20	4.2	4.8	5.8	36.8	23.2	0.3015	"
-12H	78	48	4.2	11.4	5.6	48.3	28.5	0.3945	"
-24A ⁽¹⁾	80	None	4.2	-	-	42.0	26.5	0.3480	Uniform, black-gray, rough, powdery deposit
-24B ^(1,4)	80	None	4.2	-	-	30.7	1.0	0.2630	Light gray, mat center; dark gray, rough edges

(1) Tests -24A and -24C were plated from a bath containing 21 g/l free H₃BO₃.

(2) Because the deposits were powdery and may have been lost in part, the efficiency values are, if anything, low.

(3) From this test through -12H, the bath was filtered each time because the deposits flaked off.

(4) 10 g/l X (a proprietary compound) added to the bath.

Notes: Work-rod agitation - 33 cycles/min, 1-1/4" stroke

Time - 10 minutes

D-C cathode current density - 100 amp/sq ft

Cathodes - Stainless steel (except -12I, which was SAE 4130), 3" x 1" (immersed area)

Anodes - Carbon flats, 4" x 2" x 1/4", in porous Alundum cups

TABLE 59. CODEPOSITION OF MANGANESE AND ZINC FROM SULFATE - TETRASODIUM ETHYLENEDIAMINE
TETRAACETATE(1) SOLUTIONS; PRELIMINARY EXPERIMENTS

No. 1 Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 44.0 g/l 44.0 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 70.0 g/l 70.0 g/l
 "Sequestrene NA4"(1) 200.0 g/l 400.0 g/l

No. 2 Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 44.0 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 70.0 g/l
 "Sequestrene NA4"(1) 400.0 g/l

Test No.	Bath	pH	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Remarks
-28A	No. 1	4.4	60	-	12.9	2.4	0.0219	Powdery, blue-gray deposit; a gelatinous precipitate having a pH of 8 formed on the cathode during the run
-30B	No. 2	4.4	1 to 60 (Hull cell)	-	-	-	-	No deposit
-31A	No. 2	9.0	> 60	-	25.4	1.5	0.0430	Uniform blue-gray mat deposit; no gelatinous precipitate
-31B	No. 2	12.5	60	6.4	26.6	1.5	0.0442	Uniform blue-gray mat deposit with powdery surface; no gelatinous precipitate

(1) Tetrasodium ethylenediamine tetraacetate is marketed under the name "Sequestrene NA4" by the Alrose Chemical Company, Providence 1, Rhode Island.

Notes: No agitation

Temperature - 80 F

Time - 10 minutes

Cathodes - Stainless steel, 1/2" x 2" (immersed area)

Anodes - Carbon rods, 1/4" diam x 4-1/2" long, in porous Alundum cups

TABLE 60. HULL CELL⁽¹⁾ ANALYSES OF MANGANESE-ZINC TETRASODIUM
ETHYLENEDIAMINE TETRAACETATE⁽²⁾ SOLUTIONS

Temperature - 80 F (Except as Noted); Time - 10 Minutes

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 44 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 70 g/l
 "Sequestrene NA44" 200 g/l

Test No.	Appearance of Hull Cell Cathodes				Additions to Bath or Treatment	Cell Current, amps	Descriptive Code for Appearance of Hull Cell Cathodes
	42	19	8	1			
	Current densities for cell current of 1 amp						
	126	57	25	3			
	Current densities for cell current of 3 amps						
-27A	VD G	B G	D G	VD G	None	4.4 1	G B b g D L M V 1 nd
-27B		D G	M G	G	None	4.4 3	
-28B	V D G	M G	g G	V D G	None	4.4 1	
-28A		B G	B G	Db G	H ₂ O ₂ treatment ⁽³⁾	4.4 1	
-29A	M D B G	M D to B G	nd		H ₃ BO ₃	60 g/l 4.4 1	

In assigning colors to the various sections of the panels, it was found best not to use all the shades necessary to describe the panels in complete detail, because the charts would be so complicated as to be useless. Accordingly, certain basic colors were chosen, and used somewhat loosely. For example, all "medium grays" are not exactly the same. Furthermore, all the minor bands are not included as this, too, would tend to make the charts complicated.

In assigning colors to the various sections of the panels, it was found best not to use all the shades necessary to describe the panels in complete detail, because the charts would be so complicated as to be useless. Accordingly, certain basic colors were chosen, and used somewhat loosely. For example, all "medium grays" are not exactly the same. Furthermore, all the minor bands are not included as this, too, would tend to make the charts complicated.

TABLE 60. (Continued)

Test No.	Appearance of Hull Cell Cathodes	Additions to Bath or Treatment	pH	Cell Current, amps	Descriptive Code for Appearance of Hull Cell Cathodes
3006-29B	b G	H ₃ BO ₃ 100 g/l Na Citrate-2H ₂ O 240 g/l	4.4	1	See p .AII-67 for descriptive code
-30B	nd	Sequestrene NA4 400 g/l	4.4	1	
-29C	M Footnote 4 G	H ₃ BO ₃ 60 g/l Borax 60 g/l	7.5	1	
-30A	D G	Sequestrene NA4 400 g/l	9.0	1	

(1) R. O. Hull and Company, Incorporated, Rocky River 16, Ohio.

(2) Alrose Chemical Company, Providence 1, Rhode Island.

(3) 4 ml/1 30% H₂O₂ added and solution boiled.

(4) Mottled gray and white.

TABLE 61. MISCELLANEOUS EXPLORATORY EXPERIMENTS ON THE CODEPOSITION OF MANGANESE AND ZINC

Test No.	pH	Temp, F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, per cent	Manganese in Deposit, per cent	Remarks
Bath Composition:							
			$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	110.6 g/l			
			$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	52 g/l			
			$\text{NH}_2\text{SO}_3\text{H}$	100 g/l			
0245-61A	0.6		82			< 1%	Polarization vs. Current Density. Current density from 2 amp/sq ft to 470 amp/sq ft. Maximum polarization is -1.390 volts (sat. cal. scale). Gray crystalline deposit. See Figure 9.
Bath Composition:							
			$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	110.6 g/l			
			$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	52 g/l			
			$\text{NH}_2\text{SO}_3\text{H}$	200 g/l			
0245-64A	0.3		82			< 1%	Polarization vs. Current Density. Current density from 2 amp/sq ft to 360 amp/sq ft. Maximum polarization is -1.182 volts (sat. cal. scale). Mat-gray deposit. See Figure 9.
Bath Composition:							
			$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	55.3 g/l			
			$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	26 g/l			
			Gluconic Acid	150 g/l			
0245-40G	4.0		85 40		35.8	5.06	Mat-gray center, dark edges.
Bath Composition:							
			$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	20 g/l			
			$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	6 g/l			
			$\text{K}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$	360 g/l			
0420-18A	10.8		76 100	4.8	9.4	29.7	Black powdery center, brown powdery edge.
Bath Composition:							
			$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	110.6 g/l			
			$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	52 g/l			
			NH_4HF_2	200 g/l			
			NaF	40 g/l			
0420-20C	0.7-1.0		78 100	4.2	39.0	< 1%	Mat center, crystalline blue-gray edges.

TABLE 62. CODEPOSITION OF MANGANESE AND ZINC FROM A CHLORIDE-CITRATE SOLUTION; EFFECT OF SULFATE

Bath Composition: $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ 130 g/l
 ZnCl_2 25 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250 g/l
pH 5.3

Test No.	Additions to Bath	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Remarks
6429-96A(1,2)	None	4.6	14.5	8.6	0.0405	Gray, mat center; no deposit on edges
-96B(2)	Cone H_2SO_4 10 drops(4)	4.6	28.3	29.4	0.0764	Gray, mat center; edge effect
-96C(2,3)	None	4.6	34.4	29.4	0.0930	Gray, mat center, surrounded by flaky deposit; no deposit on edges
-96D(3)	None	5.0	26.6	31.5	0.0718	Gray, mat center, surrounded by flaky deposit; no deposit on edges
-96E(3)	None	5.0	26.9	34.5	0.0726	Gray, mat center, surrounded by flaky deposit; no deposit on edges
-96F(4,5)	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ 27 g/l	4.0	21.1	29.2	0.0582	Gray, mat center, surrounded by flaky deposit; no deposit on edges
-96G(4,3)	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ 135 g/l	4.4	16.6	54.2	0.0432	Dark center; pronounced edge effect
-96H(4,3)	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ 270 g/l	4.0	16.2	80.5	0.0402	Light center; black edges

(1) Fresh bath.

(2) Anolyte - $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (322 g/l).

(3) Anolyte - Same as catholyte.

(4) The solution was buffered sufficiently so that the pH remained at 5.3.

Notes: Duration of all tests - 10 minutes.

Work rod agitation 33 cycles/minute, 1-1/4" stroke.

Temperature - 80 F.

Current density - 100 amp/sq ft.

Anodes - Round carbon rods 1/4" diam x 4-1/2" long.

Cathodes - Stainless steel 2" x 1/2" (immersed area).

TABLE 63. CODEPOSITION OF MANGANESE AND ZINC FROM A SULFATE-FLUORIDE SOLUTION; PRELIMINARY EXPERIMENTS

Bath Composition: $\text{MnSO}_4 \cdot 11\text{H}_2\text{O}$ 110 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52 g/l
 NaF 40 g/l
 pH 2.0 (paper)

Test No.	Temp, F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Microappearance of Deposit	Macroappearance of Deposit
-60B	80±2	50	3.6	57.2	< 1	0.0833	Large, uneven crystals at 40X	Coarsely crystalline deposit
-60A	80±2	100	6.0	37.9	3.2	0.1084	Ditto	Ditto
-60D	140±2	50	3.0	78.0	< 1	0.1112	"	"
-60C	140±2	100	5.8	73.3	< 1	0.1676	"	"
-60F	160±2	50	2.6	84.3	< 1	0.1202	"	"
-60G	160±2	100	4.8	97.3	< 1	0.2232	"	"

Notes: No agitation

Anodes - round carbon rods in porous Aluminum cups

Anolyte - same as catholyte

Time - 10 minutes

Cathodes - stainless steel 2" x 1/2" (plated area)

TABLE 64. CODEPOSITION OF MANGANESE AND ZINC FROM A CONCENTRATED CAUSTIC-METAL OXIDE-SULFATE SOLUTION

Bath Composition: NaOH 300 g
H₂O 300 g
MnSO₄·H₂O 100 g
ZnO 25 g

Test No.	Agitation	Time, min	Temp, F	Current Density, amp/sq ft	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Remarks
-100A	200 rpm	10	192	200	--	--	--	Thick nonadherent spongy deposit; no analysis made
-100B	200 rpm	10	192	50	104	2.3	0.1046	Light-gray mat deposit
-100C	None	10	186	50	39	6.3	0.0409	Gray, powdery deposit

Notes: Anode - steel rod

Cathode - 3/16" diameter round stainless steel rod, 2-1/2" immersed in solution

TABLE 65. CODEPOSITION OF MANGANESE AND ZINC FROM A SULFATE-BORATE SOLUTION USING AN ACID INHIBITOR AS AN ADDITION AGENT

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52 g/l
 H_3BO_3 20 g/l
 Reilly #22(1) As Given Below
 pH 1.0

Test No.	Addition of Reilly #22(1), g/l	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Appearance of Deposit
6922-64G	0.05	25	3.6	7.4	0.0	0.0059	Golden nodular
-64H	0.10	25	4.0	20.0	0.0	0.0157	Ditto
-64I	0.50	25	3.6	--	--	--	No deposit
-66E	1.0	25	3.6	--	--	--	Ditto
-66F	2.0	25	4.2	--	--	--	"
-64D	0.05	50	4.2	16.2	0.0	0.0258	Golden nodular
-64E	0.10	50	4.6	23.8	0.0	0.0378	Ditto
-64F	0.50	50	4.6	--	--	--	No deposit
-66C	1.0	50	5.4	3.1	50.2	0.0045	Golden nodular deposit along edges only
-66D	2.0	50	4.8	14.9	59.5	0.0216	Golden nodular deposit along edges only
-64A	0.05	100	6.5	20.2	0.0	0.0039	Golden nodular
-64B	0.10	100	6.2	26.4	0.0	0.0833	Ditto
-64C	0.50	100	7.0	18.8	17.8	0.0579	Golden nodular deposit; slightly treed edges
-66A	1.0	100	6.8	23.5	58.8	0.0669	Golden nodular deposit; slightly treed edges
-66B	2.0	100	6.0	34.6	60.7	0.0989	Golden nodular deposit; slightly treed edges
-66I	0.5	150	10.0	20.2	25.9	0.0832	Golden nodular deposit; slightly treed edges
-66G	1.0	150	8.6	24.4	60.5	0.0956	Golden nodular deposit; slightly treed edges
-66H	2.0	150	7.0	34.0	66.5	0.1321	Golden nodular deposit; slightly treed edges

Footnotes appear on following page.

(1) Reilly Tar and Chemical Corporation, Indianapolis, Indiana.

Notes: Agitation - none

Anodes - carbon rods in porous Alundum cups

Anolyte - Na_2SO_4 142 g/l

Cathodes - stainless steel, 2" x 9/16" (plated area)

Temperature - 80 F

Time - 10 minutes

TABLE 66. COMPOSITION OF MANGANESE AND ZINC FROM A SULFATE-BORATE SOLUTION, USING AN ACID INHIBITOR AS AN ADDITION AGENT AT VARIOUS pH VALUES

Test No.	pH	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Appearance of Deposit
Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110 g/l $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 52 g/l H_3BO_3 20 g/l Reilly 25(1) 2.0 g/l							
- 70A	2.0	50	5.2	110	19.2	0.1688	Black, nodular
- 70B	3.0	50	5.2	137	15.6	0.2134	Black, nodular, and powdery
- 70C	2.0	100	8.2	123	19.1	0.3775	Black, powdery
- 70D	3.0	100	6.6	172	12.4	0.5206	Ditto
- 70E	2.0	150	11.0	87.5	21.1	0.3987	"
- 70F	3.0	150	12.5	31.2	33.7	0.1390	Black, flaky

(1) Reilly Tar and Chemical Corporation, Indianapolis, Indiana.
(2) All of the deposit did not dissolve in dilute nitric acid solution (30 ml 70% HNO_3 , 500 ml H_2O).

