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Investigation of Electrodeposited Alloys and Pure Metals as Substitutes for Zinc and Cadmium for Protective Finishes for Steel Parts of Aircraft - Final Report -*

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Eight alloys, selected as being superior to pure zinc or cadmium for protecting steel, were evaluated on the basis of static and dynamic electrode potentials and corrosion current densities in three media. Of these eight, the most outstanding corrosion resistant properties were shown by a zinc-silver alloy of 25% silver. A tabulated summary of the testing program on all cast and electrodeposited alloys tested is included.

* and Appendixes I and II

Copies of this report obtainable from CADO.

Production (36)
Fabrication Processes & Methods (8)
Materials (8)
Dopes, Paints and Finishes (7)

Electrode coatings - Development (31497.5)
Coatings, Protective (23503.2)
Coatings, Protective - Testing (23503.9)

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INVESTIGATION OF ELECTRODEPOSITED ALLOYS AND PURE METALS AS SUBSTITUTES FOR ZINC AND CADMIUM FOR PROTECTIVE FINISHES FOR STEEL PARTS OF AIRCRAFT

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UNITED STATES AIR FORCE
AIR MATERIEL COMMAND
Wright-Patterson Air Force Base, Dayton, Ohio

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ABSTRACT

This supplement covers the evaluation of eight alloys that were previously selected from 81 alloys, as being superior to pure zinc or cadmium for protecting steel, on the basis of static and dynamic electrode potentials and corrosion current densities in three media. The zinc-silver alloy of 25 percent silver has shown the most outstanding corrosion resistant properties of the eight selected alloys as shown by the accelerated tests reported herein. This report also covers a tabulated summary of the testing program on all cast and electrodeposited alloys tested, development of methods for codeposition of alloys, and future investigational work suggested for an additional year's research.

PUBLICATION APPROVAL

For the Commanding General:

J. B. JOHNSON
Chief, Materials Laboratory
Engineering Division
Air Materiel Command

TABLE OF CONTENTS

TABLE OF CONTENTS (CONTINUED)

TABLE OF CONTENTS (CONTINUED)

TABLE OF CONTENTS (CONTINUED)

FINAL REPORT

on

AN INVESTIGATION OF ELECTRODEPOSITED ALLOYS AND PURE METALS AS SUBSTITUTES FOR ZINC AND CADMIUM FOR PROTECTIVE FINISHES FOR STEEL PARTS OF AIRCRAFT

to

UNITED STATES AIR FORCE
MATERIALS LABORATORY
WRIGHT-PATTERSON AIR FORCE BASE

From

BATTELLE MEMORIAL INSTITUTE

by

A. B. Tripler, Jr., and C. L. Faust

June 28, 1949

AUTHORITY FOR PROJECT

This is the Final Report on the project being conducted under U. S. Government Contract W-33-038 ac-21107 (20145), dated May 14, 1948.

OBJECTIVES FOR THE PROJECT

The ultimate objective is to develop electrodeposited coatings which will provide better protection for aircraft steel parts than zinc or cadmium plate, particularly in tropical regions.

As stated in the First Progress Report, dated July 14, 1948, the objectives for the year's work which has just terminated were:

(1) Continuation of the exposure of alloys and pure metals, selected on the basis of potential and corrosion current-density measurements, in accelerated "wet-dry program" test with the view toward determining those showing prospects for improved resistance to chemical deterioration in tropical atmospheres.

(2) Measurement of electrode potentials of alloys and pure metals (other than those already tested) in 3 per cent sodium chloride solution, in distilled water, and in distilled water saturated with carbon dioxide. Such other alloys to be added or completed were: those in binary combination of zinc with lead, chromium, manganese, and antimony; those of manganese and of aluminum appearing to have some prospects; and those of other metals that nominally may be considered remote in possibilities, but included for completeness in survey data. These tests were to be made at a temperature of 90°F. in accordance with data obtained during the initial phase of the investigation on binary alloys of zinc and cadmium with tin, silver, indium, nickel, and copper.

(3) Electrodeposition methods were to be examined for any alloys recommended by the results of work described under paragraphs (1) and (2) above. This study was to include a survey of existing knowledge for application of recommending alloys by electrodeposition methods and an experimental examination of plating baths for these alloys.

INTRODUCTION

The previous work done on this project was related, for the greater part, to the measurement of static and dynamic electrode potentials and corrosion current densities in three media: 3 per cent sodium chloride solution; distilled water; and distilled water saturated with carbon dioxide. In all, 81 alloys, representing 14 binary systems, were investigated. The measurements indicated that the following alloys had prospects of being superior to either zinc or cadmium when used within the composition range given.

Alloy System	Range
Zinc-Copper	8-28 per cent copper
Cadmium-Zinc	3-90 per cent cadmium
Zinc-Silver	4-25 per cent silver
Cadmium-Silver	3-8 per cent silver
Zinc-Tin	25-90 per cent tin
Zinc-Nickel	10-12 per cent nickel
Zinc-Chromium	2-5 per cent chromium
Zinc-Manganese	2-5 per cent manganese

It is known that potential and current-density measurements alone are not clearly indicative of the behavior of a substance under all corroding conditions. Consequently, the necessity arose for supplementing these data with knowledge derived from other tests. In view of the difficulties involved in exposing the above alloys to the actual tropical atmosphere, it was necessary to resort to a simulated exposure test which could be accelerated to some degree. Experience in the tropics has singled out certain conditions as the primary cause of the failure of zinc and cadmium. A daily cycle of alternating periods of moisture condensation and dryness at relatively high temperatures provides the conditions for maximum rate of corrosion. A "wet-dry program" unit was constructed during the first year of investigation to provide the alternating conditions, but at a more rapid rate than found in the tropics. The time remaining to the project, upon completion of the potential measurements, did not permit evaluation of all the alloys in the "wet-dry program" unit. Completion of this work, therefore, was given first consideration in the present phase of the project.

A tabulated summary of the testing program will be found in Table 5, Appendix II. This includes all the cast alloys and electrodeposited alloys tested to date. Also included are several miscellaneous pure metals. Pure zinc and cadmium have been omitted from this table.

Work reported in progress in this report is to be continued under a one-month contract extension and, beyond that, it is expected to continue under a new contract which is being negotiated.

RESULTS ACCOMPLISHED

All tests performed to date on the cast, zinc-silver system show the alloy containing 25 per cent silver to have outstanding corrosion resistant properties. This alloy, after 50 days, exposure in the "wet-dry program" test, lost less weight than either zinc or cadmium. This alloy has not been electrodeposited as yet. Codeposition of zinc and silver has been accomplished from an iodide solution, and analysis shows the deposits to contain approximately 50 per cent silver. The initial deposit was powdery, but subsequent deposits have been improved somewhat by addition of thiourea to the bath.

It is recognized that this silver alloy might be an expensive item, but, assuming it to be the answer to the problem, the cost could be small in comparison with losses incurred because of the inadequacy of zinc or cadmium coatings. Furthermore, the United States being a large silver-producing country, supplies are assured.

Electrodeposited zinc-tin alloys, containing 30 per cent zinc, withstood the attack in the "wet-dry" cabinet approximately six times as long as pure zinc coatings. A 20 per cent zinc, balance tin alloy was also superior to pure zinc, but it was inferior to the 30 per cent alloy. None of the zinc-tin alloys proved to be as resistant as pure cadmium which lasted more than twice as long as the 30 per cent zinc alloy. However, pure zinc and zinc-tin alloys protect damaged areas much better than does pure cadmium. Furthermore, cadmium is known to have an undue resistance in accelerated tests which is not evidenced in outdoor exposure.

Cast cadmium-silver alloys containing about 8 per cent silver appeared to be highly resistant when tested in the wet-dry cabinet. It was not possible to differentiate between these alloys and pure cadmium by visual means. Additional exposure of cast and electrodeposited alloys is now under way. Weight-loss measurements will be made on the cast alloys and, between the two types of tests, the merits of the alloy, if any, should be discernible.

Potential and corrosion current-density measurements on cast zinc-antimony alloys showed little to be expected in the way of improved performance over pure zinc, and this was borne out by the weight-loss results in the "wet-dry program" test.

Potential and corrosion current-density measurements revealed the cast manganese-nickel alloys to polarize to such an extent that insufficient current was available for protection of the coupled steel. It is believed that nonmetallic inclusions in the cast alloys may have influenced the results and tests are planned with electrodeposited alloys. Exposure of two of the alloys in the "wet-dry" cabinet caused a fairly rapid rate of corrosion. Removal of the corrosion products showed the underlying metal to be badly pitted.

Potential and corrosion current density tests on electrodeposited aluminum demonstrated this type of coating to have good possibilities. The coatings provide sacrificial protection for SAE 4130 steel in 3 per cent sodium chloride solution. The potentials in distilled water and CO_2-saturated water are such that protection by pure aluminum in these media could not be expected. The potential of aluminum can be made more electronegative by small additions of zinc and this presents a possibility for increasing the protection.

Preliminary tests on manganese-tin alloy plating disclosed that codeposition occurs from tartrate or fluoborate solution. However, the manganese is present in trace amounts only. This was only a preliminary study, and the plating work should be continued.

DISCUSSION OF ESSENTIAL DATA

"Wet-Dry Program" Tests on Cast Alloys

Introduction

The accelerated exposure tests described herein were made in the "wet-dry program" cabinet, full details of which are given in Appendix I.

Insufficient time was available during the first year of the investigation to complete the "wet-dry" exposure tests. The seven alloy groups described immediately below comprise the "left-overs". The rapid cycling was used for these specimens. Each cycle consisted of a wet period of 1 hour and 58 minutes, and a dry period of 42 minutes. The specimens were examined after 267 cycles or 711.5 hours. The extent of corrosion was estimated visually. All alloys in this group were exposed simultaneously.

Cast Cadmium-Silver Alloys

Two alloys, containing 3 per cent and 8 per cent silver, respectively (the percentage figures given here have been rounded off to the nearest whole number), were, together with the pure cadmium control specimens, the least corroded. No difference in the extent of corrosion was observed between the cadmium-silver alloys and the pure cadmium. For this reason, it was believed that more aggressive conditions were necessary and that they could possibly be achieved by a change in the cycling. Following the testing of this group, such a change was made and is described later in this report.

Tests under way at present with an electrodeposited cadmium-silver alloy are expected to show the difference, if any, between the alloy and pure cadmium. Weight-loss measurements on cast alloys are also being conducted to determine if a significant difference exists.

Cast Zinc-Silver Alloys

Three alloys containing 5 per cent, 18 per cent, and 25 per cent silver, respectively, were tested. The 25 per cent silver alloy showed none of the bulky white corrosion products characteristic of pure zinc, but it had developed a dark gray, adherent film through which light machining marks on the underlying metal could be seen. On the basis of visual examination, this alloy is superior to pure zinc and appeared, by visual examination, to be only slightly inferior to pure cadmium. (See weight-loss results below). The 18 per cent silver alloy was lighter gray in color than the 25 per cent silver alloy but it had more "zinc-type" corrosion products on the surface, although less than pure zinc would acquire. The 5 per cent silver alloy was corroded to the same extent as the pure zinc.

Cast Zinc-Tin Alloys

Four alloys of this series were exposed. The 25 per cent tin alloy corroded to the same extent as pure zinc. The 51 per cent tin alloy showed an increase in resistance to attack. The 80 per cent tin and 90 per cent tin alloys corroded the least but were not so resistant as the zinc-silver alloy containing 25 per cent silver. The Tin Research Institute has recommeded a zinc-tin alloy containing 78 per cent tin for protection of steel. In electrodeposited form, it is claimed to be superior to zinc plate in the salt-spray test, a humidity and condensation test, the hot water test, and the outdoor exposure test. It is interesting to note that, unlike zinc, its potential is not reversed with respect to iron in hot water.