Notes:

- No agitation
- Anodes - carbon rods in porous Alundum cups
- Anolyte - Na_2SO_4 142 g/l
- Cathodes - stainless steel, 2" x 9/16"
- Temperature - 50 F
- Time - 10 minutes

TABLE 67. CODEPOSITION OF MANGANESE AND ZINC FROM SULFATE-GLUCONIC ACID SOLUTIONS

Bath Composition: MnSO ₄ · H ₂ O ZnSO ₄ · 7H ₂ O Gluconic Acid (50% soln) As Given Below												
Test No.	Gluconic Acid (50% Aqueous Soln), g/l	Agitation	pH	Temp, F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Appearance of Deposit		
6922-50A	100	33 cpm, 1-1/4" stroke	4.0	85	25	3.4	94.7	0.6	0.0752	Milky to mat gray; slightly powdery		
-50B	100	Ditto	4.0	85	50	5.0	53.3	2.1	0.0845	Gray mat; slightly powdery		
-50C	100	"	4.0	85	100	6.0	30.6	4.1	0.0969	Like 50B, but more powdery		
-50D	100	"	6.0	85	25	3.7	83.0	0.9	0.0660	Milky center; gray mat edges		
-50E	100	"	6.0	85	50	5.0	51.5	1.1	0.0819	Powdery, brown-gray mat		
-50F	100	"	6.0	85	100	6.2	31.1	3.5	0.0983	No deposit in center; powdery edges		
-50G(1)	100	"	7.5	85	25	3.9	--	--	--	No deposit		
-50H	100	"	7.5	85	50	6.0	2.6	46.7	0.0034	Powdery, light brown		
-50I	100	"	7.5	85	100	6.2	1.9	33.0	0.0078	Ditto		
-60A	100	"	2.0	85	25	4.2	55.7	0.0	0.0443	Semibright		
-60B	100	"	2.0	85	50	4.8	64.5	<1.0	0.1023	Milky center, mat edges		
-60C	100	"	2.0	85	100	7.6	45.0	<1.0	0.1422	Milky center, edges varied from no de- posit to gray mat		
-60D	200	"	4.0	85	50	4.8	50.6	3.0	0.0803	Gray mat		
-60E	200	"	4.0	85	100	7.8	27.2	7.3	0.0852	Gray mat center; nodular and powdery edges		
-60F	300	"	4.0	85	50	5.2	31.4	6.2	0.0495	Milky gray		
-60G	300	"	4.0	85	100	7.2	11.7	9.7	0.0371	Gray mat		

TABLE 67. (Continued)

Test No.	Gluconic Acid (50% Aqueous Soln), g/l	Agitation	pH	Temp, F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Appearance of Deposit
0922-60H	300	33 cpm, 1-1/4" stroke	4.0	120	100	7.2	23.4	0.5	0.0714	Gray mat center; no deposit on edges
-60I	300	33 cpm, 1-1/4" stroke	4.0	120	100	7.5	48.3	< 1.0	0.1524	Gray mat center; powdery and nodular edges
-60J	300	33 cpm, 1-1/4" stroke	4.0	180	100	7.5	48.3	< 1.0	0.1524	Gray mat center; powdery and nodular edges
-60K	300	33 cpm, 1-1/4" stroke	4.0	180	100	7.5	48.3	< 1.0	0.1524	Gray mat center; powdery and nodular edges
-60L	300	33 cpm, 1-1/4" stroke	4.0	180	100	7.5	48.3	< 1.0	0.1524	Gray mat center; powdery and nodular edges
-60M	300	33 cpm, 1-1/4" stroke	4.0	180	100	7.5	48.3	< 1.0	0.1524	Gray mat center; powdery and nodular edges
-60N	300	33 cpm, 1-1/4" stroke	4.0	180	100	7.5	48.3	< 1.0	0.1524	Gray mat center; powdery and nodular edges
-60O	300	33 cpm, 1-1/4" stroke	4.0	180	100	7.5	48.3	< 1.0	0.1524	Gray mat center; powdery and nodular edges
-60P	300	33 cpm, 1-1/4" stroke	4.0	180	100	7.5	48.3	< 1.0	0.1524	Gray mat center; powdery and nodular edges
-60Q	300	33 cpm, 1-1/4" stroke	4.0	180	100	7.5	48.3	< 1.0	0.1524	Gray mat center; powdery and nodular edges
-60R	300	33 cpm, 1-1/4" stroke	4.0	180	100	7.5	48.3	< 1.0	0.1524	Gray mat center; powdery and nodular edges
-60S	300	33 cpm, 1-1/4" stroke	4.0	180	100	7.5	48.3	< 1.0	0.1524	Gray mat center; powdery and nodular edges
-60T	300	33 cpm, 1-1/4" stroke	4.0	180	100	7.5	48.3	< 1.0	0.1524	Gray mat center; powdery and nodular edges
-60U	300	33 cpm, 1-1/4" stroke	4.0	180	100	7.5	48.3	< 1.0	0.1524	Gray mat center; powdery and nodular edges
-60V	300	33 cpm, 1-1/4" stroke	4.0	180	100	7.5	48.3	< 1.0	0.1524	Gray mat center; powdery and nodular edges
-60W	300	33 cpm, 1-1/4" stroke	4.0	180	100	7.5	48.3	< 1.0	0.1524	Gray mat center; powdery and nodular edges
-60X	300	33 cpm, 1-1/4" stroke	4.0	180	100	7.5	48.3	< 1.0	0.1524	Gray mat center; powdery and nodular edges
-60Y	300	33 cpm, 1-1/4" stroke	4.0	180	100	7.5	48.3	< 1.0	0.1524	Gray mat center; powdery and nodular edges
-60Z	300	33 cpm, 1-1/4" stroke	4.0	180	100	7.5	48.3	< 1.0	0.1524	Gray mat center; powdery and nodular edges

(1) At pH 7.5, the baths precipitated after standing overnight.

Notes: Anodes - carbon rods in porous Aluminum cups
 Anolyte - Na₂SO₄ 142 g/l
 Cathodes - stainless steel, 2" x 9/16" (plated area)
 Time - 10 minutes

TABLE 68. CODEPOSITION OF MANGANESE AND ZINC FROM MIXED ALKANE SULFONIC ACID SOLUTIONS

Bath Composition: Electrolytic Manganese 40 g/l
Granular Zinc 10 g/l
Mixed Alkane Sulfonic Acids As Given Below

Test No.	Mixed Alkane Sulfonic Acids, g/l	pH	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, grams	Appearance of Deposit
6922-46A	250	0.3	25	3.0	--	--	--	No deposit
-46B	350	< 0.0	25	2.4	--	--	--	Ditto
-46C	450	< 0.0	25	2.6	--	--	--	"
-46D	250	0.3	50	1.0	1.1	0.0	0.0018	Very slight metallic deposit
-46E	350	< 0.0	50	.4	--	--	--	No deposit
-46F	450	< 0.0	50	3.6	--	--	--	Ditto
-46G	250	0.3	100	5.2	1.3	0.0	0.0043	Very slight metallic deposit
-46H	350	< 0.0	100	4.2	< 1.0	0.0	0.0010	Ditto
-46I	450	< 0.0	100	4.4	--	--	--	No deposit
-46J	250	0.3	200	8.0	4.7	1.3	0.0297	Gray, powdery center, bright edges
-46K	350	< 0.0	200	6.2	< 1.0	0.0	0.0030	Very slight metallic deposit
-46L	450	< 0.0	200	6.0	< 1.0	0.0	0.0010	Ditto

Notes: Agitation - work rod, 33 cpm, 1 1/4" stroke

Anodes - carbon rods in porous Aluminum cups

Anolyte - same as catholyte

Cathodes - stainless steel, 2" x 9/16"

Time - 10 minutes

Temperature - 80 F

After makeup each bath was filtered.

Footnotes for Table 69

- (1) Time 5 minutes.
- (2) At this pH the bath was turbid.

Notes: Anodes - carbon rods in porous Alundum cups

Anolyte - Na_2SO_4 142 g/l

Cathodes - stainless steel, 2" x 9/16" (plated area)

Time - 10 minutes, except as noted

TABLE 66. CODEPOSITION OF MANGANESE AND ZINC FROM SULFATE-MIXED ALKANE SULFONIC ACID SOLUTIONS

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 125 g/l
 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 44 g/l
Mixed Alkane Sulfonic Acids As Given Below

Test No.	Mixed Alkane Sulfonic Acids, g/l	Agitation	pH	Temp. F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gr/m	Appearance of Deposit
6923-48A	25	33 cpm, 1-1/4" stroke	1.0	80	100	4.9	20.5	2.6	0.3634	Milky, mat gray
-48B	50	Ditto	1.0	80	100	5.4	18.9	2.3	0.3598	Milky, mat gray center; bright edged
-48C	100	"	1.0	80	100	5.2	21.8	1.8	0.0687	Milky, mat gray center; bright edged
-48D	25	"	1.0	80	200	7.4	24.4	4.7	0.1529	Gray, mat center; powdery and nodular edges
-48E	50	"	1.0	80	200	8.4	28.1	6.2	0.1764	Milky, gray center; powdery and nodular edges
-48F	100	"	1.0	80	200	8.2	34.7	13.7	0.2015	Milky, gray center; powdery and nodular edges
-48G(1)	25	"	2.2(2)	80	100	5.6	47.6	31.7	0.0717	Gray and flaky
-48H(1)	50	"	2.2(2)	80	100	5.6	28.0	31.7	0.0422	Ditto
-48I(1)	100	"	2.2(2)	80	100	5.8	16.6	22.1	0.0247	"
-58A	100	"	1.0	120	200	9.2	43.5	5.9	0.2725	Milky gray center; blue, nodular and powdery edges
-58B	100	"	1.0	180	200	7.8	43.2	1.2	0.2723	Milky gray center; blue, nodular and powdery edges
-58C	100	None	1.0	80	200	8.2	36.3	10.9	0.2251	Milky gray center; black, nodular and powdery edges
-58D	100	99 cpm, 1-1/4" stroke	1.0	80	200	--	31.7	2.6	0.1995	Milky gray center; black, nodular and powdery edges
-58E	100	146 cpm, 1-1/4" stroke	1.0	80	200	--	23.1	< 1	0.1456	Milky, gray center; black, streaked edges

Footnotes appear on following page.

TABLE 70. CODEPOSITION OF MANGANESE AND ZINC; PRELIMINARY EXPERIMENTS WITH FLUOSILICATE SOLUTIONS

Test No.	H ₂ SiF ₆ , (30.5% Soln) g/l	C ₅ H ₅ N, g/l	Zn, g/l	Mn, g/l	pH	Current Density, amp/sq ft	Remarks
6922-24A	140	None	5	None	< 0.0	100	No deposit
-24B	140	10	5	None	< 0.0	100	Ditto
-24C	100	None	None	10	< 0.0	100	"
-24D	240	20	5	10	< 0.0	100	"

Notes: Agitation - none
Anodes - carbon rods in porous Aluminum cups
Anolyte - same as catholyte
Cathodes - stainless steel, 2" x 9/16"
Temperature - 80 F
Time - 10 minutes

TABLE 71. CODEPOSITION OF MANGANESE AND ZINC; PRELIMINARY EXPERIMENTS WITH SULFATE-THIOCYANATE SOLUTIONS

Test No.	NaCNS, g/l	ZnSO ₄ · 7H ₂ O, g/l	MnSO ₄ · H ₂ O, g/l	pH	Current Density, amp/sq ft	Remarks
6922-25A	100	None	80	2.0(1)	100	No deposit
-25B	100	40	None	2.0(1)	100	Mat gray, no manganese
-25C	100	20	40	2.0	100	Ditto

(1) At pH values above 2.0, a precipitate formed.

Notes: Agitation - none
Anodes - carbon rods in porous Aluminum cups
Anolyte - same as catholyte
Cathodes - stainless steel 2" x 9/16"
Temperature - 80 F
Time - 10 minutes

APPENDIX III

HYPOTHETICAL EXAMPLE OF FACTORIAL EXPERIMENT

As an example of a very simple factorial experiment, for electroplating, and the subsequent analysis of variance to which it would be subjected, the following is cited.

Suppose a plating bath were composed and operated as follows:

Ingredient A at 25 g/l
 Ingredient B at 50 g/l
 Current density C at 25 amp/sq ft

The object is to set up an experiment to determine the relationship between the three independent variables and the cathode current efficiency (a dependent variable). First, one decides how much and in what direction the variables are to be manipulated. For example, suppose the following levels are chosen:

For ingredient A, 25 and 50 g/l
 For ingredient B, 50 and 75 g/l
 For current density, 25 and 40 amp/sq ft

Next, a schedule of experiments is set up, including all combinations of the two levels of the three variables. This would be eight experiments. The chronological order of running the experiments would be randomized by drawing cards from a hat or using a table of random numbers. Suppose that the current efficiencies were found experimentally as listed in Table A.

TABLE A. EXPERIMENTAL CURRENT EFFICIENCIES

		Ingredient A			
		25 g/l(A ₁)		50 g/l(A ₂)	
		Ingredient B		Ingredient B	
		B ₁ , 50 g/l	B ₂ , 75 g/l	B ₁ , 50 g/l	B ₂ , 75 g/l
C ₁	25 amp/sq ft	l 59.8	b 51.5	a 65.8	ab 58.6
C ₂	40 amp/sq ft	c 55.5	bc 47.0	ac 58.0	abc 53.7

To interpret these data by inspection becomes increasingly difficult as the number of variables increases; therefore, a procedure known as analysis of variance is applied. In the present example the procedure would be carried out as follows:

Effect of	(Carry out this arithmetic to find V_x)
A	$-1 + a - b - c + ab + ac - bc + abc = V_A$
B	$-1 - a + b - c + ab - ac + bc + abc = V_B$
C	$-1 - a - b + c - ab + ac + bc + abc = V_C$
AB	$+1 - a - b + c + ab - ac - bc + abc = V_{AB}$
AC	$+1 - a + b - c - ab + ac - bc + abc = V_{AC}$
BC	$+1 + a - b - c - ab - ac + bc + abc = V_{BC}$
ABC	$-1 + a + b + c - ab - ac - bc + abc = V_{ABC}$

If the above is done on the values in the present example the results are:

For this effect	V_x	$\frac{V_x}{8} =$ Deviation from Mean	$\frac{V_x^2}{8} =$ Sum of Squares
A	+22.3	+2.79	62.22
B	-28.3	-3.54	100.18
C	-21.5	-2.69	57.84
AB	+5.3	+0.66	3.50
AC	-3.9	-0.49	1.91
BC	+2.7	+0.34	0.92
ABC	-3.1	-0.39	1.21

The analysis of variance can now be set up as given in Table B.

TABLE B. ANALYSIS OF VARIANCE FOR HYPOTHETICAL EXAMPLE OF ELECTROPLATING STUDY

Source of Variance	Degrees of Freedom	Sums of Squares	Mean Square	$\frac{1}{df}$	F	F (0.01)	F (0.001)	Effect
Ingredient A	1	62.22	62.22	1.88	35.2	21.2	74.1	+2.79
Ingredient B	1	100.18	100.18	"	53.3	"	"	-3.54
Current Density C	1	57.84	57.84	"	30.6	"	"	-2.69
AB	1	3.50	1.88					
AC	1	1.91						
BC	1	0.92						
ABC	1	1.21						
Totals	7	227.78						

From these data, we decide that an increase in the amount of Ingredient A in the bath increases the cathode current efficiency of the bath; increasing Ingredient B or increasing the cathode current density decreases the current efficiency. In each of these conclusions there is a risk of error. However, the F for each of the first three lines in the analysis of variance lies between $F(0.01)$ and $F(0.001)$. This indicates that in each case there is less than one chance in a hundred that such results would have been obtained if there were no difference due to A, B, or C. It is more sensible to assume that A, B, and C had their effects, rather than not.

In Table B, under "Source of Variance" are also recorded the interactions AB, AC, etc. In this example, the sums of squares for the interactions were of such magnitude that any effects were considered to be of chance origin.

EXPERIMENTAL DESIGN FOR INVESTIGATION OF THE MANGANESE-TIN SULFATE-TARTRATE SOLUTION

A $1/8$ replicate of a 2^9 factorial experiment* was used to investigate the manganese-tin plating system.

To carry out a full 2^9 experiment, 512 plates would have to be prepared; using a $1/8$ replicate design, this number was reduced to 64. Information on interactions is sacrificed by fractional replication; in this case, the AB, AC, AD, BC, BD, and CD interactions were lost. Three-factor and higher interactions were so complicated by so-called aliases that they were not computed.

The $1/8$ replicate used was based upon the ABCD, ABEFG, and ACEHI interactions** as generators. In describing a treatment condition, any parameter which is at its high level is designated by its letter, and at its low level by no letter. For example, acd would indicate a treatment combination in which A, C, and D were each at their high level, whereas all of the other parameters were at their low levels. Using this convention, those combinations having an even number of letters in common with all of the generators were selected to be imposed on the manganese-tin plating bath. For example, such combinations as bdefgh, fg, and abef were chosen because each has an even number of letters in common with each of the generators.

Randomization was applied to the chronological order in which the conditions were run and to determine which specimen received any particular treatment.

TABLE 72. CODEPOSITION OF MANGANESE AND TIN FROM A SULFATE-TARTRATE SOLUTION;
PREPARATION OF PANELS FOR "WET-DRY" TEST

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 100 g/l
 SnSO_4 2 g/l
 $(\text{NH}_4)_2\text{SO}_4$ 250 g/l
Tartaric Acid(1) 25 or 50 g/l
 Na_2SO_3 0.5 g/l
Glue 0.3 g/l
pH 8.0

Test No.	Time, min	Cell Volts	Cathode Efficiency, %	Tin in Deposit, %	Thickness of One Side, mil	Weight of Deposit, gram	Remarks
153 -22A(2)	15	6.7	5.7	44.0	0.45	0.223	-
-22C	12	6.7	-	-	0.3	0.150	Coating tested in "wet-dry" cabinet
-22E(2)	15	6.6	5.4	47.0	0.4	0.216	-
-22G	11.5	6.5	-	-	0.35	0.145	Coating tested in "wet-dry" cabinet
-22J(2)	15	6.3	4.7	45.1	0.35	0.184	-
-22J	13	6.2	-	-	0.25	0.146	Coating tested in "wet-dry" cabinet
-22L	15	5.8	3.1	45.3	0.2	0.120	-
-24B(2)	13	6.8	-	-	0.3	0.159	Coating tested in "wet-dry" cabinet
-24E	15	6.3	3.4	40.9	0.2	0.135	-

(1) Tests -22A through -22G were run with the tartaric acid at 25 g/l; tests -22J through -24E were run with the tartaric acid at 50 g/l.

(2) Fresh bath.

Notes: Anodes - Carbon rods in Aluminum cups

Cathodes - SAE 1010, 3" x 1", for analysis; SAE 4130, 3" x 1", for "wet-dry"

Temperature - 100 F

Current Density - 240 amp/sq ft

TABLE 73. ANALYSIS OF VARIANCE OF EFFECT OF MANGANESE-TIN
PLATING CONDITIONS ON CELL VOLTAGE

Source of Variance	Degrees of Freedom	Sums of Squares	Mean Squares	Error Mean Square for F	F	F (0.05)	F (0.01)	Levels		Deviation From Mean (Mean = 7.05 volts)
								High	Low	
Clue Content of Bath (A)	1	0.29	0.29	0.205	1.4	4.0	7.3	0.3 g/l	0.1 g/l	-0.07
pH of Bath (B)	1	3.02	3.02	0.205	14.7	4.0	7.3	8.0	7.0	-0.22
Bath Temperature (C)	1	17.53	17.53	0.205	85.5	4.0	7.3	140 F	100 F	-1.05
Current Density (D)	1	37.97	37.97	0.205	185.0	4.0	7.3	360 ASF	240 ASF	+1.56
Sodium sulfite in Bath (E)	1	0.24	0.24	0.205	1.2	4.0	7.3	1.0 g/l	0.5 g/l	-0.06
Tartaric Acid in Bath (F)	1	0.70	0.70	0.205	3.4	4.0	7.3	50 g/l	25 g/l	-0.10
Ammonium Sulfate in Bath (G)	1	0.34	0.34	0.205	1.6	4.0	7.3	250 g/l	200 g/l	-0.09
Manganese Sulfate in Bath (H)	1	1.99	1.99	0.205	9.7	4.0	7.3	150 g/l	100 g/l	+0.07
Tin Sulfate in Bath (I)	1	0.26	0.26	0.205	1.2	4.0	7.3	2.0 g/l	1.0 g/l	-0.12
EH	1	0.93	0.93	0.205	4.5	4.0	7.3			
Error	53	10.85		0.205						
Totals	53	74.12								

TABLE 74. ANALYSIS OF VARIANCE OF EFFECT OF MANGANESE-TIN
PLATING CONDITIONS ON QUALITY RATING OF PLATE

Source of Variance	Degrees of Freedom	Sums of Squares	Mean Squares	Error Mean Square for F	F	F (0.05)	F (0.01)	F (0.001)	Levels		Deviation from Mean (Mean = 32.6)
									High	Low	
Glue Content of Bath (A)	1	1918.35	1918.35	160.7	11.9	4.0	7.2	12.3	0.3 g/l	0.1 g/l	-5.5
pH of Bath (B)	1	5.88	5.88	160.7	0.0	4.0	7.2	12.3	8.0	7.0	+0.3
Bath Temperature (C)	1	720.93	720.93	160.7	4.5	4.0	7.2	12.3	140 F	100 F	+3.4
Current Density (D)	1	813.67	813.67	160.7	5.1	4.0	7.2	12.3	360 ASF	240 ASF	+3.6
Sodium Sulfate in Bath (E)	1	193.21	193.21	160.7	1.2	4.0	7.2	12.3	1.0 g/l	0.5 g/l	+1.7
Tartaric Acid in Bath (F)	1	7.83	7.83	160.7	0.0	4.0	7.2	12.3	50 g/l	25 g/l	-
Ammonium Sulfate in Bath (G)	1	895.51	795.51	160.7	5.6	4.0	7.2	12.3	250 g/l	200 g/l	-3.8
Manganese Sulfate in Bath (H)	1	470.89	470.89	160.7	3.0	4.0	7.2	12.3	150 g/l	100 g/l	+2.7
Tin Sulfate in Bath (I)	1	0.36	0.36	160.7	0.0	4.0	7.2	12.3	2.0 g/l	1.0 g/l	-
BU	1	987.53	987.53	160.7	6.1	4.0	7.2	12.3			+3.9
CG	1	1272.69	1272.69	160.7	7.9	4.0	7.2	12.3			-4.4
CI	1	767.28	767.28	160.7	4.8	4.0	7.2	12.3			-3.5
EH	1	798.06	798.06	160.7	5.0	4.0	7.2	12.3			-3.5
Error	50	8049.04	160.7								
Totals	63	16901.23									

TABLE 75. ANALYSIS OF VARIANCE OF EFFECT OF MANGANESE-TIN PLATING CONDITIONS ON PER CENT TIN IN PLATE

Source of Variance	Degrees of Freedom	Sums of Squares	Mean Squares	Error Mean Square for F	F	F (0.05)	F (0.01)	Levels		Deviation From Mean (Mean = 56.2%)
								High	Low	
Glue Content of Bath (A)	1	995.32	995.32	14.00	71.0	4.1	12.4	0.3 g/l	0.1 g/l	-3.9
pH of Bath (B)	1	143.41	143.41	14.00	10.2	4.1	12.4	8.0	7.0	+1.5
Bath Temperature (C)	1	800.90	800.90	14.00	57.2	4.1	12.4	140 F	100 F	+3.6
Current Density (D)	1	19.15	19.15	14.00	1.4	4.1	12.4	360 ASF	240 ASF	-
Sodium Sulfite (E)	1	118.81	118.81	14.00	8.5	4.1	12.4	1.0 g/l	0.5 g/l	+1.4
Tartaric Acid (F)	1	18.93	18.93	14.00	1.3	4.1	12.4	50 g/l	25 g/l	-
Ammonium Sulfate (G)	1	643.90	643.90	14.00	46.0	4.1	12.4	250 g/l	200 g/l	+3.2
Manganese Sulfate (H)	1	63.61	63.61	14.00	4.5	4.1	12.4	150 g/l	100 g/l	+1.6
Tin Sulfate (I)	1	534.78	534.78	14.00	38.2	4.1	12.4	2.0 g/l	1.0 g/l	+2.9
AG	1	147.10	147.10	14.00	10.5	4.1	12.4			-1.5
AI	1	154.45	154.45	14.00	11.0	4.1	12.4			-1.6
BH	1	201.63	201.63	14.00	14.3	4.1	12.4			+1.8
CE	1	60.84	60.84	14.00	4.3	4.1	12.4			-1.6
DG	1	68.05	68.05	14.00	4.9	4.1	12.4			-1.0
EG	1	57.38	57.38	14.00	4.1	4.1	12.4			+0.9
FG	1	59.67	59.67	14.00	4.3	4.1	12.4			-1.0
FI	1	83.25	83.25	14.00	5.9	4.1	12.4			-1.1
Error	46	643.38	14.00							
Totals	63	4996.85								

TABLE 76. ANALYSIS OF VARIANCE OF EFFECT OF MANGANESE-TIN PLATING CONDITIONS ON CATHODE CURRENT EFFICIENCY

Source of Variance	Degrees of Freedom	Sums of Squares	Mean Squares	Error Mean Square for F	F	F (0.05)	F (0.01)	F (0.001)	Levels		Deviation: From Mean (Mean = 4.10%)
									High	Low	
Glue Content of Bath (A)	1	0.45	0.45	0.557	0.8	1.0	7.2	12.3	0.3 g/l	0.1 g/l	-0.62
pH of Bath (B)	1	6.64	6.64	0.557	11.9	4.0	7.2	12.3	8.0	7.0	-0.53
Bath Temperature (C)	1	4.96	4.96	0.557	8.8	4.0	7.2	12.3	140 F	100 F	-0.62
Current Density (D)	1	25.60	25.60	0.557	46.0	4.0	7.2	12.3	360 ASF	240 ASF	-
Sodium Sulfite (E)	1	0.00	0.00	0.557	0.0	4.0	7.2	12.3	1.0 g/l	0.5 g/l	-
Tartaric Acid in Bath (F)	1	0.00	0.00	0.557	0.0	4.0	7.2	12.3	50 g/l	25 g/l	-
Ammonium Sulfate in Bath (G)	1	1.13	1.13	0.557	2.0	4.0	7.2	12.3	250 g/l	200 g/l	-0.49
Manganese Sulfate in Bath (H)	1	10.00	10.00	0.557	18.0	4.0	7.2	12.3	150 g/l	100 g/l	+1.00
Tin Sulfate in Bath (I)	1	63.52	63.52	0.557	114.0	4.0	7.2	12.3	2.0 g/l	1.0 g/l	-0.38
Error	52	28.90	0.557		16.6	4.0	7.2	12.3			-0.19
Totals	63	152.34			4.1	4.0	7.2	12.3			

TABLE 77. ESSENTIAL EXPERIMENTAL DATA ON EVALUATION OF

		Independent Plating and Bath Conditions								
Specimen No.	Code	A Glue Content, g/l	B pH	C Temperature, F	D Cathode Current Density, amp/sq ft	E Na ₂ SO ₃ , g/l	F Tartaric Acid, g/l	G (NH ₄) ₂ SO ₄ , g/l	H MnSO ₄ ·H ₂ O, g/l	I SnSO ₄ , g/l
5022-80A (100S)	ABCDEFH	0.3	8.0	140	360	1.0	50	200	150	1.0
-74H (213S)	ABCDEFI	"	"	"	"	"	"	"	100	2.0
-76D (164S)	ABCDEGH	"	"	"	"	"	25	250	150	1.0
-70B (154S)	ABCDEGI	"	"	"	"	"	"	"	100	2.0
-79I (209S)	ABCDFGHI	"	"	"	"	0.5	50	"	150	"
-82B (2S)	ABCDFG	"	"	"	"	"	"	"	100	1.0
-80I (265S)	ABCDHI	"	"	"	"	"	25	200	150	2.0
-70A (250S)	ABCD	"	"	"	"	"	"	"	100	1.0
-76F (152S)	ABEFHI	"	"	100	240	1.0	50	"	150	2.0
-78B (93S)	ABEF	"	"	"	"	"	"	"	100	1.0
-78F (266S)	ABEGHI	"	"	"	"	"	25	250	150	2.0
-72E (78S)	ABEG	"	"	"	"	"	"	"	100	1.0
-82D (7S)	ABFGH	"	"	"	"	0.5	50	"	150	"
-80C (245S)	ABFGI	"	"	"	"	"	"	"	100	2.0
-74F (28S)	ABH	"	"	"	"	"	25	200	150	1.0
-70F (27S)	ABI	"	"	"	"	"	"	"	100	2.0
-80D (46S)	ACEFGH	"	7.0	"	"	1.0	50	250	150	1.0
-78A (223S)	ACEFGI	"	"	"	"	"	"	"	100	2.0
-80B (43S)	ACEH	"	"	"	"	"	25	200	150	1.0
-74E (202S)	ACEI	"	"	140	"	"	"	"	100	2.0
-74I (97S)	ACFHI	"	"	"	"	0.5	50	"	150	"
-76B (185S)	ACF	"	"	"	"	"	"	"	100	1.0
-70C (113S)	ACGHI	"	"	"	"	"	25	250	150	2.0
-84A (241S)	ACG	"	"	"	"	"	"	"	100	1.0
-72C (175S)	ADEFGHI	"	"	100	360	1.0	50	"	150	2.0

PERFORMANCE OF MANGANESE-TIN ALLOY-PLATING BATH

Resultant Values of Dependent Variables					
Plating Cell Voltage	Quality Rating of Plate	Per Cent Sn in Plate	Cathode Current Efficiency	Condition of Plating Bath	Description of Plate
7.4	56.3	59.6	1.65	Considerable white precipitate formed	Dark-gray, slightly round deposit with poor adherence
6.8	24.3	52.0	5.78	Ditto	Gray mat deposit with dull edges and some treeing
6.9	56.3	59.6	2.24	"	Dark-gray mat deposit with somewhat flaky edges
7.5	24.3	52.0	6.16	No precipitate	Dark-gray mat deposit with blue stains; very slightly powdery surface
6.9	33.6	62.0	2.10	Moderate amount of white precipitate formed	Light-gray mat in center; edges blistered and nonadherent
6.0	27.3	49.7	3.01	No precipitate	Moderately dark mat plate
8.4	45.6	53.1	1.92	Considerable white precipitate formed	Very poorly adherent deposit
7.1	49.0	48.1	2.16	Ditto	Golden brown at bottom center; then powdery gray zone; dark dull edges
6.7	64.6	65.4	6.17	No precipitate	Dark-gray mat deposit with rough edges
6.5	49.0	50.2	4.08	Ditto	Gray mat deposit with dark edge
6.5	30.0	48.7	4.73	"	Medium-brown mat deposit, gray on other side, slight powdering
5.4	24.3	58.9	3.58	No precipitate	Gray mat with some shininess; blistered and flaked edges
6.2	18.3	47.3	3.34	Ditto	Dark mat, seems to have fairly good adherence
6.1	23.3	50.0	5.99	"	Powdery over a mat; dark-brownish gray
6.8	21.3	47.8	3.27	Considerable white precipitate formed	Light-gray mat with darker edges
7.0	6.3	47.5	6.25	No precipitate	Light, hard dense mat with slight edge treeing
6.2	44.0	58.2	3.76	Ditto	Golden mat in center; edges nonadherent
5.4	8.0	57.4	6.02	Very small amount of white precipitate formed	Golden mat with darker edges
6.3	38.0	43.4	4.19	Considerable white precipitate formed	Dark-gray mat in center; non-adherent edges
6.2	32.0	55.5	7.25	No precipitate	Light mat with slightly blistered edges and slight treeing
5.9	32.3	54.9	6.03	Considerable white precipitate formed	Smooth mat with blistered edges and deep-blue center
5.8	31.0	57.6	3.28	No precipitate	Gray mat in center; blistered edges
6.7	9.0	62.5	6.84	Ditto	Light-gray mat with some brown stains; dense and hard
5.4	17.3	52.7	3.89	"	Dark mat with blisters on edges; center with good appearance
8.4	9.3	50.4	3.81	"	Light-gray mat with slightly treed edges