Cast Zinc-Lead Alloys

Zinc-lead alloys, containing one-half per cent lead and one per cent lead, had slightly less corrosion products than pure zinc, and these corrosion products had a finer structure than those which formed on the pure zinc.

Cast Zinc-Nickel Alloys

The alloys containing from 11 to 12 per cent nickel had the same type corrosion products as pure zinc, but the amount was less.

Cast Zinc-Manganese Alloys

Three to five per cent manganese in zinc did not improve the corrosion resistance.

Cast Zinc-Chromium Alloys

Two to five per cent chromium in zinc did not improve the corrosion resistance.

Change in Cycling of "Wet-Dry Program" Cabinet

A change in cycling was believed to increase the rate of attack, and possibly make it easier to differentiate between metals such as cadmium and cadmium alloys. Results by other investigators have indicated that a smaller number of cycles per day provides a longer continuous exposure to condensation with a consequently more aggressive attack. Accordingly, the number of cycles was changed to two per day. The wet portion of each cycle then was of eleven hours, duration, while the dry portion lasted one hour.

A comparison of the rapid and slow cycling was obtained through the exposure of like thicknesses of zinc plate on steel. The time required for rust to appear was the same in both cases, showing that no acceleration was obtained by this change.

Weight-Loss Measurements on Cast Specimens Exposed in the "Wet-Dry Program" Cabinet

The use of visual inspection of the cast specimens to determine the extent of corrosion is open to the objection that nonadherent corrosion products may fall off or partially soluble compounds can be dissolved away, leaving a surface which appears relatively free of corrosion. For this reason, an experiment was made using weight-loss measurements in combination with the "wet-dry" test. Such measurements were believed to give, at least, semiquantitative data on the relative resistances of the alloys.

For this series of measurements, one previously exposed alloy series and two unexposed systems were used. The zinc-silver series was re-exposed because it appeared so promising in all previous tests. Four cast zinc-antimony alloys, two cast manganese-nickel alloys, and control specimens of zinc and cadmium completed the lot. All specimens were in duplicate. Before exposure, the specimens were cleaned and weighed accurately. Following an exposure of fifty days or one-hundred cycles, the corrosion products were removed chemically (see Appendix I) and the specimens reweighed. Weight losses were expressed as milligrams per square decimeter per day. The average results are graphed in Figure 1 (also see Tables 6, 7, and 8, Appendix II).

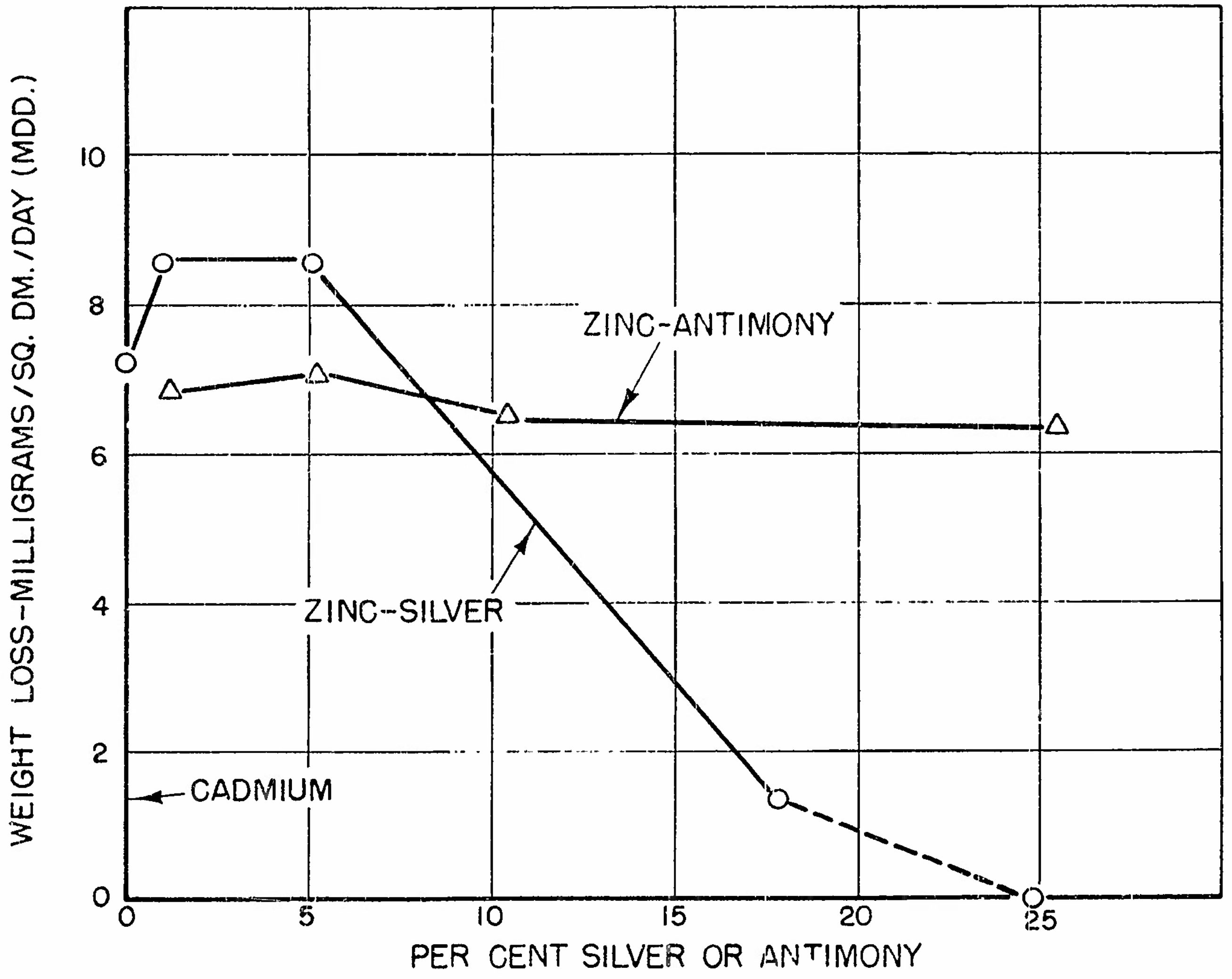

FIGURE I. RELATIONSHIP BETWEEN ALLOY COMPOSITION AND WEIGHT LOSS FOR CAST ZINC-ANTIMONY AND CAST ZINC-SILVER ALLOY SPECIMENS AFTER FIFTY DAYS' EXPOSURE IN THE "WET-DRY PROGRAM" TEST

0-11178

Cast Zinc-Antimony Alloys

The addition of antimony to zinc, in amounts up to 25 per cent had only a small effect in hindering corrosion. The small drop in weight loss is not considered significant.

Cast Zinc-Silver Alloys

The addition of silver to zinc in amounts up to 5 per cent appears to increase the corrosion rate. This correlates with results obtained during the measurements of corrosion current densities. (See Final Report, Nov. 30, 1947, p. 49). With the silver content at 18 per cent, the weight loss decreases to approximately the same level as pure cadmium. When the silver content is increased to 25 per cent, the corrosion rate is well below that of pure cadmium.

The 25 per cent silver alloy actually showed a slight weight gain after removal of the corrosion products. This gain was small and is well within the limits of experimental error. This might just as well have been a small loss. For the reason that the exact location of the final point in Figure 1 is uncertain within small limits (± 0.1 mdd), the final portion of the curve is dotted.

The results of this test are in agreement with the visual estimation made prior to removal of the corrosion products and with the previous test described on page 8 , this report.

Removal of the corrosion products disclosed the zinc-silver alloys containing one and five per cent silver, respectively, to be pitted to the same extent as pure zinc. The 18 per cent silver alloy had only a few pits while the 25 per cent silver alloy was free of pits, although it was stained somewhat.

Cast Manganese-Nickel Alloys

The manganese-nickel alloys, containing 14 per cent and 30 per cent nickel, respectively, acquired a fairly thick, adherent, dark brown, corrosion layer. No satisfactory procedure was found for removal of the corrosion products. Acidified, 15 per cent hydrogen peroxide solution removed enough of the coating to allow observation that the underlying metal was pitted, but the attack on the basis metal was too great for quantitative measurements. It is estimated that the corrosion rate of these alloys is fairly high.

"Wet-Dry Program" Tests on Electrodeposited Specimens

A complete evaluation of the results of exposure of the electrodeposited specimens in the "wet-dry" test was not given in the Sixth Progress Report, because the test was still under way when the report was being written. The test has now been completed and the resultant data are given here.

The number of cycles elapsing to the first appearance of rust has been arbitrarily chosen as the criterion of failure and the data are given in Table 1. This table does not include the manganese specimens for reasons which will be discussed below. With the exception of the 10 per cent zinc - 90 per cent tin specimens, there were four specimens of each type. The thickness of coating was 0.3 mil. Half of the specimens were exposed intact while the other half were scored with two diagonal scratches, thus exposing the basis steel. This was done to test the galvanic protective power of the coating.

The data in Table 1 show that for zinc and zinc-tin alloys the average number of cycles to the first appearance of rust is about the

TABLE 1. RESULTS OF EXPOSURE OF PLATED SPECIMENS IN THE "WET-DRY PROGRAM" TEST. THICKNESS OF COATING 0.3 MIL.

Type	Specimen No.	No. Cycles to First Rust	Average No. Cycles to First Rust	Remarks
		(Specimens Unscratched)		
Pure zinc	3363-55A	6		
	-55D	10	8	Typical pin-hole type rust spots.
Zinc-tin 10-90	-49A	10	10	Ditto
20-80	-68C	24		
	-68F	18	21	"
30-70	-54C	42		
	-54D	56	49	"
Pure cadmium	-56A	100		
	-56E	126	113	"
		(Specimens Scratched)		
Pure Zinc	3363-55B	8		Rust in scratches and on plate.
	-55C	8	8	3 rust spots on plate only.
Zinc-tin 10-90	-49B	20	20	Large rust spot in scratch.

TABLE 1. (Continued)

Type	Specimen No.	No. Cycles to First Rust	Average No. Cycles to First Rust	Remarks
20-80	-68A	22		One rust spot in scratch. Two on plate.
	-68B	24	23	Ditto
30-70	-54A	36		Three rust spots in scratch.
	-54B	56	46	One rust spot in scratch.
Pure cadmium	-56C	6		Rust in scratches only.
	-56F	2	3	Ditto

same for equivalent specimens, whether scratched or unscratched. The conclusion can be drawn that these coatings give sacrificial protection to exposed areas of the basis metal. Pure cadmium, however, behaves quite differently. The specimens with the scratches showed rust after a few cycles while the unscratched cadmium required an average of 113 cycles for rust to appear. The conclusion in this case is that cadmium does not provide adequate protection at breaks in the coating.

The 20-80 and the 30-70 zinc-tin alloys are both superior to pure zinc, with the 30-70 alloy being the better of the two.

While undamaged cadmium coatings are superior to pure zinc and zinc-tin alloys, the same cannot be said for the damaged coating. In this wet-dry test, even pure zinc is superior to the cadmium if both coatings are damaged.

Clear-cut observations were not possible on the manganese-coated panels because of the similarity in color of the corrosion products of manganese and iron. For this reason, the exact number of cycles to the first appearance of rust was not determined and no data are given in Table 1. Observation of the manganese-coated panels during the exposure period disclosed two important facts. Iron rust appeared in the scratches after one cycle, but the unscratched specimens remained free of iron rust for a period approximately twice as long as the unscratched zinc specimens. Dipping in dichromate solution, prior to exposure, improves the resistance of the manganese coating. Aside from this, the brittleness of the manganese deposits would make them undesirable, since there is great possibility of their being chipped off.

The preparation of the electrodeposited specimens is described in Appendix I.