TABLE 77

Specimen No.	Code	Independent Plotting and Bath Conditions								
		A	B	C	D	E	F	G	H	I
		Glue Content, g/l	pH	Temperature, F	Cathode Current Density, amp/sq ft	Na ₂ SO ₃ , g/l	Tartaric Acid, g/l	(NH ₄) ₂ SO ₄ , g/l	MnSO ₄ · H ₂ O, g/l	SnSO ₄ , g/l
5022-72H (151S)	ADEFG	0.3	7.0	100	360	1.0	50	250	100	1.0
-72B (226S)	ADEHI	"	"	"	"	"	25	200	150	2.0
-80F (167S)	ADE	"	"	"	"	"	"	"	100	1.0
-70H (15)	ADFH	"	"	"	"	0.5	50	"	150	"
-78C (68S)	ADFI	"	"	"	"	"	"	"	100	2.0
-76C (63S)	ADGH	"	"	"	"	"	25	250	150	1.0
-80H (180S)	ADGI	"	"	"	"	"	"	"	100	2.0
-72G (120S)	BCFGHI	0.1	8.0	140	240	1.0	50	"	150	"
-70I (231S)	BCEFG	"	"	"	"	"	"	"	100	1.0
-76E (252S)	BCEHI	"	"	"	"	"	25	200	150	2.0
-76H (233S)	BCE	"	"	"	"	"	"	"	100	1.0
-82E (227S)	BCFH	"	"	"	"	0.5	50	"	150	"
-82I (47S)	BCFI	"	"	"	"	"	"	"	100	2.0
-78E (69S)	BCGH	"	"	"	"	"	25	250	150	1.0
-72I (254S)	BCGI	"	"	"	"	"	"	"	100	2.0
-74A (52S)	BDEFGH	"	"	100	360	1.0	50	"	150	1.0
-76G (6S)	BDEFGI	"	"	"	"	"	"	"	100	2.0
-72A (229S)	BDEH	"	"	"	"	"	25	200	150	1.0
-76I (196S)	BDEI	"	"	"	"	"	"	"	100	2.0
-76A (230S)	BDFHI	"	"	"	"	0.5	50	"	150	"
-70E (3S)	BDF	"	"	"	"	"	"	"	100	1.0
-78B (40S)	BDEHI	"	"	"	"	"	25	250	150	2.0
-74G (44S)	BEG	"	"	"	"	"	"	"	100	1.0
-82G (221S)	CDEFHI	"	7.0	140	"	1.0	50	200	150	2.0
-82H (215S)	CDEF	"	"	"	"	"	"	"	100	1.0
-74H (197S)	CDEGHI	"	"	"	"	"	25	250	150	2.0
-72D (143S)	CDEG	"	"	"	"	"	"	"	100	1.0

(Continued)

Plating Cell Voltage	Quality Rating of Plate	Resultant Values of Dependent Variables			
		Per Cent Sn in Plate	Cathode Current Efficiency	Condition of Plating Bath	Description of Plate
8.2	58.3	48.7	2.70	Slight amount of precipitate formed	Poorly adherent, slightly shiny mat; slightly treed edges; dark near edges
8.3	10.3	49.0	4.83	Considerable white precipitate formed	Light-gray mat with slightly treed edges
8.9	37.3	42.9	2.84	No precipitate	Dark-gray mat overlaid with powdery layer
9.2	12.6	45.9	2.86	Considerable white precipitate formed	Dense, slightly shiny mat with blue and purple marks
8.5	10.3	44.8	5.55	No precipitate	Gray mat with slightly treed edges
8.7	7.3	47.0	2.89	Ditto	Ditto
8.7	41.3	50.0	4.58	"	Slightly blistered mat with dark center and lighter edges
5.5	23.6	75.7	2.53	Moderate amount of white precipitate formed	Powdery, light-gray mat
5.4	31.0	69.8	3.27	No precipitate	Light-gray slightly powdery mat
5.7	41.0	68.0	2.94	Considerable white precipitate formed	Dark-gray mat with powdery overlay and nonadherent edges
5.8	38.3	54.6	4.69	Ditto	Gray mat with dark nonadherent edges
5.6	57.0	60.0	2.12	"	Dark with very poor adherence; cracked and flaked
5.3	23.6	58.3	6.82	Small amount of precipitate formed	Gray mat with lighter edges
6.1	25.0	67.0	2.28	Ditto	Dark-gray mat with slightly powdery edges
5.4	36.3	77.7	4.57	No precipitate	Light-gray powdery mat
7.7	42.6	61.6	2.42	Ditto	Dark-gray powdery mat with treed edges
8.6	26.0	66.3	4.63	"	Dark-gray powdery mat
9.1	42.6	57.3	2.41	"	Ditto
8.2	51.6	55.5	5.01	"	Dark-gray mat; nonadherent in places
7.8	51.3	59.1	4.29	Small amount of white precipitate formed	Golden-brown mat with some flaking and blistering in center
8.3	17.0	45.7	3.68	Considerable white precipitate formed	Gray, slightly powdery mat with treed edges
8.6	48.0	68.3	3.55	No precipitate	Dark-gray mat with slightly powdery, nonadherent edges
7.9	28.3	50.1	3.10	Ditto	Very dark-gray, slightly powdery mat; treed edges
7.5	63.3	58.4	4.37	Moderate amount of white precipitate formed	Light-gray mat with blistered and flaked edges
7.3	64.3	59.8	1.96	Ditto	Very poorly adherent, cracked and flaked mat
7.3	25.6	74.0	3.98	Moderate amount of white precipitate formed	Light-gray, slightly powdery mat with treed edges
7.4	42.6	63.3	2.76	No precipitate	Light-gray powdery center; edges dark and flaking

TABLE 77.

		Independent Plating and Bath Conditions								
Specimen No.	Code	A	B	C	D	E	F	G	H	I
		Glue Content, g/l	pH	Temperature, F	Cathode Current Density, amp/sq ft	Na ₂ SO ₃ , g/l	Tartaric Acid, g/l	(NH ₄) ₂ SO ₄ , g/l	MnSO ₄ ·H ₂ O, g/l	SnSO ₄ , g/l
5022-80G (201S)	CDGH	0.1	7.0	140	360	0.5	50	250	150	2.0
-80E (16S)	CDFGI	"	"	"	"	"	"	"	100	1.0
-82F (111S)	CDH	"	"	"	"	"	25	200	150	2.0
-70G (228S)	CDI	"	"	"	"	"	"	"	100	"
-78G (22S)	EFH	"	"	100	240	1.0	50	"	150	1.0
-72F (189S)	EFI	"	"	"	"	"	"	"	100	2.0
-74C (149S)	EGH	"	"	"	"	"	25	250	150	1.0
-74D (228S)	EGI	"	"	"	"	"	"	"	100	2.0
-82C (79S)	FGHI	"	"	"	"	0.5	50	"	150	"
-70D (178S)	FG	"	"	"	"	"	"	"	100	1.0
-82A (95S)	HI	"	"	"	"	"	25	200	150	2.0
-78H (106S)	O	"	"	"	"	"	"	"	100	1.0

(Continued)

Resultant Values of Dependent Variables					
Plating Cell Voltage	Quality Rating of Plate	Per Cent Sn in Plate	Cathode Current Efficiency	Condition of Plating Bath	Description of Plate
8.2	47.3	61.5	2.44	Small amount of precip- itate formed	Medium-gray mat center with dark nonadherent edges
7.3	26.3	70.0	4.12	No precipitate	Medium-gray, somewhat powdery mat
8.0	55.6	48.3	2.31	Considerable amount of white precipitate formed	Very poorly adherent, cracked and flaked mat
6.7	35.3	61.7	4.70	Considerable amount of precipitate formed	Light-gray powdery deposit with dark edges and some treeing
6.7	13.6	46.1	3.81	No precipitate	Gray mat center with dark edges
6.8	61.0	59.9	6.60	Ditto	Light-gray mat with poor adherence
6.8	30.6	53.5	3.53	Moderate amount of white precipitate formed	Light mat with powdery overlay; some treeing at edges
6.8	23.6	70.8	6.05	No precipitate	Ditto
8.9	47.3	58.9	7.39	Ditto	Powdery, blistered and flaking
6.7	19.0	48.2	4.54	"	Hard, light-gray mat with dark and dull edges
7.8	50.6	50.2	7.38	"	Powdery, slightly flaked and blistered
7.1	28.0	43.8	4.09	"	Dark-gray mat with powdery overlay

TABLE 78. ESSENTIAL EXPERIMENTAL DATA ON "PREDICTED"

Specimen Number	Code	Independent Plating and Bath Conditions						
		A	B	C	D	E	F	G
		Glue Content, g/l	pH	Tempera- ture, F	Cathode Current Density, amp/sq ft	Na ₂ SO ₃ , g/l	Tartaric Acid, g/l	(NH ₄) ₂ SO ₄ , g/l
6530-40I	aegh	0.3	7.0	100	240	1.0	25	250
-40A	aefgh	0.3	7.0	100	240	1.0	50	250
-40C	abg	0.3	8.0	100	240	0.5	25	250
-40E	abfg	0.3	8.0	100	240	0.5	50	250
-40H	aeh	0.3	7.0	100	240	1.0	25	200
-40B	aefh	0.3	7.0	100	240	1.0	50	200
-40D	ab	0.3	8.0	100	240	0.5	25	200
-42A	abf	0.3	8.0	100	240	0.5	50	200
-40G	aceghi	0.3	7.0	140	240	1.0	25	250
-42D	acefghi	0.3	7.0	140	240	1.0	50	250
-42B	abcgi	0.3	8.0	140	240	0.5	25	250
-42C	abcfgi	0.3	8.0	140	240	0.5	50	250

H	I	Resultant Values of Dependent Variables				
		Plating Cell Voltage	Per Cent Sn in Plate	Cathode Current Efficiency, per cent	Condition of Plating Bath	Description of Plate
MnSO ₄ ·H ₂ O, g/l	SnSO ₄ , g/l					
150	1.0	7.6	46.2	7.6	Clear	Hard, almost semibright mat plate with slightly dark edges.
150	1.0	7.3	47.9	7.3	Slightly cloudy	Semibright mat plate with irregular brown stains, very uniform.
100	1.0	7.0	45.1	7.0	Fairly clear	Dull, hard, uniform mat deposit. Light-gray, very slightly dark edges.
100	1.0	7.2	44.1	7.2	Clear	Semibright mat deposit with dull and darkened edges.
150	1.0	7.8	43.9	7.8	Slightly cloudy	Dark-stained, almost semibright plate with a light border next to a darker edge.
150	1.0	7.8	44.2	7.8	Fairly clear	Bluish colored, semibright mat plate with slightly dark edges.
100	1.0	7.5	45.1	7.0	Clear	Dull, hard, uniform gray mat deposit with very slightly darkened edges.
100	1.0	7.1	43.7	7.1	Slight, white precipitate	Semibright mat plate in center with fairly wide, dark, dull edges.
150	2.0	6.3	57.9	6.3	Clear	Dull, hard, uniform mat deposit with a series of small blisters and chips around edges; very slight treeing.
150	2.0	7.2	49.7	6.0	Considerable crystalline precipitate	Semibright mat plate with dull but not dark edges.
100	2.0	6.2	61.0	6.2	Slightly cloudy	Dull mat plate, slightly powdery.
100	2.0	5.8	60.3	5.8	Slightly cloudy	Dull mat plate, slightly powdery.

Method Used in Locating Lines A and A'
in Figures 11, 12, and 13

To show how the Lines A and A' were located on Figure 11, consider the analysis of variance for cell voltage on page AIII-5 (Appendix III). The mean square error for voltage was reported 0.205 with 52 degrees of freedom. Entering a table for F at the 5 per cent probability level and with one degree of freedom for the variate, it is found that the $F = 4.02$. This is the ratio of square of the random variation of an observation to the mean square of the error of the 52 observations. Therefore, the error of an individual measurement at a 5 per cent level is

$$\pm \sqrt{4.02(0.205)} = \pm 0.910 \text{ voltage.}$$

At this distance vertically from Line B, the Lines A and A' are drawn. The corresponding lines on Figures 12 and 13 were located similarly.

Method Used in Estimating Performance of "Predicted" Baths

The performance of the 12 "predicted" baths was estimated by computation from the analyses of variance. For this computation*, additivity of effects of variables was assumed although it was known that actually the effects are probably not additive. This approximation was used because a better one is not known.

To show this computation, an example is given. To find the expected voltage for one of the "predicted" baths, aegh, Table 9, the analysis of variance showed that the significant effects on voltage were:

<u>Source of Variance</u>	<u>Deviation from Mean</u>
pH of Bath (B)	-0.32
Bath Temperature (C)	-1.05
Current Density (D)	+1.56
Manganese Sulfate in Bath (H)	+0.16
DG**	-0.12

*This method is that given in The Design and Analysis of Factorial Experiments, Imperial Bureau of Soil Science, Harpenden, England, 1937, p 13.

**Where G is the factor designator for the manganese sulfate concentration (level) in the bath.

Then the voltage to be expected across the bath aegh is:

7.05	= Mean plating voltage
+0.22	= Effect of low level of B
+1.05	= Effect of low level of C
-1.56	= Effect of low level of D
+0.16	= Effect of high level of H
+0.12	= Effect of low level of D in the presence of a high level of G
7.04	Total = Predicted voltage

This predicted value will not be the same as the experimental value except in rare cases. The difference between the two will vary subject to the standard error found in the analysis of variance and perhaps to an additional constant error due to differences between batches of specimens run at different times and, therefore, by slightly different techniques.

Agreement Between Predicted and Experimental Results

Except for the plating voltage, the agreement between the predicted and experimental values is within the margins of error established by the analyses of variance. The values for the plating voltage averaged 0.9 volt higher than expected. This is attributed to a slight change in the design of the anode in the cell.

The design of the cell was changed by attachment of rubber tubes to the anodes to carry away any foam produced inside the Alundum thimbles. Drilled holes in the anodes connected the tubes with the free space inside the thimbles. Each anode was held in its thimble by a drilled rubber stopper plugging the open end of the thimble. This design probably tended to lower the liquid level around the anodes thereby tending to increase anodic voltage. Lowering of the liquid level might have been due to back gas pressure caused by the length of rubber tubing and/or loss of liquid from the thimble in the foam.

Quality ratings of the plates were not graphed because all were expected to be of nearly the same rating. It would not have been possible to evaluate the new specimens in the original quality-rating system because the original specimens were destroyed for analysis.

TABLE 79. CODEPOSITION OF MANGANESE AND TIN FROM
A SULFATE-FLUORIDE BATH

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110 g/l
 SnSO_4 21.6 g/l
 NaF 40 g/l
pH 1.9-2.1

Test No.	Addition Agent	Temp, F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Appearance of Deposit
6606-64B	None	80	50	--	--	< 1	--	Muddy, nonadherent deposit
-64A	None	80	100	--	--	< 1	--	Ditto
-64D	None	160	50	--	--	> 1<5	--	"
-64C	None	160	100	--	--	> 1<5	--	"
-64F	X(1) 2 g/l	80	50	3.0	--	--	--	"
-64I	Gelatin(2) 2 g/l	80	50	3.6	--	20	0.0494	Powdery center, treed edges; best deposit thus far
-64G	Alrosol(3) 2 g/l	80	50	3.4	43.1	4.5	0.0587	Uniform brown-gray mat
-64H	Hide Glue 2 g/l	80	50	3.4	45.5	30	0.0338	Coarsely crystalline center, heavily treed edges; due to poor adherence, part of the deposit was lost making efficiency determination impossible
-708	Alrosol(3) 2 g/l	80	100	4.4	--	--	--	

Notes: No agitation

Anodes - round carbon rods in porous Alundum cups

Anolyte - same as catholyte

Cathodes - SAE 1010 steel, 2" x 1/2" (plated area)

Time - 10 minutes

(1) X is a proprietary compound, still under development. Its composition has not been revealed.

(2) Keystone No. 431, purchased from R. O. Hull and Company, Inc., Rocky River 16, Ohio.

(3) Alrosol is a nonionic wetting agent of the fatty acid amide type. Manufactured by Alrose Chemical Company, Providence, Rhode Island.

TABLE 80. CODEPOSITION OF MANGANESE AND TIN FROM A SULFATE-FLUORIDE SOLUTION;
EFFECT OF AGITATION AND ADDITION AGENT MIXTURES

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110 g/l
 SnSO_4 21.6 g/l
 NaF 40 g/l
 pH 1.9-2.1

Test No.	Addition Agent	Agitation	Temp. F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Appearance of Deposit
-70A	Alrosol	2 g/l 33 cpm, 1-1/4" stroke	80	100	4.2	20.4	18	0.0930	Coarsely crystalline center, treed edges, poor adherence, slightly better cohesion than 70B (Table 10)
-70C	Alrosol	2 g/l None	150	100	3.7	77.8	47	0.2920	Coarsely crystalline center, treed edges, fair adhesion and cohesion
-70D	Alrosol	2 g/l 33 cpm, 1-1/4" stroke	150	100	3.4	83.7	51	0.3145	Uniformly and coarsely crystalline, fair adherence and cohesion
-70E	Alrosol	2 g/l 99 cpm, 1-1/4" stroke	150	100	3.8	71.0	32	0.3061	Like 70D but with finer crystals
-70F	Alrosol	2 g/l 146 cpm, 1-1/4" stroke	150	100	3.8	85.5	9.5	0.4209	Ditto
-84A	Alrosol	0.25 g/l 33 cpm, 1-1/4" stroke	150	100	3.3	64.7	0.5	0.3413	Coarsely crystalline center, treed edges, poor adhesion and cohesion
-84B	Hide Glue	0.25 g/l 33 cpm, 1-1/4" stroke	150	100	4.4	46.2	2.0	0.2382	Fine-grained, mat center, treed edges, poor adherence and cohesion
-84C	Alrosol Hide Glue	0.25 g/l 33 cpm, 1-1/4" stroke 0.25 g/l	150	100	3.6	70.2	9.5	0.3459	Coarsely crystalline center, treed edges, poor adherence and cohesion
-84D	Alrosol	5.0 g/l 33 cpm, 1-1/4" stroke	150	100	5.0	39.5	33	0.1852	Gray, flaky deposit
-84E	Hide Glue	5.0 g/l 33 cpm, 1-1/4" stroke	150	100	4.0	67.0	17.5	0.3223	Fine-grained center, treed edges, poor adherence and cohesion
-84F	Alrosol Hide Glue	5.0 g/l 33 cpm, 1-1/4" stroke 5.0 g/l	150	100	4.5	47.5	83.0	0.2227	Gray, flaky deposit

Footnotes appear on the following page.

Footnotes for Table 80

Notes: Anodes - round carbon rods in porous Alundum cups
Anolyte - same as catholyte
Cathode - SAE 1010 steel, 2" x 1/2" (plated area)
Time - 10 minutes

TABLE 81. CODEPOSITION OF MANGANESE AND TIN FROM SULFATE-FLUORIDE SOLUTIONS; EFFECT OF ACTIVATED CARBON TREATMENT AND HYDROFLUORIC ACID ADDITIONS

Bath Composition: $MnSO_4 \cdot H_2O$ 110 g/l
 $SnSO_4$ 21.6 g/l
 NaF 40 g/l
 pH 1.9-2.1

Test No.	Addition of 50% HF Solution, g/l	Temp, F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Appearance of Deposit
6606-92A	None	150	40	3.0	14.7	6.8	0.0449	Fine-grained deposit with nonadherent overlay of long needle-like crystals
-92B	5	150	40	2.6	29.5	9.0	0.0871	Ditto
-92E	10	150	40	2.4	40.6	5.0	0.1227	"
-92F	20	150	40	--	31.0	5.0	0.0936	"
-92C	None	150	100	4.9	4.7	5.0	0.0355	"
-92D	5	150	100	3.9	9.1	4.0	0.0688	"
-92G	10	150	100	4.1	7.6	9.2	0.0559	"
-92H	20	150	100	5.0	10.7	6.5	0.0808	"

Notes: Work-rod agitation - 33 cpm, 1-1/4" stroke
Anodes - round carbon rods in porous Alundum cups
Anolyte - same as catholyte
Cathodes - SAE 1010 steel, 1-1/2" x 1" (plated area)
Time - 10 minutes
All baths treated with activated carbon

TABLE 82. CODEPOSITION OF MANGANESE AND TIN FROM SULFATE-FLUORIDE SOLUTIONS:
EFFECT OF AMMONIUM BIFLUORIDE WITH AND WITHOUT ADDITION AGENT 5

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110 g/l
 SnSO_4 21.6 g/l
 NaF 40 g/l
pH 1.9-2.1

Test No.	Addition of $\text{NH}_4\text{F} \cdot \text{HF}$, g/l	Addition Agent	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Appearance of Deposit
6606-94A	10	None	40	2.0	10.8	5.6	0.0326	Fine-grained deposit with nonadherent overlay of long needlelike crystals
-94B	20	None	40	2.2	23.4	21.6	0.0643	Ditto
-94C	10	None	100	4.0	2.3	0.0	0.0178	"
-94D	20	None	100	3.5	18.9	30.0	0.1231	Nonuniform, dull-gray, rough deposit
-94E	10	Alrosol (1) 2 g/l	40	3.9	65.5	64.0	0.1340	Nonuniform, dull-gray, rough crystalline deposit
-94F	20	Ditto	40	3.0	63.9	17.0	0.1789	Lustrous mat to black deposit; coating flaky
-94G	10	"	100	7.0	56.0	83.5	0.2451	Dull-gray crystalline deposit with treed edges
-94H	20	"	100	5.6	49.7	34.6	0.3040	

(1) Alrosol is a nonionic wetting agent of the fatty acid amide type. Alrose Chemical Company, Providence, Rhode Island.

Notes: Work-rod agitation - 33 cpm, 1-1/4" stroke
Anodes - round carbon rods in porous Aluminum cups
Anolyte - same as catholyte
Cathodes - SAE 1010 steel, 1-1/2" x 1" (plated area)
Time - 10 minutes
Temperature - 150 F
All baths treated with activated carbon

TABLE 83. CODEPOSITION OF MANGANESE AND TIN FROM SULFATE-FLUORIDE SOLUTIONS;
EFFECT OF VARIATIONS IN AGITATION, WITH AND WITHOUT AN ADDITION AGENT

Bath Composition:				MnSO ₄ · H ₂ O	110 g/l				
				SnSO ₄	21.6 g/l				
				NaF	40 g/l				
				pH	2.0				
Test No.	Addition Agent	Work-Rod Agitation ⁽¹⁾	Paddle Agitation ⁽²⁾	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Appearance of Deposit	
6922-10D	Altrosol ⁽³⁾	2 g/l	33 cpm, 1-1/4" stroke	--	3.9	44.0	13.0	0.3188	Medium gray, finely crystalline deposit; slightly powdery.
-10E	Altrosol	2 g/l	99 cpm, 1-1/4" stroke	--	--	70.0	13.0	0.5093	Ditto
-10F	Altrosol	2 g/l	146 cpm, 1-1/4" stroke	--	--	96.0	12.0	0.6958	"
-10A	None		33 cpm, 1-1/4" stroke	--	3.1	13.5	6.5	0.1012	Long needle overlay on gray mat base
-10B	None		99 cpm, 1-1/4" stroke	--	--	49.0	3.5	0.3696	Medium coarse crystal overlay on gray mat base.
-10C	None		146 cpm, 1-1/4" stroke	--	--	92.5	23.5	0.6034	Ditto
-16A	Altrosol	2 g/l	33 cpm, 1-1/4" stroke	--	5.3	72.5	60.2	0.3771	Medium gray, rough deposit; slightly powdery and treed edges.
-16B	Altrosol	2 g/l	--	33 cpm, 1-1/4" stroke	5.3	91.5	61.2	0.4754	Ditto
-16C	Altrosol	2 g/l	--	66 cpm, 1-1/4" stroke	5.2	86.6	1.6	0.6545	"
-16D	Altrosol	2 g/l	--	99 cpm, 1-1/4" stroke	5.3	98.0	11.7	0.7052	"
-16E	Altrosol	2 g/l	--	33 cpm, 3" stroke	5.3	67.0	7.0	0.4935	"
-16F	Altrosol	2 g/l	--	66 cpm, 3" stroke	5.3	103.5	0.0	0.7961	Nonuniform, mat center; rough, gray edges.

(1) Cathode moves linearly between anodes.

(2) See section on experimental work for description of paddles.

(3) Altrose Chemical Company, Providence, Rhode Island.

Notes: Anodes - carbon rods in porous Alundum cups

Anolyte - same as catholyte

Temperature - 180 F

Current density - 100 amp/sq ft

Time - specimens 10A, 10B, 10C, 10D, 10E, 10F 10 minutes

specimens 16A, 16B, 16C, 16D, 16E, 16F 5 minutes

Cathodes - SAE 1010 steel for specimens; 10A, 10B, 10C, 10D, 10E, 10F -

1" x 1-1/2"; for specimens 16A, 16B, 16C, 16D, 16E, 16F - 3" x 1"

TABLE 84. CODEPOSITION OF MANGANESE AND TIN FROM SULFATE-FLUORIDE SOLUTIONS; EFFECT OF FLUORIDE-ION CONCENTRATION

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110 g/l SnSO_4 21.6 g/l As Given in Table NaF 2 g/l $\text{Alroso}(\text{l})$ 2.0 pH 2.0								
Test No.	NaF, g/l	Temp, F	Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Appearance of Deposit
6922-18A	80	150	25	2.0	103.0	3.0	0.0961	Smooth, light-gray mat center; rough edges
-18B	80	150	50	2.4	87.4	4.0	0.1648	Leaf-like crystals overlaying a mat gray deposit; overlay flaked off easily
-18C	80	150	100	3.2	70.5	7.0	0.2514	Dirto
-18D	80	180	25	2.0	109.5	4.0	0.1023	Same as 18A above
-18E	80	180	50	2.6	93.5	7.5	0.1725	Same as 18B above but overlay slightly more adherent
-18F	80	180	100	3.6	79.5	14.0	0.2722	Dirto
-22A	20	150	25	2.4	105.0	1.5	0.0998	Smooth, gray mat
-22B	20	150	50	3.4	70.5	0.5	0.1360	Light to medium gray, rough, nodular deposit
-22C	20	150	100	4.4	31.8	10.0	0.1170	Rough, ridge-like structure, overlaying a gray mat deposit
-22D	20	180	25	2.4	106.0	1.7	0.1000	Same as 22A
-22E	20	180	50	3.2	66.0	3.5	0.1268	Same as 22B
-22F	20	180	100	4.6	47.0	26.5	0.1565	Same as 22C

(1) Alrose Chemical Company, Providence, Rhode Island.

Notes: Agitation - work rod, 33 cpm, 1-1/4" stroke
Anodes - carbon rods in porous Alundum cups
Anolyte - same as catholyte
Cathodes - SAE 1010 steel, 1-1/2" x 1" (plated area)
All solutions treated with activated carbon
Time - 10 minutes

TABLE 85. CODEPOSITION OF MANGANESE AND TIN FROM SULFATE-FLUORIDE SOLUTIONS; EFFECT OF ADDITION AGENTS

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110 g/l
 SnSO_4 21.6 g/l
 NaF 40 g/l
 pH 2.0

Test No.	Addition Agent and Concentration	Cell Volts	Appearance of Deposits
6922-26A	None	3.2	Gray mat overlaid with long needlelike deposit
-26B	Resorcinol 2 g/l	3.4	Ditto
-26C	Miranol ⁽¹⁾ 2 g/l	3.5	Gray, finely crystalline deposit with poor cohesion
-26D	Urea 2 g/l	3.2	Same as 26A
-26E	β -Naphthol 1 g/l	3.2	Same as 26A, but needles were shorter.
-26F	Sulfonated Cresol 2 g/l	3.4	Same as 26A
-27A	Coumarin 2 g/l	3.3	Ditto
-26G	Thiourea 2 g/l	2.9	"
-26H	Resorcinol 10 g/l	3.2	Same as 26A, but needles were shorter
-26I	Miranol ⁽¹⁾ 10 g/l	3.2	Same as 26C
-26J	Urea 10 g/l	3.2	Same as 26A
-26L	Sulfonated Cresol 10 g/l	3.2	Same as 26A, but needles were shorter
-26M	Sulfonated Cresol 50 g/l	3.7	Same as 26C
-26K	Thiourea 10 g/l	3.2	Same as 26A
-27B	Coumarin 10 g/l	3.2	Same as 26A, but needles were shorter
-27C	Sulfonated Cresol 100 g/l	--	Same as 26C
-27D	Miranol ⁽¹⁾ 24 g/l	--	Same as 26 C

TABLE 85. (Continued)

Test No.	Addition Agent and Concentration	Cell Volts	Appearance of Deposit
6522-27E	Alrosol ⁽²⁾ 2 g/l Sulfonated Cresol 100 g/l	--	Fine-grained gray deposit with poor cohesion
-27F	Alrosol ⁽²⁾ 2 g/l Miranol ⁽¹⁾ 24 g/l	--	Like 27 E but with better (but still not satisfactory) cohesion
-27G	Alrosol ⁽²⁾ 2 g/l Sulfonated Cresol 100 g/l Hide Glue 3.2 g/l	--	Like 27E
-27H	Alrosol ⁽²⁾ 2 g/l Miranol ⁽¹⁾ 24 g/l Hide Glue 3.2 g/l	--	Powdery gray deposit
-28A	Sb ₂ O ₃ 2 g/l	2.8	Gray, finely crystalline deposit with poor cohesion
-28B	Sb ₂ O ₃ 2 g/l Alrosol ⁽²⁾ 2 g/l	3.2	Like 27E but with better (still unsatisfactory) cohesion
-28C	Sb ₂ O ₃ 2 g/l Alrosol ⁽²⁾ 2 g/l Hide Glue 2 g/l	3.8	Powdery gray deposit
-28D	Sb ₂ O ₃ 2 g/l Alrosol ⁽²⁾ 2 g/l Hide Glue 6.4 g/l	4.0	Ditto

(1) The Miranol Chemical Corporation, Irvington, New Jersey.
(2) Alrore Chemical Company, Providence, Rhode Island.