Static and Dynamic Potential and Corrosion Current-Density Measurements

Introduction

The apparatus and methods used in making these potential and current-density measurements are described in detail in Appendix I

The static potentials were measured in 3 per cent sodium chloride solution, in water saturated with carbon dioxide, and in distilled water, at 90°F., against saturated calomel electrodes. From these measurements are drawn conclusions as to whether an alloy can be expected to protect steel sacrificially.

The dynamic potential measurements were made in 3 per cent sodium chloride solution at 90°F. They provide information relative to polarization and corrosion current density as influenced by alloying. In developing substitute alloys, it is desired to provide the lowest possible corrosion current density commensurate with sacrificial protection. Such alloys should also retain an electrode potential appreciably less noble (more anodic) than that of steel. The larger the difference, the more effective will the alloy coating be in protecting "bare" areas of steel. Alloys more noble than steel will not give the type of protection desired in this work.

Cast Zinc-Antimony Alloys

The static potential measurements of the zinc-antimony alloys in 3 per cent sodium chloride solution, in CO_2-saturated water, and in distilled water are given graphically in Figure 2. (Also see Tables 9 and 10, Appendix I).

Up to approximately 50 per cent antimony, the alloys are anodic

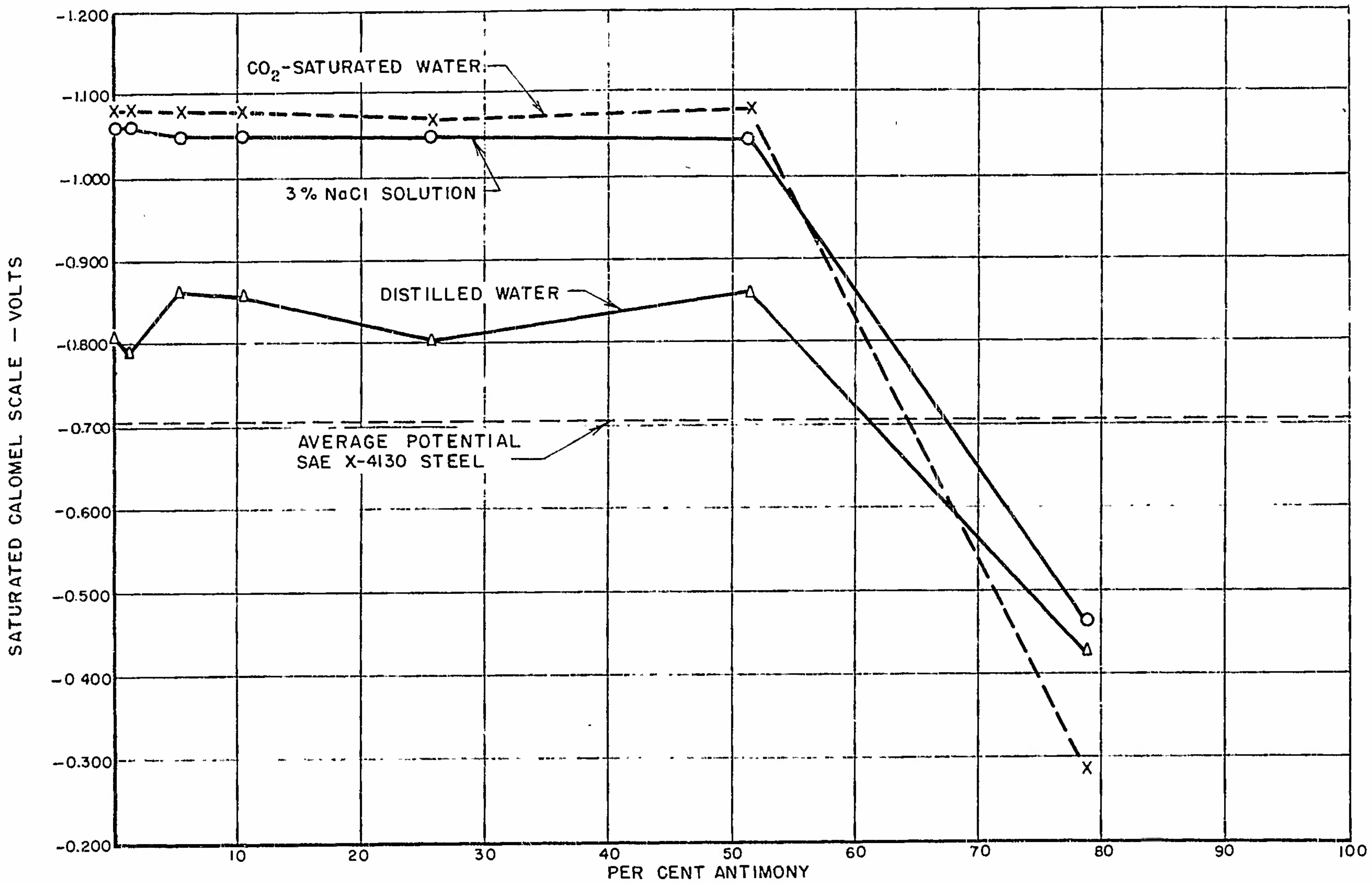

FIGURE 2. GRAPH SHOWING STATIC ELECTRODE POTENTIALS OF CAST ZINC-ANTIMONY ALLOYS IN 3% NaCl SOLUTION, CO_2-SATURATED WATER, AND DISTILLED WATER. MEASURED AGAINST A SATURATED CALOMEL HALF-CELL. TEMPERATURE 90 °F., 60-MINUTE IMMERSION.

0-9474

to SAE 4130 steel and can be expected to provide protection for the steel in the three media. Figures 3 and 4 show the polarization and corrosion current densities, respectively, when the alloys were coupled with steel in 3 per cent sodium chloride solution. Figure 3 shows a small increase in polarization up to about 10 per cent antimony, but, after that, no additional polarization occurs. (See also Table 11, Appendix II). The current density of the coupled cells (Figure 4) decreases from 6 ma./sq.in. for pure zinc to 4 ma./sq.in. for the 50 per cent antimony alloy. This decrease in current density indicates that the 50 per cent alloy would show a somewhat increased resistance to corrosion. Because of its extreme brittleness, however, it is doubtful if its use would be practicable.

Cast Manganese-Nickel Alloys

Figure 5 shows the change in static potentials with increase in nickel content for the manganese-nickel alloys in the same three media, in which the change to more noble values is quite abrupt with increase in nickel content. Furthermore, the potential-time data (see Tables 12, 13, and 14, Appendix II) show that, for the alloys which are anodic to steel, the potential values become more noble with time. This information predicts that sacrificial protection would be established only in the 3 per cent sodium chloride solution. However, the results of the dynamic tests did not confirm this. Figures 6 and 7 show the polarization and corrosion current densities for the alloys. (Also see Table 15, Appendix II). There is a large shift in polarization with increase in nickel content, and the current density drops to practically zero (actually a very minute current was flowing). Observation of the steel specimens after 24 hours showed them to be slightly rusted.

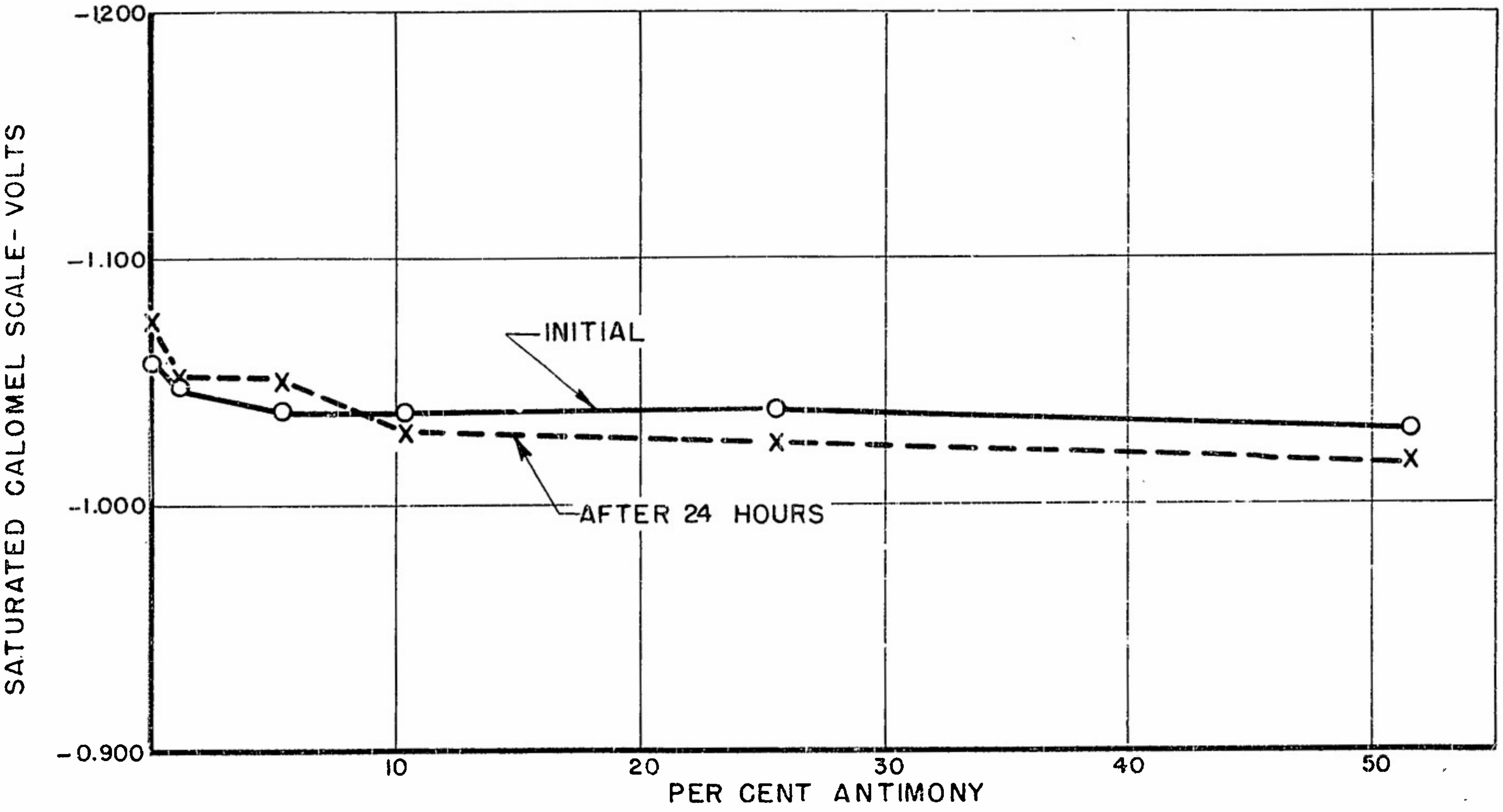

FIGURE 3. GRAPH SHOWING DYNAMIC ELECTRODE POTENTIALS OF CAST ZINC-ANTIMONY ALLOYS COUPLED WITH STEEL IN 3% NaCl SOLUTION. MEASURED AGAINST A SATURATED CALOMEL HALF-CELL. TEMPERATURE 90 °F.

0-9475

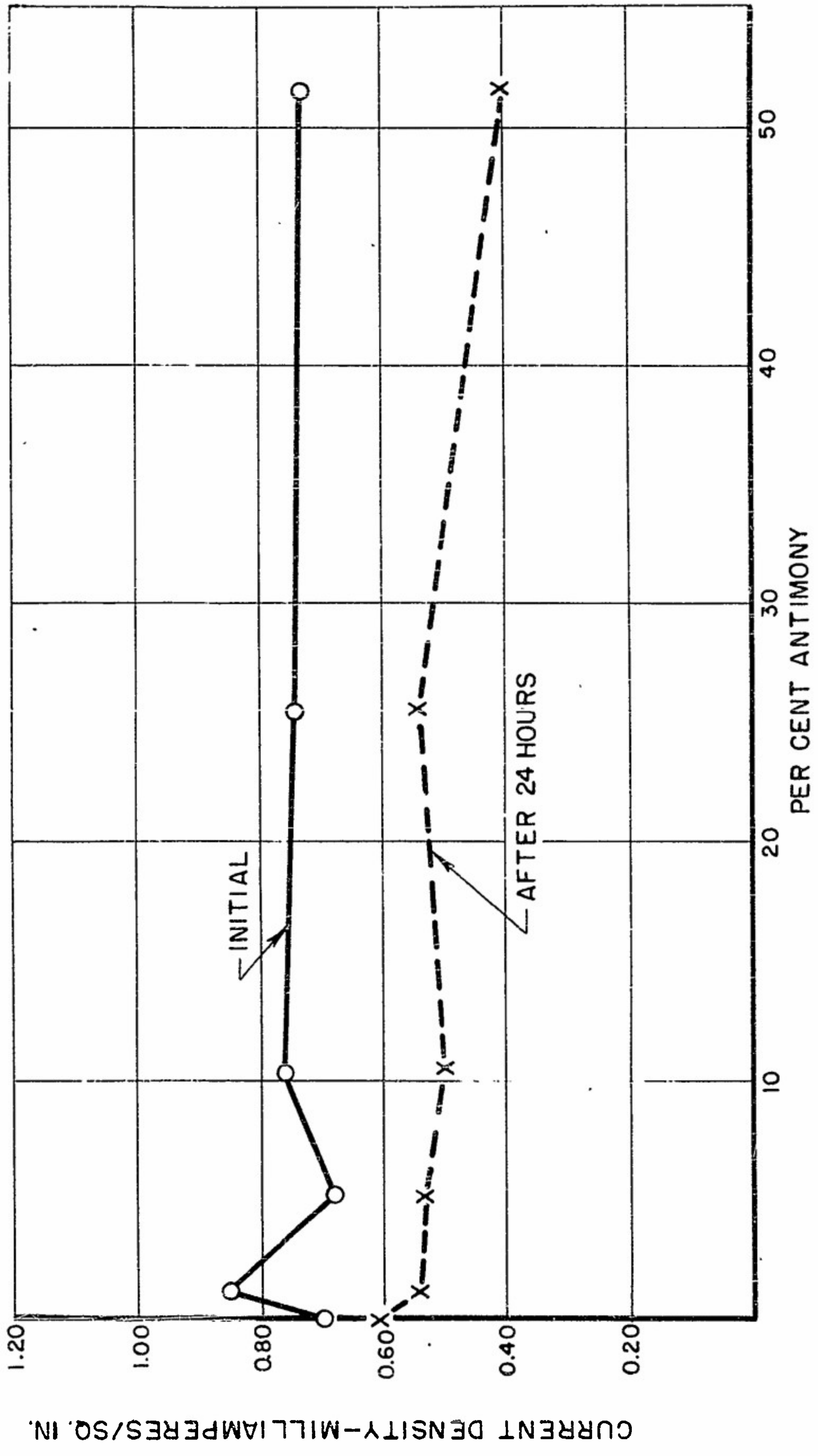

FIGURE 4. CORROSION CURRENT DENSITY IN CELLS CONSISTING OF CAST ZINC-ANTIMONY ALLOYS COUPLED WITH STEEL, IN 3 % NaCl SOLUTION AT 90 °F.

0-9476

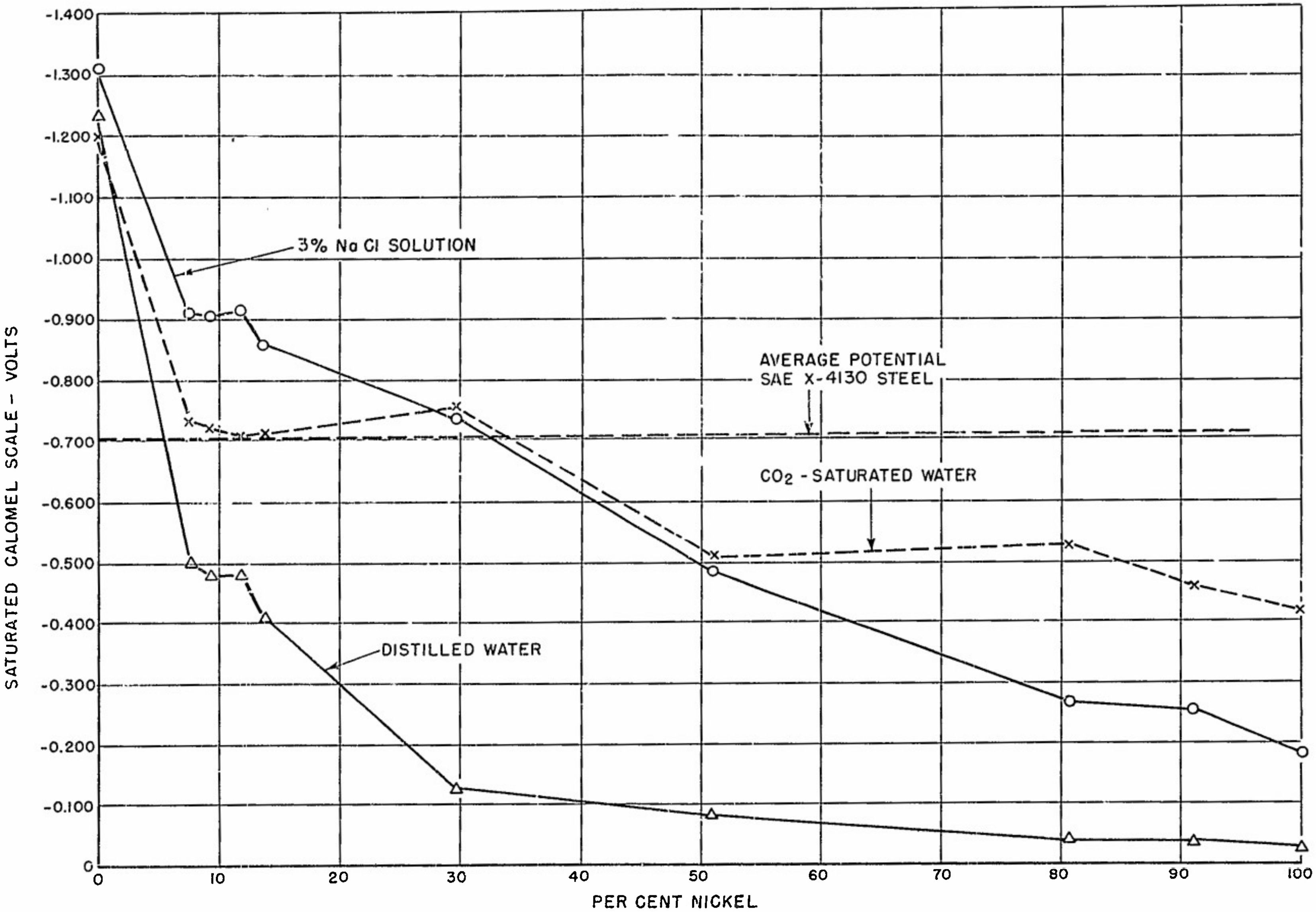

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FIGURE 5. STATIC ELECTRODE POTENTIALS OF CAST MANGANESE-NICKEL ALLOYS IN 3% NaCl SOLUTION, CO_2-SATURATED WATER, AND DISTILLED WATER, MEASURED AGAINST A SATURATED CALOMEL HALF-CELL. TEMPERATURE 90° F., 60-MINUTE IMMERSION

0-9946

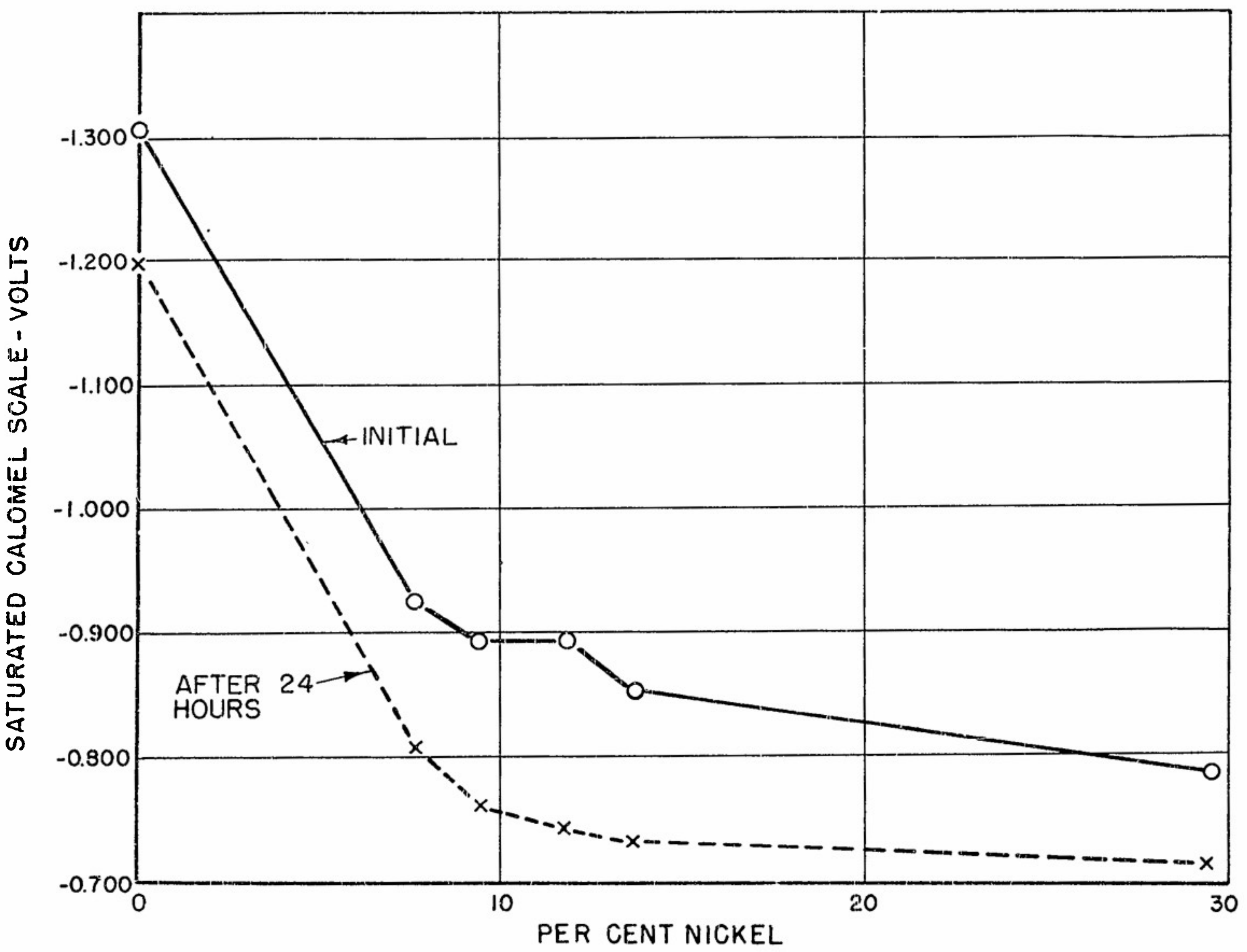

FIGURE 6. DYNAMIC ELECTRODE POTENTIALS OF CAST MANGANESE - NICKEL ALLOYS COUPLED WITH STEEL IN 3% NaCl SOLUTION. MEASURED AGAINST A SATURATED CALOMEL HALF-CELL. TEMPERATURE 90° F.