Notes: Agitation - work rod, 33 cpm, 1-1/4" stroke
Anodes - carbon rods in porous Aluminum cups
Anolyte - same as catholyte
Cathodes - SAE 1010 steel, 2" x 1/2" (plated area)
Time - 10 minutes
Temperature - 180 F
Current Density - 100 amp/sq ft
All baths treated with activated carbon prior to adding addition agents

TABLE 86. CODEPOSITION OF MANGANESE AND TIN FROM A SULFATE-FLUORIDE SOLUTION AT LOWER pH

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110 g/l
 SnSO_4 21.6 g/l
 NaF 40 g/l
 $\text{Alroso}(1)$ 2 g/l
 pH 0.5

Test No.	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Appearance of Deposit
6922-6D	25	2.2	91.3	4.5	Smooth, gray, mat center; treed edges
-6E	50	2.8	55.3	6.0	Rough, medium-gray deposit; only fair cohesion
-6F	100	3.5	39.6	8.0	Ditto

(1) Alroso Chemical Company, Providence, Rhode Island.

Notes: Agitation - work rod, 33 cpm, 1-1/4" stroke
 Anodes - carbon rods in porous Alundum cups
 Anolyte - same as catholyte
 Temperature - 150 F
 Cathodes - SAE 1010 steel, 1-1/2" x 1"
 Time - 10 minutes
 Baths treated with activated carbon

TABLE 87. CODEPOSITION OF MANGANESE AND TIN FROM SULFATE-FLUORIDE SOLUTIONS;
EFFECTS OF ADDITION AGENTS

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110 g/l
 SnSO_4 21.6 g/l
 NaF 40 g/l

Test No.	Addition Agent	pH	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Appearance of Deposit
6922-84A	Sulfoxide ⁽¹⁾	15 g/l	2.0	6.4	14.3	1.0	0.0734	Gray mat with leaflike crystalline overlay on lower portion of panel
-84B	Sulfide ⁽²⁾	2 g/l	Ditto	--	4.1	0.0	0.0212	Gray mat with heavy spongy overlay
-84C	Sulfoxide Disulfide ⁽³⁾ Sulfide	15 g/l 8 g/l 0.6 g/l	"	5.2	17.5	2.5	0.0395	Gray mat with powdery overlay
-90A	Sulfoxide	15 g/l	0.0	3.4	9.4	2.0	0.0483	Gray mat with leaflike crystalline overlay
-90B	Sulfide	2 g/l	Ditto	5.0	12.9	2.0	0.0660	Gray mat center; heavily used edges
-90C	Sulfoxide Disulfide Sulfide	15 g/l 8 g/l 0.6 g/l	"	4.2	6.7	0.0	0.0342	Gray mat with powdery overlay

- (1) Sulfoxide = sulfonated di - p - tolyl sulfoxide.
(2) Sulfide = sulfonated sodium salt of di - p - tolyl sulfide.
(3) Disulfide = sulfonated di - p - tolyl disulfide.

Notes: Agitation - work rod, 33 cpm, 1-1/4" stroke
Anodes - carbon rods in porous Alundum cups
Anolyte - same as catholyte
Cathodes - SAE 1010 steel, 2" x 1"
Temperature - 150 F

Time - 5 minutes

All baths treated with activated carbon.
Where deposit had overlay some of the deposit may have been lost in drying, hence efficiency figures may be low.

TABLE 88. CODEPOSITION OF MANGANESE AND TIN FROM SULFATE-POTASSIUM FLUORIDE SOLUTIONS

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110 g/l
 SnSO_4 21.6 g/l
 $\text{KF} \cdot 2\text{H}_2\text{O}$ As Given Below

Test No.	$\text{KF} \cdot 2\text{H}_2\text{O}$, g/l	Addition Agent	pH	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Appearance of Deposit
6922-81A	40	None	2.0	100	6.2	25.2	3.5	0.1266	Gray mat with long needlelike overlay
-81B	80	Ditto	Ditto	Ditto	5.4	44.4	4.0	0.2203	Ditto
-81C	120	"	"	"	5.0	37.5	3.5	0.1882	"
-81D	200	"	"	"	3.8	56.7	12.0	0.2749	"
-82A	Ditto	Allosol ⁽¹⁾	"	"	5.9	50.5	1.0	0.2583	Coarsely crystalline; fair cohesion
-82B	"	Allosol	"	"	6.0	30.0	0.0	0.1533	Powdery deposit
-82C	"	Sulfoxide ⁽²⁾	"	"	6.6	--	--	--	Gray mat with heavy powdery overlay
-82D	"	Sulfide ⁽³⁾	"	"	5.0	36.1	3.5	0.1814	Nonuniform, gray mat with beaded edges
-82E	"	Sulfide Allosol	"	"	8.0	29.9	12.8	0.2587	Nonuniform, dark gray mat
-82F	"	Sulfoxide	15 g/l	"	--	--	--	--	Sulfoxide precipitated upon addition to bath
-82G	"	Disulfide ⁽⁴⁾	2 g/l	"	4.8	7.1	3.0	0.0356	Gray mat with long needlelike crystalline overlay

TABLE 88. (Continued)

Test No.	KF · 2H ₂ O, g/l	Addition Agent	pH	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Appearance of Deposit	
6922-82H	200	Disulfide Sulfide	2 g/l 2 g/l	2.0	100	5.1	44.3	9.0	0.2166	Gray mat center; dark gray edges
-90D	"	Sulfide	2 g/l	0.0	"	4.4	44.5	3.0	0.2287	Gray mat
-90E	"	Disulfide Sulfide	2 g/l 2 g/l	0.0	"	4.2	43.8	2.5	0.2248	Ditto
-90F	"	Disulfide Sulfide Alrosol	2 g/l 2 g/l 2 g/l	0.0	"	4.2	42.1	3.0	0.2161	Gray mat center; dark edges

(1) Alrose Chemical Company, Providence, Rhode Island.
(2) Sulfoxide = sulfonated di - p - tolyl sulfoxide.

- (1) Alrose Chemical Company, Providence, Rhode Island.
 (2) Sulfoxide = sulfonated di - p - tolyl sulfoxide.
 (3) Sulfide = sulfonated sodium salt of di - p - tolyl sulfide
 (4) Disulfide = sulfonated di - p - tolyl disulfide

Notes: Agitation - work rod, 33 cpm, 1-1/4" stroke
 Anodes - carbon rods in porous Alundum cups
 Anolyte - same as catholyte
 Cathodes - SAE 1010 steel, 2" x 1"
 Temperature - 150 F
 Time - 5 minutes

All baths treated with activated carbon.
 Where deposit had overlay some of the deposit may have been
 lost in drying, hence efficiency figures may be low.

TABLE 89. CODEPOSITION OF MANGANESE AND TIN FROM CHLORIDE-FLUORIDE SOLUTION

Bath Composition: $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ 128 g/l
 $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ 22.6 g/l
 NaF 40 g/l
 pH 1.9-2.1

Test No.	Bath Treatment	Temp, F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Appearance of Deposit
6922-2A	None	100	25	3.6	50.5	4.0	0.0951	Finely crystalline to coarsely crystalline deposit
-2B	None	100	50	4.9	11.2	12.3	0.0391	Long, needlelike crystals overlaying a mat deposit
-2C	None	100	100	5.2	14.0	9.5	0.1900	Ditto
-2D	None	150	25	2.6	102	27.0	0.1672	Same as 2A
-2E	None	150	50	2.6	48.2	35.4	0.1471	Same as 2B
-2F	None	150	100	3.6	64.0	28.6	0.4173	Ditto
-2G	AC ⁽¹⁾	100	25	2.4	24.0	2.0	0.0474	Same as 2A
-2H	AC	100	50	3.2	8.0	12.6	0.0281	Same as 2B
-2I	AC	100	100	4.2	2.8	17.7	0.0215	Gray powdery deposit
-2J	AC	150	25	2.0	40.5	15.0	0.0739	Same as 2A
-2K	AC	150	50	2.2	103	20.2	0.3657	Same as 2B
-2L	AC	150	100	3.8	86.0	23.7	0.5478	Same as 2I

(1) AC = activated carbon treatment.

Notes: Work-rod agitation = 33 cpm, 1-1/4" stroke

Anodes = round carbon rods in porous Aluminum cups

Anolyte = same as catholyte

Cathodes = SAE 1010 steel, 1-1/2" x 1" (plated area)

Time = 10 minutes

TABLE 90. CODEPOSITION OF MANGANESE AND TIN FROM CHLORIDE-FLUORIDE SOLUTIONS

Bath Composition: $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ 128 g/l
 $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ 22.6 g/l
 NaF 40 g/l
 $\text{Airosol}(1)$ 2 g/l
pH 1.5 - 1.8

Test No.	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Appearance of Deposit
6922-6A	25	2.1	102.0	4.2	Smooth mat center; slightly treed edges
-6B	50	2.6	66.3	7.0	Rough deposit; only fair cohesion
-6C	100	3.1	64.0	18.5	Dirto

(1) Alrose Chemical Company, Providence, Rhode Island

Notes: Agitation - work rod, 33 cpm, 1-1/4" stroke
Anodes - carbon rods in porous Alundum cups
Anolyte - same as catholyte
Cathodes - SAE 1010 steel, 1-1/2" x 1"
Temperature - 150 F
Time - 10 minutes
Baths treated with activated carbon

TABLE 91. CODEPOSITION OF MANGANESE AND TIN FROM A SULFATE-FLUORIDE-TARTRATE SOLUTION

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110 g/l
 SnSO_4 21.6 g/l
 NaF 40 g/l
 $\text{Na Tartrate} \cdot 2\text{H}_2\text{O}$ As Given in Table

Test No.	Na Tartrate $\cdot 2\text{H}_2\text{O}$, g/l	pH	Temp, F	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Appearance of Deposit
6922-30A	10	2.0	80	3.8	42.3	0.0	0.1098	Gray, spongy deposit
-30B	50	2.0	80	4.0	54.2	1.0	0.1408	Ditto
-30C	100	2.0	80	4.2	41.8	1.0	0.1088	"
-30D	10	3.0	80	3.6	43.5	2.8	0.1101	"
-30E	50	3.0	80	3.8	34.8	4.5	0.0882	"
-30F	100	3.0	80	4.0	44.8	1.0	0.1163	"
-30G	10	2.0	120	3.0	31.5	3.0	0.0796	Gray, mat, deposit with long needlelike overlay
-30H	50	2.0	120	3.2	65.9	0.0	0.1667	Ditto
-30I	100	2.0	120	3.0	88.5	5.5	0.2240	"
-30J	10	3.0	120	3.4	27.4	11.4	0.0676	"
-30K	50	3.0	120	3.4	38.6	4.8	0.0977	
-30L	100	3.0	120	3.8	66.0	4.2	0.1670	"

Notes: Agitation - work rod, 33 cpm, 1-1/4" stroke
 Anodes - carbon rods in porous Aluminum cups
 Anolyte - same as catholyte
 Cathodes - SAE 1010, 2" x 1/2" (plated area)

Time - 5 minutes
 Current density - 100 amp/sq ft
 All baths treated with activated carbon

TABLE 92. CODEPOSITION OF MANGANESE AND TIN FROM
SULFATE-CITRATE SOLUTIONS

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110 g/l
 SnSO_4 21.6 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250 g/l

Test No.	pH	Current Density, amp/sq ft	Estimate of Per Cent Manganese in Deposit	Appearance of Deposit
6922-39B	5.0	25	< 10	Mat gray
-39A	5.0	100	> 10	Gray and powdery
-39D	7.0	25	< 10	Ditto
-39C	7.0	100	> 10	"

Notes: Agitation - work rod, 33 cpm, 1-1/4" stroke
 Anodes - carbon rods in porous Alundum cups
 Anolyte - Na_2SO_4 142 g/l
 Cathodes - stainless steel, 2" x 1/2"

APPENDIX IV

TABLE 93. PRELIMINARY EXPERIMENTS ON THE CODEPOSITION OF MANGANESE AND NICKEL FROM SULFATE SOLUTIONS

Test No.	Concentration of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, g/l	pH	Temp, F	Current Density, amp/sq ft	Cathode Efficiency, %	Per Cent Manganese in Deposit	Remarks
Bath Composition:							
	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$ - 40 g/l						
	$(\text{NH}_4)_2\text{SO}_4$ - 135 g/l						
6245-30C	4	7.5	80	45	13.3	8.7	Like bright nickel in appearance; good adhesion
-36A	4	7.5	83	45	12.6	8.6	Like bright nickel in appearance; good adhesion
-32C	8	7.5	83	45	8.0	8.3	Bright edges; dull center
-34A	12	7.5	82	45	9.6	11.5	Partly bright; dark edges
-34E	16	7.5	84	45	22.3	7.2	Full bright; excellent adhesion
-38C(1)	8	7.5	88	45	19.3	10.1	Bright deposit; blistered at edges
Bath Composition:							
	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$ - 40 g/l						
	$(\text{NH}_4)_2\text{SO}_4$ - 135 g/l						
	$\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ - 0.5 g/l						
6245-30B	4	7.5	80	45	15.2	1.8	Powdery; light gray deposit
-32F	8	7.5	82	45	11.1	4.0	Powdery; light gray deposit
-34D	12	7.5	84	45	20.2	3.7	Powdery; light gray deposit

(1) Platinum cathode, 2" x 1/2" (immersed area).

Notes: Duration of all tests - 10 minutes

Anodes - Carbon disks in porous Alundum cups.

Cathodes - Stainless steel sheet, 2" x 1/2" (immersed area).

TABLE 94. CODEPOSITION OF MANGANESE AND NICKEL
FROM FLUOROBORATE SOLUTIONS

Bath Composition: HBF_4 (42.3%) 810 g/l
Mn 95.4 g/l
Ni 10 g/l
 H_3BO_4 20 g/l

Test No.	Addition	pH(1)	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Remarks
6429-88A	None	0.0	-	-	-	-	No deposit
-88B	NaOH to change the pH	2.1-2.5	5.0	27.8	20.2	0.0595	Brown, flaky deposit
-88C	Hide glue 2 g/l	2.1-2.5	-	-	-	-	Brown, flaky deposit

(1) pH measured by papers.

Notes: For all tests:

Temperature - 80 F.

Current density - 100 amp/sq ft.

Time - 10 minutes.

Agitation - None.

Anodes - Carbon rods 1/4" diam x 4-1/2" long in porous Alundum cups.

Cathodes - Stainless steel 1/2" x 2" (immersed area).

TABLE 95. CODEPOSITION OF MANGANESE AND NICKEL FROM SULFATE-CITRATE, SULFATE-BOROCITRATE, SULFATE-TARTRATE, AND SULFATE-ACETATE SOLUTIONS

Basic Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.6 g/l
 $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 40.0 g/l

Test No.	Addition	pH	Temp, F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit,		Remarks
							%	gram	
6429-84A ⁽¹⁾	Na Citrate · 2H ₂ O 250 g/l	5.0	72	50	5.0	1.2	72	0.0015	Brown center; black edges
-84B	Na Citrate · 2H ₂ O 250 g/l	2.0	85	50	5.4	-	-	-	No deposit
-84C	Na Citrate · 2H ₂ O 250 g/l	8.0	85	50	5.4	-	-	-	No deposit
-84D	Na Citrate · 2H ₂ O 250 g/l	2.0	80	100	5.0	<1.0	-	-	Very slight, brown deposit
-84E	Na Citrate · 2H ₂ O 250 g/l	5.0	80	50	3.4	<1.0	-	-	Very slight, brown deposit
-84F	Na Citrate · 2H ₂ O 250 g/l H ₃ BO ₃ 99 g/l	5.0	80	100	4.8	<1.0	-	-	Very slight, brown deposit
-84G	Na Citrate · 2H ₂ O 250 g/l H ₃ BO ₃ 99 g/l	5.0	80	200	-	1.0	64	0.0047	Un. form, brown deposit
-84H	Na Acetate 200 g/l	5.0	80	50	4.2	3.0	30	0.0036	Nonuniform, black center; black edges
-84I ⁽¹⁾	NaK Tartrate 200 g/l	5.0	80	50	4.2	-	-	-	No deposit

(1) Bath precipitated upon standing after electrolysis.