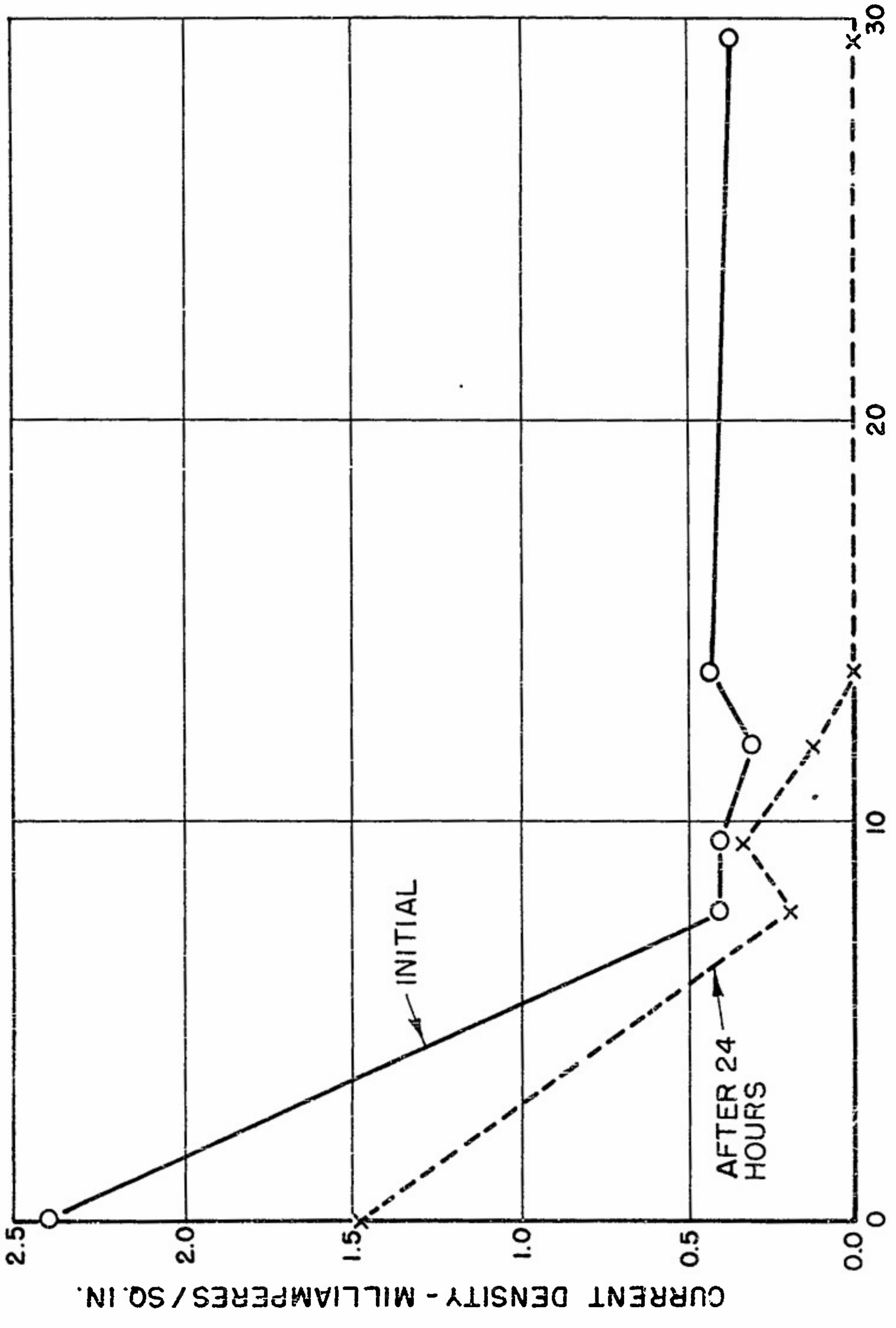

FIGURE 7. CORROSION CURRENT DENSITY IN CELLS CONSISTING OF CAST MANGANESE-NICKEL ALLOYS COUPLED WITH STEEL, IN 3% NaCl SOLUTION AT 90° F.

0-9945

The results of the potential measurements, together with the results of the "wet-dry" tests, leave small hope for manganese-nickel alloys as substitute coatings. There is one factor, however, which indicates that additional tests should be made on electrodeposited alloys before this alloy system is dropped entirely. Metallographic examination of some of the cast alloys showed a small percentage of nonmetallic inclusions which could have had a marked and detrimental effect on the corrosion rate. Such a condition, conceivably, would be minimized with plated alloys.

Electrodeposited Aluminum

Several processes for electrodepositing aluminum have been developed recently by Hurley and Weir*. Essentially, the aluminum is deposited from a toluene solution of anhydrous aluminum chloride-ethyl pyridinium bromide eutectic. The process involves a modification of customary electrodeposition practice, in that moisture must be excluded from the plating cell. The solutions have been under investigation in these laboratories for over a year, in work conducted for the Bureau of Aeronautics, U. S. Navy.

After some preliminary work to determine the proper conditions for adhesion on the steel basis metal, several specimens were plated with 0.001 inch of aluminum, which had satisfactory qualities as to appearance and adhesion. Subsequent attempts to reproduce adherent deposits failed and no reason is known for this failure. However, the first attempt had provided sufficient satisfactory specimens for the potential and corrosion current-density measurements.

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* U. S. Patents 2,446,331, 2,446,349, and 2,446,350

The results of the static potential measurements are recorded in Table 2. At 120 minutes, the aluminum was approximately 300 millivolts more negative than SAE 4130 steel when immersed in 3 per cent sodium chloride solution. Also, the aluminum potential became less noble with time. Hydrogen peroxide was not used in these measurements.

In both distilled water and CO_2-saturated water, the aluminum is shown to be more noble than the steel and, therefore, not protective. In both media, the over-all change with time is in the noble direction.

These measurements predict that the electrodeposited aluminum will protect 4130 steel sacrificially in 3 per cent sodium chloride solution, but not in distilled water or water saturated with CO_2.

Table 3 shows the results of the polarization and corrosion current-density measurements made on the coupled cell in 3 per cent sodium chloride solution. The current density was quite low compared to that of many of the alloy specimens. After 24 hours, the steel was not rusted. A second couple was set up and, after four days, the steel was not rusted.

Zinc-Silver Alloy Plating

Of the several factors involved in alloy plating, usually the first to be considered is the problem of respective deposition potentials. Reference to the table of standard potentials shows that zinc and silver are separated by 1.56 volts. It is recognized, however, that the static potentials alone are not indicative of the probability of codeposition. Under the influence of the current, polarization plays an important role. With these general ideas in mind, a preliminary attack was made on the problem.

TABLE 2. POTENTIAL-TIME DATA FOR STEEL ELECTROPLATED WITH ALUMINUM, MEASURED AT 90°F., IN 3 PER CENT SODIUM CHLORIDE SOLUTION, IN DISTILLED WATER SATURATED WITH CARBON DIOXIDE, AND IN DISTILLED WATER. SATURATED CALOMEL SCALE, VALUES IN VOLTS*.

Specimen No.	Volts at Elapsed Time of: 1 Min.	30 Min.	60 Min.	90 Min.	120 Min.
	(3% Sodium Chloride Solution)				
3942-87F	0.916	0.945	0.970	---	---
	(Distilled Water Saturated With Carbon Dioxide)				
3942-87I	0.597	0.660	0.668	---	---
	(Distilled Water)				
3942-87J	---	---	0.623	0.618	0.563

* All values are negative.

TABLE 3. INITIAL AND 24-HOUR DYNAMIC POTENTIAL AND CORROSION CURRENT-DENSITY DATA FOR ELECTRODEPOSITED ALUMINUM COUPLED WITH STEEL. COUPLE IMMERSED IN 3 PER CENT SODIUM CHLORIDE SOLUTION AT 90°F. FOR THE 24-HOUR PERIOD. SATURATED CALOMEL SCALE.

	Initial Measurements		24-Hour Measurements	
Specimen No.	Coupled Alloy (Volts)	Corrosion Current Density (Ma./In.^{2})	Coupled Alloy (Volts)	Corrosion Current Density (Ma./In.^{2})
3942-87F	-0.813	0.46	-0.740	0.22

Assuming, for the present, that the deposition potential for a metal is close to its reversible potential, then the deposition potential is dependent on the ionic concentration in accordance with the Nernst equation. This relationship states that an increase in ion concentration will make the deposition potential more positive (indicating easier deposition), whereas a decrease in ion concentration has the opposite effect. If the zinc-ion concentration were increased and the silver-ion concentration were decreased, the net result would be to lessen the disparity in their respective reversible potentials. The obvious way to accomplish this is to "complex" the silver but not the zinc. A study of the literature revealed that an iodide solution might fulfill the requirements. Good deposits of silver have been obtained from complex iodide solutions*, while no evidence was found indicating that zinc formed a complex iodide.

As a basis for comparison, separate sulfate solutions of zinc and silver, respectively, were prepared. These were patterned after a commercial zinc, acid-sulfate, plating solution. (The details of this work will be found in Appendix I). The static potentials of these solutions were measured, and then the polarization values were determined. The results are plotted in Figure 8 (See also Tables 16 and 17 in Appendix II). The respective static potentials for zinc and silver in these sulfate solutions are 1.43 volts apart. The polarization curves show that this value is increased when the current flows. The zinc polarizes slightly while the silver polarization is insignificant. With iodide solutions, however, the situation changes. The static potential difference has been reduced to 0.55 volts,

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* C. W. Fleetwood and L. F. Yntema, Ind. Eng. Chem., 27, 340(1935).

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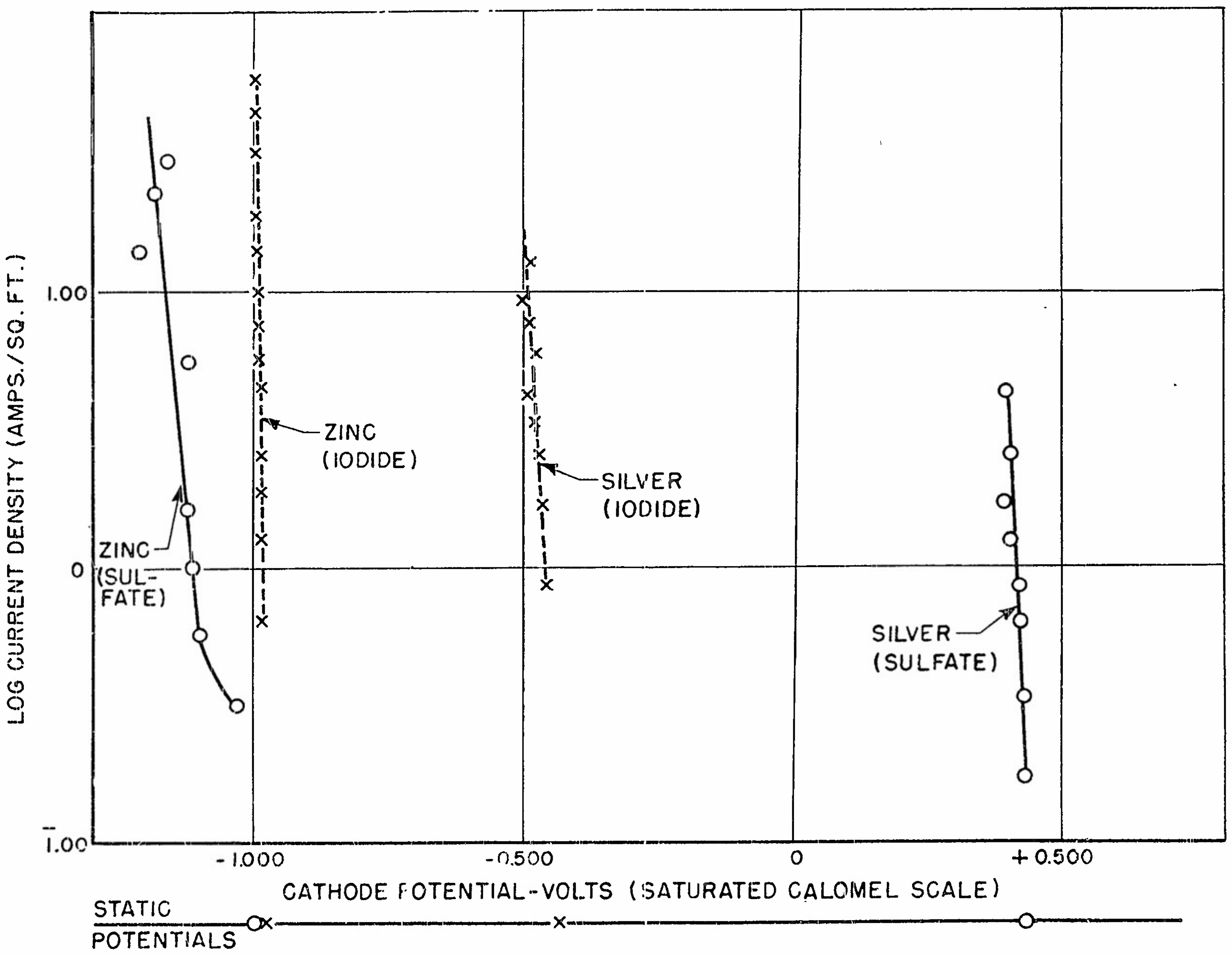

FIGURE 8. POLARIZATION CURVES FOR ZINC AND SILVER IN SEPARATE SULFATE AND IODIDE SOLUTIONS

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but neither of the elements shows appreciable polarization, so that with the current flowing there is still no common potential at which codeposition may be expected to occur. However, the change in potentials is in a favorable direction in the solutions containing only a single heavy-metal element, so that it is possible, where both elements are present, one element may polarize the other with resultant codeposition. Such a trial was carried out, and codeposition did occur.

This method of investigating prospective plating solutions, while limited as to definite predictions, can, nevertheless, indicate the probability of obtaining a codeposit from a given type of solution.

Subsequent experiments with the iodide solution resulted in powdery deposits containing 50 per cent zinc. The use of agitation, or changes in temperature and current density, did not ameliorate the nature of the deposit, but addition of thiourea caused some improvement. This lead should be followed up in future work, with trials of various other addition agents.

Details of the apparatus and methods used in the zinc-silver plating experiments are given in Appendix I.

Zinc-Tin Alloy Plating

Instructions for electrodepositing 22 per cent zinc - 78 per cent tin alloy have been given by R. M. Angles[1] J. W. Cuthbertson and R. M. Angles[2]. The recommended solution, when used in this work, gave an alloy having 95 per cent tin. Experiments resulted in the bath described on page 56 of Appendix I, which produced the desired alloy plate. The

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[1] J. Electrodep. Tech. Soc., 21, 45, (1946)

[2] J. Electrochem. Soc., August, 1948, p. 73

zinc-tin alloys of other compositions can be produced by maintaining a constant tin and "free cyanide" content and adjusting the zinc and "free caustic" concentrations. Increasing the zinc or "free caustic" concentrations increases the zinc content of the deposit.

Manganese-Tin Alloy Plating

Experiments with fluoborate and tartrate solutions resulted in a deposit containing traces of manganese. The experiments and results are given in Table 4, Appendix I.

Investigation of the manganese pyrophosphate solution showed that manganese could be deposited from such a solution. No codeposition experiments were made from the pyrophosphate complexes.

FUTURE WORK

The contract period was extended to July 31, 1949, at no additional cost. This permitted continuation of the exposure tests and the zinc-silver alloy deposition work. The results of experiments completed during this period will be reported in the First Progress Report under a new contract being negotiated at present.

EXPERIMENTAL WORK*

The apparatus and methods used for this work are described in detail in Appendix I.

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* Laboratory Record Book No. 3363, pp. 31-100
Laboratory Record Book No. 3393, pp. 15-56
Laboratory Record Book No. 3942, pp. 24-100
Laboratory Record Book No. 4557, pp. 1-3

APPENDIX I

APPENDIX I

This Appendix contains descriptions of all apparatuses and all methods used for this project.

Preparation of the Media in Which the Electrode Potentials Were Measured

Three Per Cent Sodium Chloride Solution

The water used for the sodium chloride solution was the regular laboratory distilled water having a pH of 6.3. The salt used was "Baker's Analysed", chemically pure sodium chloride. The solution was filtered and the concentration checked by accurate specific gravity measurement.

Distilled Water

The distilled water, which was used alone for potential measurements, was a specially purchased product having a specific conductivity of $5\text{x}10^{-6}$ reciprocal ohms and a pH of 6.9-7.0. It was protected by a tube containing "Ascarite", a carbon dioxide-absorbing substance.

Distilled Water Saturated with Carbon Dioxide

Compressed carbon dioxide was bubbled through the special distilled water, using a water trap in series with the solution under preparation. The solution had a pH of 4.1 after one hour and additional bubbling of carbon dioxide through the solution did not change this value. Numerous checks showed this pH value to be reproducible.

Static Electrode Potential Measurements

Apparatus

Figure 9 is a picture of the apparatus as set up for measuring static electrode potentials of four specimens concurrently. Also, pictured in this figure are the additional pieces of equipment used in the dynamic potential measurements which are described later.

A Leeds and Northrup, student-type potentiometer was used for measuring potential differences in 3 per cent sodium chloride solution and in CO_2-saturated water. For potential measurements in distilled water, a Leeds and Northrup No. 7660 Electrometer-Potentiometer was used. This instrument is of the vacuum-tube type and was specially designed for use in high-resistance circuits. Four No. 4970 saturated calomel cells, designed for use with the Beckman pH meter*, were used as reference electrodes. When measurements were made in distilled water or in distilled water saturated with carbon dioxide, the test-tube-like calomel electrodes dipped directly into these media. For the measurements in 3 per cent sodium chloride solution, the calomel electrode dipped into a small cup containing a saturated solution of potassium chloride. A bent, 7-mm.-diameter glass tube, containing a 3 per cent sodium chloride solution, connected this cup, as a bridge, to the beaker filled with a 3 per cent sodium chloride solution, into which dipped the specimen. The end of the glass tube, which dipped into the 3 per cent sodium chloride solution, was drawn down to a small bore into which a

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* Manufactured by the National Technical Labs., Pasadena, California.

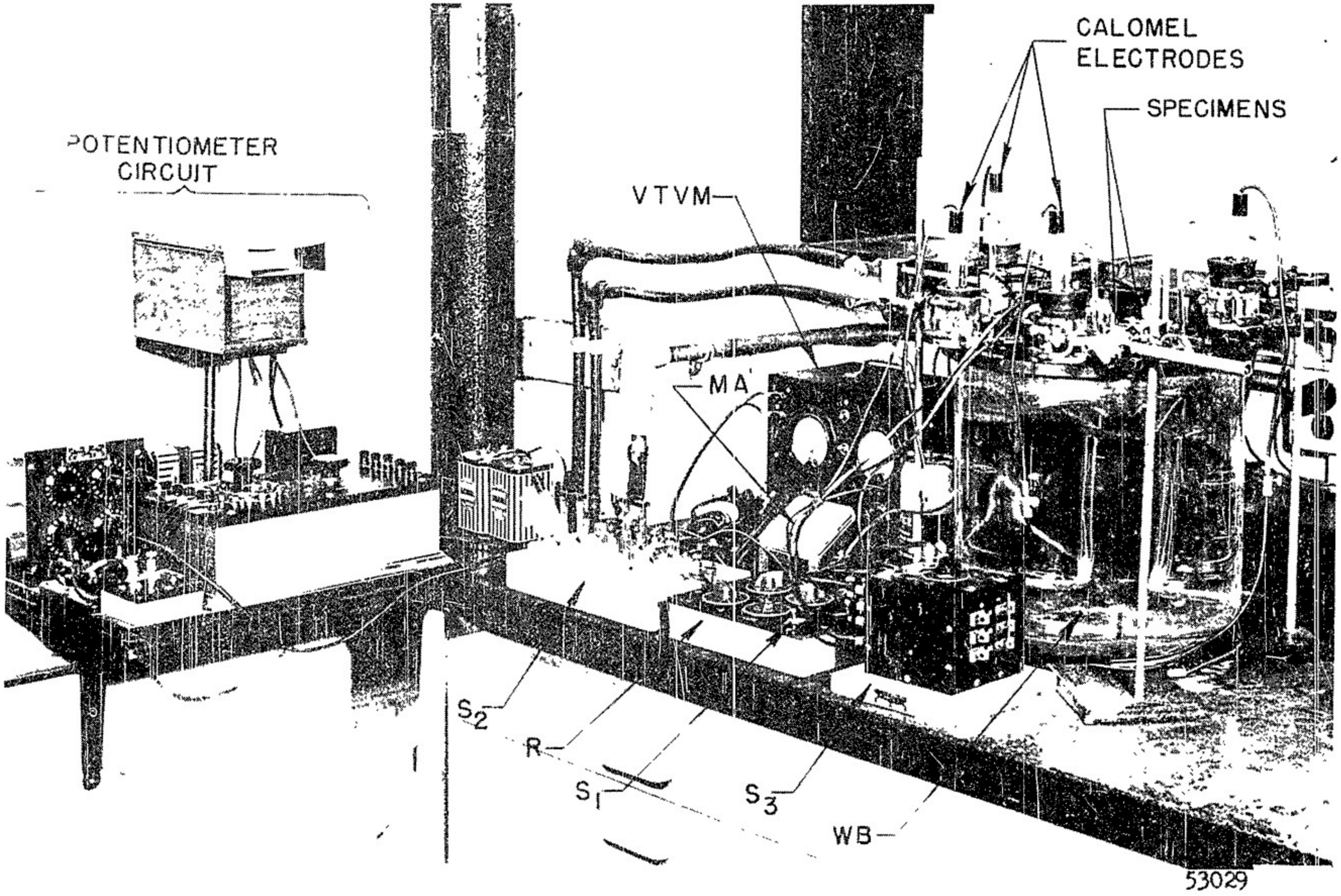

Figure 9. Apparatus for the Measurement of Static and Dynamic Electrode Potentials and Corrosion Currents. As Pictured, the Apparatus is Connected to Measure Static Electrode Potentials

5-mm. length of fibrous asbestos was sealed. The asbestos tip reduced diffusion and, by having the calomel electrode dip into the saturated potassium chloride solution, contamination of the calomel electrode by sodium ions is minimized.

The corrosive media were contained in 250-ml. beakers, which were immersed in a thermostatically controlled water bath (WB in Figure 9), which operated within ±1°F. of the desired temperature.

The specimens were supported in bakelite clamps which rested on the edges of the beakers. A four-way, rotating, double-pole switch (S_3 in Figure 9) was used so as to make possible the concurrent measurement of four specimens.

The poteniometric circuit was calibrated twice by the Battelle Instrument Laboratory and was found to be accurate to 0.5 millivolt.

Method

The calomel electrodes were placed so that the tips were immersed in the corrosive medium to a depth of 3/4 inch. The clamped specimens were then immersed vertically to a depth of 1-1/2 inches and placed so as to be 1/4 inch from the calomel electrode tip. After one minute, the initial potential measurement was made (except for measurements in distilled water; see below). Subsequent measurements were then made at 10-minute intervals, following the instant of immersion, up to 60 minutes. After this, measurements were made at 30-minute intervals.