Notes: Time for all runs - 10 minutes.

Agitation - None.

Anodes - Round carbon rods 1/4" diam x 4-1/2" long enclosed in porous Alundum cups.

Cathodes - Stainless steel 1/2" x 2" (immersed area).

TABLE 96. CODEPOSITION OF MANGANESE AND NICKEL FROM SULFATE-CITRATE SOLUTION; EFFECT OF AMMONIUM IONS

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 40 g/l
 $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 16 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 90 g/l

Test No.	Addition of $(\text{NH}_4)_2\text{SO}_4$, g/l	pH	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Remarks
6429-88E	None	7.5	4.2	-	-	-	No deposit
-90A	50	7.5	3.4	7.6	7.2	0.0087	Semibright deposit
-88F	135	7.5	3.6	7.7	6.2	0.0088	Light-brown, semibright deposit
-90B	200	7.5	3.0	8.9	6.4	0.0102	Semibright deposit
-90C	300	7.5	3.5	10.7	8.5	0.0123	Semibright deposit
-90D	50	5.0	3.4	2.5	20.0	0.0029	Semibright deposit
-90E	135	5.0	3.4	3.9	19.2	0.0044	Semibright deposit
-90F	200	5.0	4.0	3.1	7.0	0.0036	Semibright deposit
-90G	300	5.0	3.0	4.3	10.0	0.0049	Semibright deposit
-90H	50	2.0	3.0	-	-	-	No deposit
-90I	135	2.0	4.2	-	-	-	No deposit
-90J	200	2.0	3.0	-	-	-	No deposit
-90K	300	2.0	-	-	-	-	Bath precipitated at pH 2.0

Notes: Time for all tests - 10 minutes, except 90H, 90I, 90J which were 20 minutes.

No agitation.

Anodes - Round carbon rods 1/4" diam x 4-1/2" long enclosed in porous Alundum cups.

Cathodes - Stainless steel 1/2" x 2" (immersed area).

Current density for all tests - 45 amp/sq ft.

Temperature for all tests - 80 F.

TABLE 97. CODEPOSITION OF MANGANESE AND NICKEL FROM A SULFATE-FLUORIDE SOLUTION

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.0 g/l
 $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 52.0 g/l
 NaF 40.0 g/l

Test No.	pH ⁽¹⁾	Temp. F	Current Density, amp/sq ft	Cell Volts	Agitation	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Microappearance of Deposit	Macroappearance of Deposit
6606-68B ⁽²⁾	2.0 (Electromet.) 1.9 - 2.1 (Paper)	80 ± 2	50	4.4	None	8.8	< 1	0.0115	Marls from basis metal visible	Uniform, semibright
-68A ⁽³⁾	Ditto	80 ± 2	100	4.0	None	7.5	9.7	0.0193	Ditto	Semibright center; black edges
-68D ⁽²⁾	"	150 ± 5	50	2.2	None	31.8	< 1	0.0413	"	Like 68B
-68C ⁽³⁾	"	150 ± 5	100	3.0	None	33.4	8.4	0.0851	"	Like 68A
-68G ⁽⁴⁾	"	Ditto	100	3.6	33 cpm, 1-1/4" stroke	19.3	20.0	0.0488	Dark background with gray spots	Blue-black with gray spots
-68H ⁽⁵⁾	"	"	10	3.4	Ditto	29.6	< 1	0.0754	Fine grained	Uniform, semibright
-68E ⁽⁴⁾	"	"	1	2.8	99 cpm, 1-1/4" stroke	33.3	1.2	0.0845	Uneven with high and low areas	Ditto
-68F ⁽⁴⁾	"	"	100	2.8	146 cpm, 1-1/4" stroke	24.1	< 1	0.0612	Ditto	"
-89A ⁽⁶⁾	1.7 - 2.0 (Paper)	"	100	3.0	None	24.0	5.4	0.0548	Fine grained	Lustrous dark gray to lustrous light gray
-89B ⁽⁷⁾	1.3 (Electromet.)	"	100	3.6	None	12.7	< 1	0.0292	Ditto	Semibright
-90A ⁽⁷⁾	1.5 (Ditto)	"	100	3.4	None	13.9	1.5	0.0320	"	Ditto
-90B ⁽⁷⁾	1.7	"	100	3.0	None	31.9	38.0	0.0715	Black background with gray blots	Blue-black with gray blots
-90C ⁽⁷⁾	1.9	"	100	3.6	None	43.0	36.7	0.0963	Ditto	Ditto

(1) Electrometric pH determinations were made with a quinhydrone electrode.
 For further details see section on "Experimental Work".

Notes: Anodes - round carbon rods in porous Alundum cups

Cathodes - 6606-68 series - stainless steel 2" x 1/2" (plated area),
 6606-89 and 6606-90 series - stainless steel 2" x 3/8" (plated area)

Time - 10 minutes

(2) (3) (4) (5) (6) (7) Tests having same footnote number were plated from
 same bath.

TABLE 98. ATTEMPTS TO PREPARE MANGANESE-NICKEL PLATING BATHS FROM ETHYLENEDIAMINE, ETHANOLAMINE, AND TRIETHANOLAMINE

Test No.	Solvent(1)	Solute(2)	Results	Effect of Water Addition(3)	Effect of Heating After Water Addition
6429-86A	Ethylenediamine	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	Insoluble	Salt dissolved but shortly afterward a brown precipitate formed	No effect
-86B	"	NiO	"	--	--
-86C	"	NiCO_3	Slightly soluble; faint-red solution	All the salt went in solution	--
-86D	"	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	After some time, the salt went in solution and later precipitated	--	--
-86E	Triethanolamine	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	Insoluble	Salt dissolved and then a brown precipitate formed	No effect
-86F	"	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	"	Slightly soluble	No effect
-86G	"	NiCO_3	"	Ditto	--
-86H	"	$\text{MnSO}_4 \cdot \text{H}_2\text{O} + \text{NiCO}_3$	"	Brown precipitate	--
-86I	Ethanolamine	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	Soluble; pink solution formed	--	Heating the nonaqueous solution produced a darker pink color
-86J	"	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	Insoluble	Salt dissolved	Precipitate formed
-86K	"	NiO	"	--	--
-86L	"	$\text{MnSO}_4 \cdot \text{H}_2\text{O} + \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	Ni salt insoluble	Water added a drop at a time until Ni salt dissolved, required about 0.5 ml	--

(1) About 10 ml

(2) About 0.1 gram

(3) About 2 ml

TABLE 99. CODEPOSITION OF MANGANESE AND NICKEL FROM SULFATE-GLUCONIC ACID SOLUTIONS

Bath Composition: $MnSO_4 \cdot H_2O$ 110 g/l
 $NiSO_4 \cdot 6H_2O$ 52 g/l
 Gluconic Acid (50% Soln) 100 g/l

Test No.	pH	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit (Estimated), %	Weight of Deposit, gram	Appearance of Deposit
6922 - 52A	4.0	25	3.8	< 1.0	< 50	0.0008	Nonuniform, blue stain
- 52B	4.0	50	6.0	Ditto	< 50	0.0010	Nonuniform, blue-brown stain
- 52C	4.0	100	8.9	"	< 50	0.0019	Blue-black center; no deposit on edges
- 52D	6.0	25	3.9	"	< 50	0.0006	Similar to 52B
- 52E	6.0	50	5.0	"	< 50	0.0005	Ditto
- 52F	6.0	100	6.8	"	"	--	No deposit

Notes:

Agitation - work rod, 33 cpm, 1-1/4" stroke
 Anodes - Carbon rods in porous Aluminum cups
 Anolyte - Na_2SO_4 142 g/l
 Cathodes - stainless steel, 2" x 9/16" (plated area)
 Temperature - 80 F
 Time - 10 minutes

TABLE 100. CODEPOSITION OF MANGANESE AND CHROMIUM FROM SIMPLE SULFATE SOLUTIONS
AND FROM SULFATE-CITRATE SOLUTIONS; PRELIMINARY ATTEMPTS

Test No.	Solution	pH	Temp, F	Current		Cell Volts	Remarks
				Density, amp/sq ft			
Solution No. 1: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 60 g/l Solution No. 2 ⁽¹⁾ : $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 55 g/l $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ 30 g/l $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ 30 g/l pH (as made) 2.8 Na Citrate $\cdot 2\text{H}_2\text{O}$ 125 g/l pH (as made) 5.1							
6606-59A	1	2.8	72	57.5		9.0	Nonmetallic appearing deposit; positive test for Mn; negative test for Cr
-59B	1	2.8	135	86.5		8.4	Green nonmetallic deposit; positive test for Mn; negative test for Cr
-57A	2	5.1	78	86.5		8.4	Very light metallic deposit; positive test for Mn; negative test for Cr
-57B	2	5.1	78	86.5		8.4	Somewhat heavier deposit than 57A; positive test for Mn; negative test for Cr
-57C ⁽²⁾	2	2.4	87	86.5 → 130	8.6 → 8.9		Very light metallic deposit; positive test for Mn; negative test for Cr
-57D ⁽²⁾	2	0.0	76	86.5		4.0	No deposit

(1) The pH of this bath was 5.1 as made up, and the solution had a green color. After a couple of hours, the color changed to a reddish purple. A check of the pH revealed it to be 4.7.

(2) At pH 2.4, the color of the solution is a mixture of reddish purple and green, and at pH 0.0, the color is green.

Notes: No agitation

Anode - one round 4-1/2" x 1/4" carbon rod in a porous Alundum cup

Cathode - stainless steel 2" x 1/2" (plated area)

Time - 10 minutes

TABLE 101. CODEPOSITION OF MANGANESE AND CHROMIUM FROM SULFATE-CITRATE SOLUTIONS

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110 g/l
 $\text{Cr}_2\text{K}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ 120 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250 g/l
 $(\text{NH}_4)_2\text{SO}_4$ As Given Below

Test No.	$(\text{NH}_4)_2\text{SO}_4$, g/l	pH	Temp, F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Appearance of Deposit
6922-74A	None	4.5	80	50	4.5	8.4	97.5	0.0099	Gray, mat center; powdery black edges
-74B	Ditto	Ditto	Ditto	100	5.5	6.0	87.3	0.0140	Gray, mat center of small area; powdery black edges
-74C	"	"	"	200	7.0	4.8	90.5	0.0227	Powdery, gray center, no deposit on edges
-74D	"	"	140	50	3.4	9.7	97.0	0.0115	Gray mat with dark streaks along edges
-74E	"	"	Ditto	100	4.0	8.4	103.0	0.0199	Mulky gray; slightly powdery gray edges
-74F	"	"	"	200	5.4	6.7	94.5	0.0316	Powdery gray with areas having no deposit
-74G	"	1.5	80	50	5.2	--	--	--	No deposit
-74H	"	Ditto	Ditto	100	4.6	--	--	--	No deposit; gray stain on cathode
-74I	"	"	"	200	10.0	6.5	94.0	0.0308	Mat gray deposit with black streaks
-74J	"	"	"	300	9.0	6.8	88.5	0.0471	Ditto
-76A	17	4.5	"	50	4.6	26.1	104.0	0.0314	Mulky gray
-76B	50	Ditto	"	50	3.8	23.3	102.0	0.0280	Ditto
-76C	17	"	"	100	6.2	35.0	97.0	0.0843	"
-76D	50	"	"	100	4.6	30.6	98.5	0.0736	Semibright center; bright edges
-76E	17	"	"	200	8.2	28.8	97.7	0.1379	Mulky center; gray mat edges
-76F	50	"	"	200	6.4	18.5	97.8	0.0883	Mulky center; blue edges

Footnotes appear on following page.

NOTES FOR TABLE 101

Notes: Agitation - none
Anodes - carbon rods in porous Alundum cups
Cathodes - brass sheet, 2" x 1/2"
Anolyte - Na_2SO_4 142 g/l
Time - 10 minutes

TABLE 102. CODEPOSITION OF MANGANESE AND CHROMIUM FROM CHLORIDE-CITRATE SOLUTIONS

Bath Composition: $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ 128 g/l
 $\text{CrCl}_3(1)$ 34.6 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ 250 g/l
 NH_4Cl As Given Below
pH 4.5

Test No.	NH_4Cl , g/l	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Appearance of Deposit
6922-78A	None	50	4.6	--	--	0.0064	Gray mat with powdery brown overlay
-78B	Ditto	100	5.8	--	--	0.0064	Powdery brown
-78C	"	200	7.4	--	--	0.0075	Ditto
-78D	50	50	3.4	3.0	71.0	0.0031	White powdery center; gray mat edges
-78E	50	100	4.0	4.4	101.0	0.0106	Blue-gray mat
-78F	50	200	5.4	4.7	113.0	0.0224	Ditto
-78G	17	50	4.0	6.0	78.5	0.0062	Same as 78D
-78H	17	100	4.6	5.2	99.0	0.0124	Blue-gray mat
-78I	17	200	6.0	6.6	105.0	0.0315	Ditto

(1) No assay or analysis was given for this material so the exact chromium content was unknown. The salt was manufactured by J. T. Baker and Company, Phillipsburg, N. J.

Notes: Agitation - none

Anodes - carbon rods in porous Alundum cups

Anolyte - NaCl 142 g/l

Cathodes - brass sheet, 2" x 1/2"

Time - 10 minutes

Temperature - 80 F

TABLE 103. CODEPOSITION OF MANGANESE AND CHROMIUM FROM A CHLORIDE-FLUORIDE BATH

Bath Composition: $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ 127.0 g/l
 CrCl_3 36.4 g/l
 NaF 40.0 g/l
pH 1.9 - 2.1

Test No.	Bath No.	Temp. F	Current Density, amp/sq ft	Cell Volts	Agitation	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Micro appearance of Deposit	Macro appearance of Deposit
6606-80A	A	80 ± 2	50	3.2	None	10.5	25.8	0.0090	--	No deposit in center, black edges
-80B	A	150 ± 5	50	2.5	None	--	--	--	--	No deposit
-80C	A	150 ± 5	100	--	None	7.4	17.9	0.0122	--	Nonuniform, black deposit
-80D	A	80 ± 2	100	4.0	None	--	--	--	--	No deposit
-80E	B	80 ± 2	100	4.0	None	54.5	38.7	0.1106	Pitted	Nonuniform, black deposit
-80F	B	150 ± 5	100	3.0	None	--	--	--	--	No deposit
-80G	C	80 ± 2	100	5.2	33 cpm ⁽¹⁾ 1-1/4" stroke	56.0	44.5	0.1152	Slightly nodular	Nonuniform, gray-black deposit
-80H	C	80 ± 2	100	--	99 cpm ⁽¹⁾ 1-1/4" stroke	1.6	100	0.0028	Only basic metal pattern is visible	Ditto
-80I	C	80 ± 2	100	--	146 cpm ⁽¹⁾ 1-1/4" stroke	17.4	54.5	0.0374	Ditto	"

(1) Work-rod agitation.