When the specimens were being tested in distilled water, the initial measurements were made after 60 minutes had elapsed and subsequent measurements were made at 75 and 90 minutes. The reason for waiting 60

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When the specimens were being tested in distilled water, the initial measurements were made after 60 minutes had elapsed and subsequent measurements were made at 75 and 90 minutes. The reason for waiting 60 minutes before making the initial measurements was originally connected with the fact that the student-type potentiometer was not capable of making measurements in high-resistance systems. Therefore, it was necessary to allow some time to elapse in order that some of the test electrode material might dissolve, thus increaseing the conductivity. This was not necessary when using the Leeds and Northrup electrometer, but was done only to conform with the original set of measurements. The calomel electrodes were removed from the water when the measurements were not being made so that no contamination would result from potassium chloride solution.

Dynamic Potential and Corrosion Cell Current-Density Measurements

Apparatus

The circuit developed by Brown & Mears*, for measuring potentials and currents in coupled cells, was used in this work. A schematic diagram of this so-called "zero-resistance" circuit is given in Figure 10. As shown in Figure 9, the apparatus was connected for the measurement of static electrode potentials. By disconnecting the potentiometer leads from the four-way switching box and reconnecting them to terminals 2 and 5 of S_2 (Figure 10), and connecting two calomel electrodes, the apparatus is ready for dynamic measurements. MA is a 0-10 milliammeter, if relatively high currents are to be measured. For low currents, a multi-range microammeter can be switched into the circuit. The battery between

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* Trans. Electrochem. Soc., 74, 495, (1938)

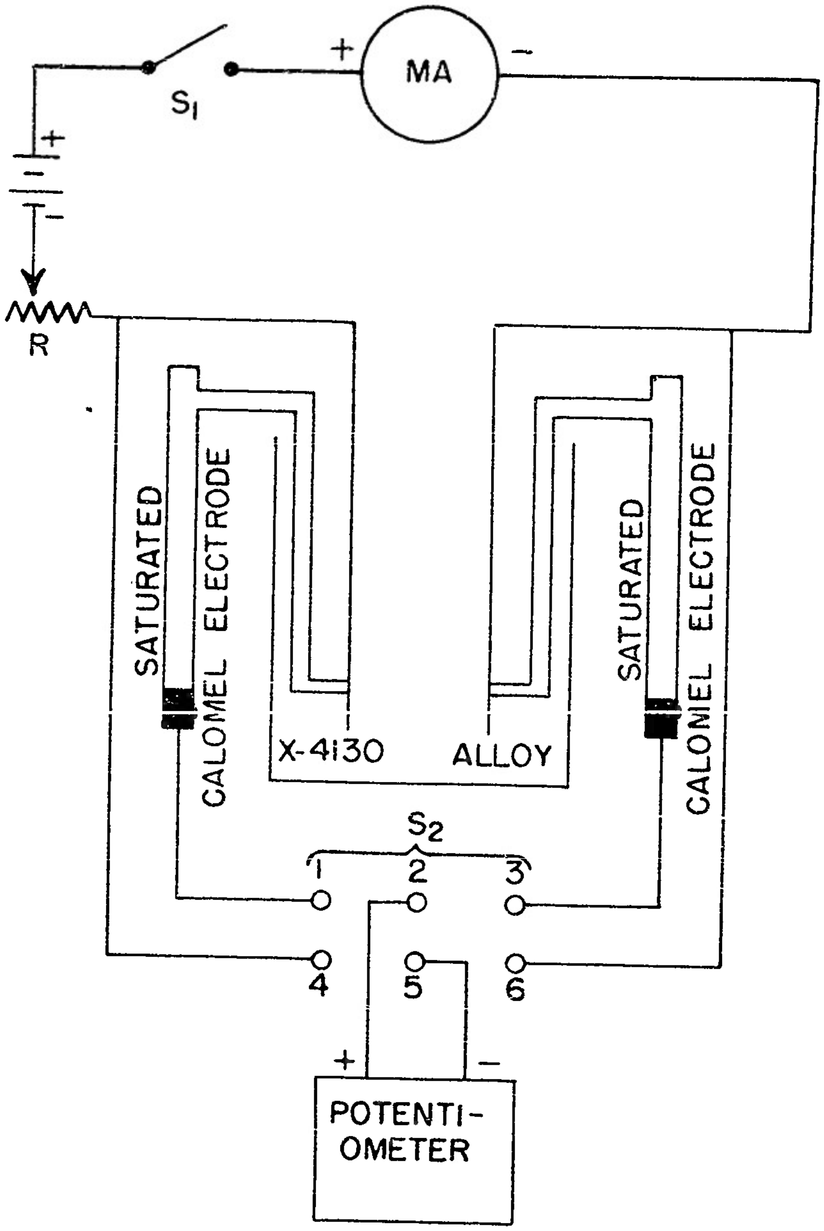

FIGURE 10. SCHEMATIC REPRESENTATION OF THE "ZERO-RESISTANCE" CIRCUIT FOR MEASUREMENT OF CORROSION CURRENTS AND ELECTRODE POLARIZATION

resistance R and switch S_1 is a 1-1/2-volt dry cell. Resistance, R, comprised a 5000-ohm, a 3000-ohm, and two 1000-ohm variable radio-type resistors connected in series. For very low current measurements, additional fixed resistors were available and could be plugged in at the terminals of R. Switch, S_2, was constructed from two knife switches, one a double-pole, double-throw type, and the other a double-pole, single-throw type. It should be noted that switch, S_2, as drawn in Figure 10 is not meant to represent a simple double-pole, double-throw switch. Reference to the method of using this apparatus, as given below, will make this clear. In addition to the Leeds and Northrup student-type potentiometer circuit, a simple slide-back, vacuum-tube voltmeter (VTVM in Figure 9) was used for attaining a rough null adjustment.

The specimens were supported by bakelite clamps which held the steel and alloy (or pure metal) one inch apart.

Method

The clamped specimens were immersed in the sodium chloride solution and the circuit connections were then made. The two calomel electrodes were placed so that the tips were against the surfaces of the steel and alloy, respectively. A period of twenty minutes elapsed, following the instant of immersion, and the measurements were made according to the following procedure:

1. With switch, S_1, open and switch, S_2, thrown so that contacts 1 and 4 were connected to 2 and 5, respectively, potential of the S.A.E. 4130 steel was measured.

2. With switch, S_1, open and switch, S_2, thrown so that contacts 3 and 6 were connected to 2 and 5, respectively, the potential of the alloy was measured.

3. With switch, S_1, open and switch, S_2, thrown so that contacts 4 and 6 were connected to 2 and 5, respectively, the difference in potential between the steel and the alloy was measured. This value should be very close (1 mv.) to the calculated difference obtained from Steps 1 and 2.

4. With switch, S_2, connected as in Step 3, switch, S_1, was closed and resistance, R, was adjusted, so that the potential difference between the steel and the alloy was zero. The corrosion current for the cell was then read on the milliammeter (or the microammeter).

5. With S_1 closed, and with zero potential difference as in Step 4, the separate potentials of the steel and alloy were measured as in Steps 1 and 2.

Preparation of Specimens for Potential Measurements

Zinc-Antimony Alloys

The as-cast ingots were machined on a shaper so as to produce a smooth surface. The specimens were then cleaned by rubbing with a clean cloth saturated with carbon tetrachloride or acetone. This was followed by vapor degreasing in trichlorethylene. The same specimens were used for measurements in the several media; between measurements, the light corrosion products were removed by rubbing with fine steel wool. The machined surfaces of the specimens facilitated this and no significant

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Manganese-Nickel Alloys

These alloys were too brittle to be worked on the shaper. The sawed specimens were smoothed on abrasive belts, ending up with 325 grit. They were then rubbed with a clean cloth saturated with carbon tetrachloride, and were then vapor degreased in trichlorethylene.

Steel Cathodes for Corrosion Current-Density Measurements

The SAE 4130 specimens had good surfaces to begin with, so the treatment consisted of rubbing with fine steel wool and then dipping for 20 seconds in 1-1 hydrochloric acid just prior to using.

Cathode Potential Measurements

Apparatus

A schematic representation of the apparatus used for these experiments is given in Figure 11. Cylindrical cathodes were used in order to minimize point-to-point potential differences. A rubber cap was placed over the lower end of the cathode to minimize "edge effects". Two probing-tip, saturated calomel reference electrodes touched the cathode on opposite sides. One of the tips was one inch below the surface, while the second was 1-7/8 inches below the surface of the solution. The bare portion of the cathode was immersed to a depth of two inches. Two anodes were used, each being enclosed in porous Alundum thimbles. Carbon anodes

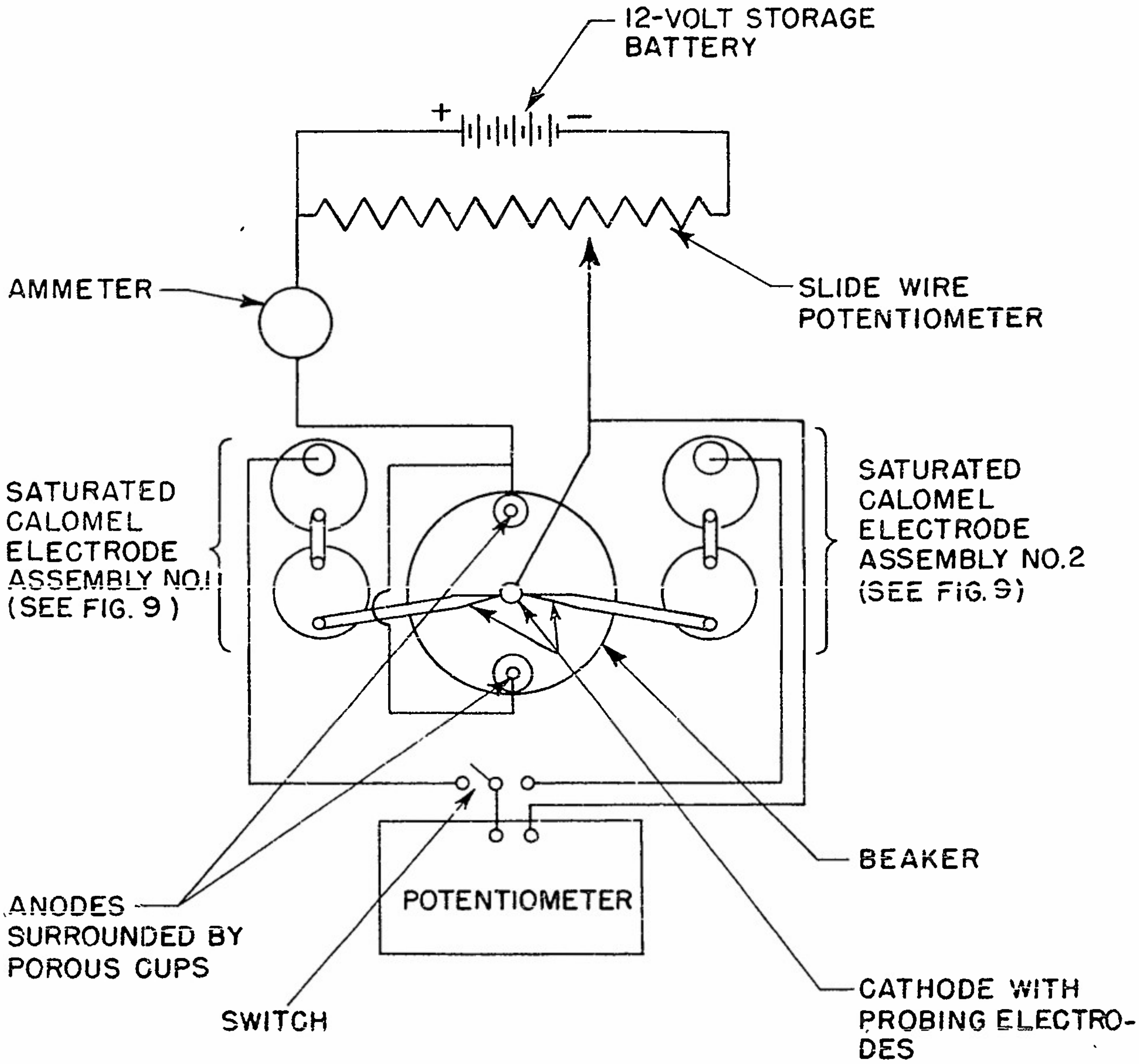

FIGURE 11. SCHEMATIC REPRESENTATION OF THE APPARATUS USED TO MEASURE CATHODE POLARIZATION

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were used for the sulfate solutions, but soluble silver or zinc anodes were necessary for the silver iodide or zinc iodide solutions, respectively, because molecular iodine will form at an insoluble anode.