Notes: Anodes - round carbon rods in porous Alundum cups

Anolyte - same as catholyte

Cathodes - stainless steel 2" x 1/2" (plated area)

Time - 10 minutes

TABLE 104. CODEPOSITION OF MANGANESE AND CHROMIUM FROM A CHLORIDE-FLUORIDE (Cr III) SOLUTION

Bath Composition: $MnCl_2 \cdot 4H_2O$ 127 g/l
 $CrCl_3$ 36.4 g/l
 NaF 40 g/l
 pH 2.0

Test No.	Addition Agent	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Appearance of Deposit
-8A	None	25	--	--	--	--	No deposit
-8B	None	50	--	--	--	--	Ditto
-8C	None	100	3.5	2.8	28.4	0.0067	No deposit in center; black edges
-8D	None	150	4.5	56.5	42.5	0.1795	Black velvety center; black, slightly powdery edges
-8E	None	150	4.5	--	39.8	0.1658	Ditto
-8F	None	200	7.4	10.3	41.0	0.0463	Blue mat deposit, with blue-gray flaky overlay
-12A	Alrocol ⁽¹⁾	150	4.7	19.0	25.0	0.0680	Black, mat, slightly powdery center; no deposit on edges
-12B	Hide Glue	150	4.8	4.7	21.5	0.0168	No deposit in center; black, mat, slightly powdery edges
-12C	X ⁽²⁾	150	5.2	--	--	--	Powdery, brown deposit; analysis impractical
-12D	Sequestrene NA4 ⁽¹⁾	150	5.2	--	--	--	Ditto

(1) Alrocol Chemical Company, Providence, Rhode Island.

(2) X is a proprietary compound. Its chemical nature has not been disclosed.

Notes: Agitation - work rod, 33 cpm, 1-1/4" stroke

Anodes - carbon rods in porous Alundum cups

Anolyte - same as catholyte

Cathodes - stainless steel, 2" x 9/16"

Time - 10 minutes

Temperature - 80 F

All baths treated with activated carbon (where addition agents were used, this was done prior to their addition)

TABLE 105. CODEPOSITION OF MANGANESE AND CHROMIUM FROM CHLORIDE-FLUORIDE (Cr VI) SOLUTIONS

Bath Composition: $MnCl_2 \cdot 4H_2O$ 127 g/l
 CrO_3 22.8 g/l
 NaF As Given Below
 pH 1.0 - 2.0 (l)

Test No.	NaF, g/l	Temp, F	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese In Deposit, %	Weight of Deposit, gram	Appearance of Deposit
6922-40A	40	80	100	3.6	7.6	35.8	0.0159	Gray mat center; dark edges
-40B	40	80	200	6.2	2.6	37.0	0.0108	Brown, powdery
-40C	40	80	300	6.2	2.1	37.7	0.0126	Ditto
-40D	40	130	100	3.2	1.5	24.0	0.0033	No deposit in center; gray mat edges
-40E	40	130	200	5.2	1.5	39.4	0.0061	Brown, powdery
-40F	40	130	300	6.2	2.1	37.2	0.0125	Ditto
-40G	40	180	100	3.6	18.6	32.5	0.0387	"
-40H	40	180	200	5.2	2.2	36.6	0.0093	"
-40I	40	180	300	6.2	2.7	35.9	0.0170	"
-42A	80	80	100	4.8	29.8	29.3	0.0524	Brown, flaky
-42B	80	80	200	5.4	13.9	30.6	0.0489	Ditto
-42C	80	80	300	6.6	3.0	32.7	0.0159	"
-42D	20	80	100	5.0	1.2	44.3	0.0022	Purple stain
-42E	20	80	200	6.2	5.7	39.2	0.0203	Brown, powdery
-42F	20	80	300	7.8	4.0	32.5	0.0215	Ditto

(1) Colorimetric papers were used for pH measurements, and the yellow color of the chromic acid solution interfered with the reading. That is why the pH is given over so wide a range.

Notes: Agitation - work rod, 33 cpm, 1-1/4" stroke
 Anodes - carbon rods in porous Aluminum cups
 Anolyte - same as catholyte
 Cathodes - brass strips 2" x 1/2"
 Time - 10 minutes
 All baths treated with activated carbon

TABLE 106. CODEPOSITION OF MANGANESE AND CHROMIUM FROM CHLORIDE-
FLUOSILICATE (Cr III) SOLUTIONS. PRELIMINARY EXPERIMENTS

Bath Composition: $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ 127 g/l
 CrCl_3 36.4 g/l
 H_2SiF_6 (30.5% soln) 120 g/l
pH 1.2

Test No.	Current Density, amp/sq ft	Cell Volts	Results
6922 - 39E	50	2.6	No deposit
- 39F	100	4.2	Dirty
- 39G	150	4.4	"
- 39H	50	--	"
- 39I	100	--	"
- 39J	150	--	"

Notes: Agitation - work rod, 33 cpm, 1-1/4" stroke
Anodes - carbon rods in porous Alundum cups
Anolyte - same as catholyte
Time - 10 minutes
Cathodes - Monel sheet, 2" x 1/2"
Temperature - 80 F
Baths treated with activated carbon

TABLE 107. CODEPOSITION OF MANGANESE AND CHROMIUM FROM A SULFATE-FLUORIDE (Cr III) SOLUTION

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110 g/l
 $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ 120 g/l
 NaF 40 g/l
pH 2.0

Test No.	Current Density, amp/sq ft	Cell Volts	Results
6922 - 72A	50	4.2	No deposit
- 72B	100	4.8	Dirto
- 72C	150	5.6	"

Notes: Agitation - work rod, 33 cpm, 1-1/4" stroke
Anodes - carbon rods in porous Alundum cups
Anolyte - same as catholyte
Cathodes - brass, 2" x 1/2
Time - 10 minutes
Temperature - 120 F
Baths treated with activated carbon

TABLE 108. CODEPOSITION OF MANGANESE AND IRON FROM A SULFATE-FLUORIDE SOLUTION

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110.0 g/l
 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 59.5 g/l
 NaF 40.0 g/l
 pH 1.7-1.9

Test No.	Temp. F	Current Density, amp/sq ft	Cell Volts	Agitation	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Microappearance of Deposit	Macroappearance of Deposit
6606-78A(1)	80 ± 2	50	3.3	None	9.2	2.2	0.0111	--	Semibright mat
-78B(1)	80 ± 2	100	4.6	None	23.2	10.9	0.0563	--	Milky center, black edges
-78C(1)	150 ± 5	50	2.6	None	62.5	0.6	0.0763	--	Semibright mat
-78D(1)	150 ± 5	100	3.2	None	50.0	13.7	0.1215	Uniform, fine grain	Uniform, gray mat
-78E(2)	150 ± 5	100	3.4	33 cpm, 1-1/4" stroke	26.8	0.5	0.0694	Ditto	Ditto
-78F(2)	150 ± 5	100	3.4	99 cpm, 1-1/4" stroke	25.6	0.2	0.0663	"	Semibright mat
-78G(2)	150 ± 5	100	3.4	146 cpm, 1-1/4" stroke	24.7	0.3	0.0640	"	Ditto
-77A(3)	150 ± 5	100	--	None	22.3	1.3	0.0578	"	Semibright mat
-77B(3)	150 ± 5	100	4.0	None	48.7	6.9	0.1262	Uniform, fine grained center; edges appear pitted	Semibright mat center; dark gray, mat edges
-77C(3)	150 ± 5	100	4.0	None	103.0	18.8	0.2679	Irregularly pitted	Nonuniform gray to black mat

(1) (2) (3) Tests having same footnote number were plated from same bath.

Notes: Anodes - round carbon rods in porous Alundum cups

Anolyte - same as catholyte

Cathodes - stainless steel 2" x 1/4" (plated area)

Time - 10 minutes

TABLE 106. CODEPOSITION OF MANGANESE AND IRON FROM A SULFATE-FLUORIDE SOLUTION; USE OF CYLINDRICAL CATHODES

Bath Composition: $MnSO_4 \cdot H_2O$ 110.0 g/l
 $FeSO_4 \cdot 7H_2O$ 59.5 g/l
 NaF 40.0 g/l
 pH 1.7-2.1

Test No.	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Microappearance of Deposit	Macroappearance of Deposit
6606-86A(1)	100	3.3	21.4	1.2	0.0366	Marks from basis metal show through deposit	Uniform, milky gray
-86B(1)	150	3.6	24.1	1.2	0.0629	Uniform and regular	Uniform, semibright
-86C(1)	200	4.4	40.3	13.6	0.1384	Nearly uniform coverage; a few pin holes	Lustrous gray-black to lustrous gray
-86D(1)	200	3.9	20.3	7.8	0.0700	Poor coverage	Milky gray
-86E(2)	200	4.2	33.8	--	0.1166	Like 86C	Like 86C
-86F(2)	200	4.2	26.4	7.0	0.0908	Ditto	Ditto
-86G(2)	200	4.2	30.2	--	0.1039	"	"
-86H(2)	200	4.2	24.8	--	0.0853	Like 86C but more pitted	"
-86I(2)	200	4.2	32.0	--	0.1070	Ditto	Like 86C, Used for X-ray; see Table 7
-86J(2)	200	4.2	34.7	12.2	0.1192	"	Like 86C

(1) (2) Tests having same footnote number were plated from same bath.

Notes: No agitation

Anodes - round carbon rods in porous Aluminum cups

Anolyte - same as catholyte

Cathodes - round stainless steel rods 3/16" diam x 2" long

Time - 10 minutes

Temperature - 150 F $\pm$ 5 F

TABLE 110. CODEPOSITION OF MANGANESE AND MOLYBDENUM FROM SULFATE-FLUORIDE SOLUTIONS

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ As Given Below
 MoO_3 (87.3%) 10 g
 $\text{KF} \cdot 2\text{H}_2\text{O}$ 200 g
 HF (50% Soln) 20 ml
 H_2O 160 ml
 H_2SO_4 (conc) As Given Below

Test No.	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$, H_2SO_4 (conc).		Cathode Material and Dimensions,		Current		Cathode Efficiency,		Manganese in Deposit,		Weight of Deposit,		Appearance of Deposit
	grams	grams	inches		pH	amp/sq ft	Volts	%	%	%	gram		
6922-54A	2	None	Brass 1 x 1/2		5.0	100	3.5	--	--	--	--	--	No deposit
-54B	2	"	Ditto		5.0	200	4.6	< 1	< 1	0.0	0.0009		Center was stained purple color; edges were semibright gray
-54C	2	"	"		5.0	400	6.0	< 1	< 1	0.0	0.0016		Uniform, semibright gray
-56A(1)	10	"	"		5.0	100	3.2	--	--	--	--		No deposit
-56B(1)	10	"	"		5.0	200	4.0	< 1	< 1	0.0	0.0005		Same as 54B
-56C(1)	10	"	"		5.0	400	6.0	< 1	< 1	0.0	0.0026		Brown to gray mat
-56D	2	"	Stainless steel 2 x 9/16		5.0	400	6.2	< 1	< 1	8.8	0.0067		Powdery brown-gray
-56E(2)	2	"	Stainless steel 2 x 9/16		5.0	400	6.2	< 1	< 1	17.4	0.0296		Powdery black
-56F	2	"	Stainless steel 2 x 9/16		5.0	400	6.2	< 1	< 1	0.0	0.0042		Semibright gray
-56G(2)	2	"	Stainless steel 2 x 9/16		5.0	400	6.2	< 1	< 1	28.9	0.0271		Powdery brown-gray
-62A	2	40	Stainless steel 1 x 9/16		3.0	400	7.2	--	--	--	--		No deposit; slight brown stain
-62B	2	91	Stainless steel 1 x 9/16		2.0	400	5.6	--	--	--	--		No deposit; slight purple stain
-62C	2	40	Stainless steel 1 x 9/16		3.0	200	5.2	--	--	--	--		No deposit; slight purple stain

TABLE 110. (Continued)

Test No.	MnSO ₄ · H ₂ O, grams	H ₂ SO ₄ (conc), grams	Cathode Material and Dimensions, inches	pH	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Appearance of Deposit
6922-62D	2	91	Stainless steel 1 x 9/16	2.0	200	4.0	--	--	--	Yellow saltlike deposit
-62E ⁽³⁾	2	None	Stainless steel 1 x 9/16	5.0	400	--	< 1	0.0	0.0018	Purple stain
-62F ⁽⁴⁾	2	"	Stainless steel 1 x 9/16	5.0	400	5.7	< 1	0.0	0.0014	Brown stain in center; gray edges
-62G ⁽⁵⁾	2	"	Stainless steel 1 x 9/16	5.0	400	--	< 1	0.0	0.0020	Light-gray center; dark-gray edges
-62H ⁽⁶⁾	2	"	Stainless steel 1 x 9/16	5.0	400	5.8	< 1	0.0	0.0024	Black center; gray edges

(1) With 10 grams of MnSO₄ · H₂O, some of the salt precipitated.

(2) These two tests were plated for 60 minutes.

(3) Temperature 80 F.

(4) Temperature 180 F.

(5) Work-rod agitation, 99 cpm, 1-1/4" stroke.

(6) Work-rod agitation, 66 cpm, 1-1/4" stroke.

Notes: Agitation - none, except 62G and 62H

Anodes - carbon rods in porous Alundum cups

Anolyte - same as catholyte

Temperature - 120 F except as noted

Time - 20 minutes except as noted

Baths electrolyzed 10 minutes prior to addition of MnSO₄ · H₂O

TABLE III. CODEPOSITION OF MANGANESE AND MOLYBDENUM FROM SULFATE-CITRATE SOLUTIONS

Bath Composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 110 g/l
 $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ 48 g/l
 $\text{Na Citrate} \cdot 2\text{H}_2\text{O}$ As Given Below

Test No.	Na Citrate $\cdot 2\text{H}_2\text{O}$, g/l	pH	Current Density, amp/sq ft	Cell Volts	Cathode Efficiency, %	Manganese in Deposit, %	Weight of Deposit, gram	Appearance of Deposit
6922-87A	60	4.0	25	3.4	--	--	--	No deposit
-87B	60	Ditto	50	4.2	--	--	--	Ditto
-87C	60	"	100	5.8	--	--	--	"
-87D	120	"	25	3.3	--	--	--	"
-87E	120	"	50	--	--	--	0.0003	Nonuniform, black smudges.
-87F	120	"	100	5.6	<1	--	--	No deposit
-88A	180	"	25	3.6	--	--	0.0003	Black on edges; no deposit in center
-88B	180	"	50	4.5	<1	--	0.0002	Ditto
-88C	180	"	100	5.0	<1	--	--	No deposit
-88D	180	2.0	25	2.8	--	--	--	Ditto
-88E	180	2.0	50	3.8	--	98.0	0.0022	No deposit in center; gray to black edges
-88F	180	2.0	100	5.4	<1	90.0	0.0060	Black center; no deposit on edges
-88G	180	2.0	150	6.2	1.7	--	--	No deposit
-89A	180	6.0	25	3.4	--	--	--	No deposit in center; brown powdery edges
-89B	180	6.0	50	4.2	--	--	--	Ditto
-89C	180	6.0	100	5.8	--	--	--	Ditto

Cathodes - brass sheet, 2" x 1/2"

Time - 10 minutes

Temperature - 90 F

Notes: Agitation - none
 Anodes - carbon rods in porous aluminum cups
 Anolyte - Na_2SO_4 142 g/l

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