Pure silver rod, measuring 0.27-inch diameter, was used as a cathode in the silver solutions, and a pure cast zinc rod, measuring 0.36-inch diameter, served for the measurements in the zinc solutions.

The solution was contained in a 400-ml. beaker, and the temperature was thermostatically controlled.

Figure 12 shows a detailed side view of the saturated calomel electrode assembly. With this assembly, it is possible to keep the junction potentials as low as one or two millivolts and still eliminate contamination of the plating solution.

The inverted U-tube, labeled A, and the container, labeled B, are filled with different solutions, depending on the nature of the plating bath. In the case of the zinc sulfate solution, A and B both contained saturated KCl. With the silver sulfate solution, A and B were both filled with 2N ammonium nitrate. Like saturated KCl, ammonium nitrate practically eliminates liquid junction potentials, but, unlike KCl, it will not precipitate silver chloride at the junction containing the filter paper plug. The 2N ammonium nitrate solution was also used in both places for the zinc iodide solution. For silver iodide, "A" contained 2N ammonium nitrate, while "B" contained a solution of sodium iodide for which the concentration was 520 g./l. (same as in the plating solution). This was necessary because silver iodide would precipitate at a junction where there was no excess of sodium iodide. Actually, a

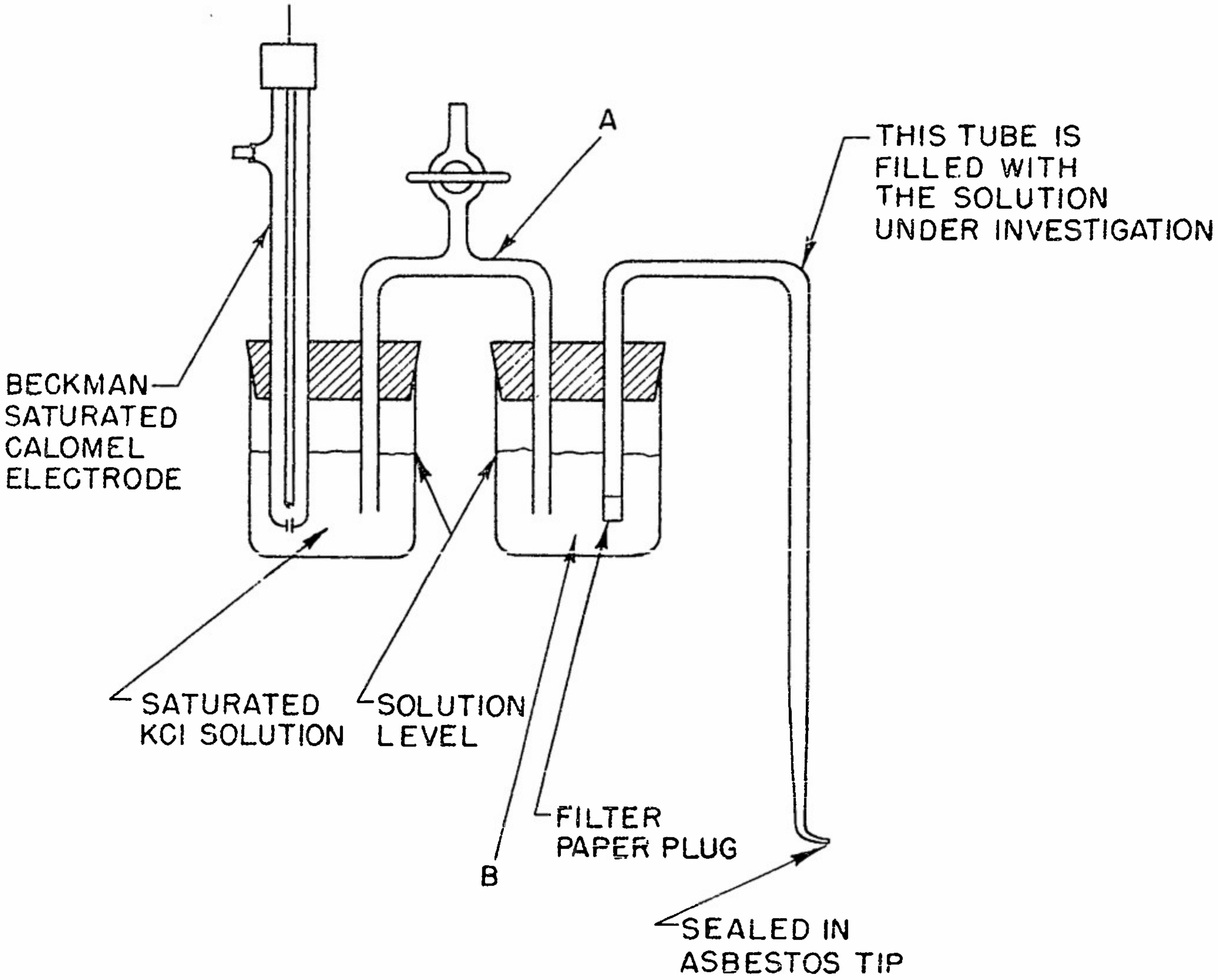

FIGURE 12. DETAILED SIDE VIEW OF SATURATED CALOMEL ELECTRODE ASSEMBLY. THE PARTS LABELED "A" AND "B" ARE EXPLAINED IN THE TEXT

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simpler assembly could be used for routine work, but the one described eliminates all possibility of contamination of the calomel cell and the plating bath.

Method

To use the apparatus represented in Figure 11, the slide wire is moved by discrete increments so as to increase the current through the cell. After each increase in current, potential measurements are made at intervals of a few minutes. When the potential reaches a steady state, the current is again increased. In the experiments described in this report, the average value of the potentials as measured by the two reference electrode assemblies was taken.

Composition of Plating Solutions used in Zinc and Silver Cathode Potential Measurements

Zinc-Sulfate Bath (3942-66B)

$ZnSO_4 \cdot 7H_2O$	240 g./l.
$(NH_4)_2SO_4$	15 g./l.
$Al_2(SO_4)_3 \cdot 18H_2O$	30 g./l.
Licorice	1 g./l.

pH raised to 4.0 with 1-1 NH_4OH. During this operation, some of the zinc precipitated but, after stirring for two hours, the precipitate dissolved.

Silver Sulfate Bath (3942-77B)

Ag_2SO_4	5 g./l.
$(NH_4)_2SO_4$	15 g./l.
$Al_2(SO_4)_3 \cdot 18H_2O$	30 g./l.
Licorice	1 g./l.

As made up, this solution had a pH of 3.6, which was not changed because of the possibility of precipitating the silver.

Zinc Iodide Bath (3942-92A)

ZnI_2	394 g./l.
NaI	520 g./l.
Citric Acid	60 g./l.

The zinc iodide was prepared in solution by reacting ZnO with HI. The other reagents were then added.

Silver Iodide Bath (3942-93A)

Ag_2O	20 g./l.
NaI	520 g./l.
Citric Acid	60 g./l.

The sodium iodide and the citric acid were dissolved first and the Ag_2O was then added in small quantities with stirring. The stirring caused some air oxidation of the iodide.

Preparation of Cast Alloys

Low-Melting Alloys

The low-melting alloys were prepared directly in a gas-fired crucible furnace. This furnace was composed of a fire clay crucible which fitted in a larger graphite crucible, with about one-half-inch air space between the two crucibles. The graphite crucible was supported in a 10-quart galvanized bucket by an insulating layer of Sil-O-Cel. The nozzle of a blast burner passed through a one-inch hole, which was bored through the bucket, insulation, and the graphite crucible side wall. The flame swirled around the inner crucible, thus distributing the heat.

Measured amounts of two chemically pure metals were placed in the inner crucible and covered with charcoal. During melting, the inner crucible was covered and the outer crucible partly covered. After melting was complete, the temperature was maintained for 10-15 minutes. The melt was then stirred thoroughly with a carbon rod and poured into a carbon mold. The ingots measured 1 inch x 3 inches x 1/8 inch.

High-Melting Alloys

Manganese-Nickel Alloys. Two methods were used in the preparation of these alloys. In both cases, alloying was effected by induction heating, the differences being in the size of the melt and other factors described below.

The first group of manganese-nickel alloys to be prepared were the five alloys ranging in composition from 13.7% nickel to 91% nickel, inclusive. An Alundum thimble, measuring 1-1/2 inches in diameter by 5 inches in length, was "rammed in" a small induction furnace with mangnesia sand. A single furnace lining lasted for two heats. The manganese was melted first and then electrolytic nickel was added in small pieces. No slag was used. An alundum rod was used to stir the molten metal. The melts were poured into a heated (1000°F.) carbon mold having three sections, each measuring 3 inches x 1 inch x 1/8 inch. A carbon pouring head aided in directing the stream of molten metal to the mold. Temperatures were measured with an optical pyrometer and the heats were poured at a temperature 200°F. above the melting point. The total weight of each heat was 300 grams.

The experience gained in making these first manganese-nickel heats demonstrated the inadvisability of working with such small quantities for high-melting alloys. The small mass of metal cools so quickly as to make the casting difficult. Accordingly, in making the second group of heats (7.6, 9.4, and 11.9% nickel, respectively), larger quantities were used. Electrolytic manganese and pure nickel rod were used in preparing the alloys. The manganese was first melted in the magnesia-lined furnace under a neutral slag consisting of 50 per cent lime, 42 per cent alumina, and 8 per cent magnesia. The nickel was then added, the nickel rod making a convenient stirrer. A small amount of nickel-magnesium was used as a deoxidizing agent. The heats were poured into a chill mold constructed from five pieces of one-inch-thick steel plate. The inside dimensions of the mold were 2 inches x 2 inches x 6 inches. The mold was provided with a shrink head and, after the heats were poured, "Riser X"* was added to keep the metal in the shrink head molten, thus preventing "piping" in the ingot. The ingots weighed approximately eight pounds each.

When the ingots had been cooled, they could not be sawed or machined. Because nickel has been reported to stabilize manganese in the ductile, gamma form, it was believed that, by heating to the temperature

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* Chromium Mining and Smelting Corp., Ltd., Sault Sainte Marie, Ontario, Canada

where the gamma manganese forms, and then quenching, it would be possible to anneal the alloys. A preliminary test piece, heated to 2050°F. and quenched in 10 per cent brine solution, was softened so that it could be sawed or filed, but not drilled. Oxidation was confined to the surface. Since this treatment resulted in sufficient softening, the ingots were then annealed in the same way.

Apparently, the ingots were unsound for they shattered during the annealing. Some of the larger pieces were saved, however, and specimens for use in the potential measurements were prepared.

The "Wet-Dry Program" Cabinet

A lead-lined, cork-insulated plywood box, measuring 34 inches x 25 inches x 25 inches, is the basis for the "wet-dry program" cabinet pictured in Figure 13. This box is equipped with a 1/2-inch-thick Lucite door (A) (letters in parenthesis refer to Figure 13), on which the specimens are supported by being clamped between Lucite washers in such a way that the test pieces do not make contact with the 18-8 stainless steel machine screws which pass through the washers. Twenty-four specimens can be exposed simultaneously. To prevent warping of the Lucite door, the edges were bound with angle iron.

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

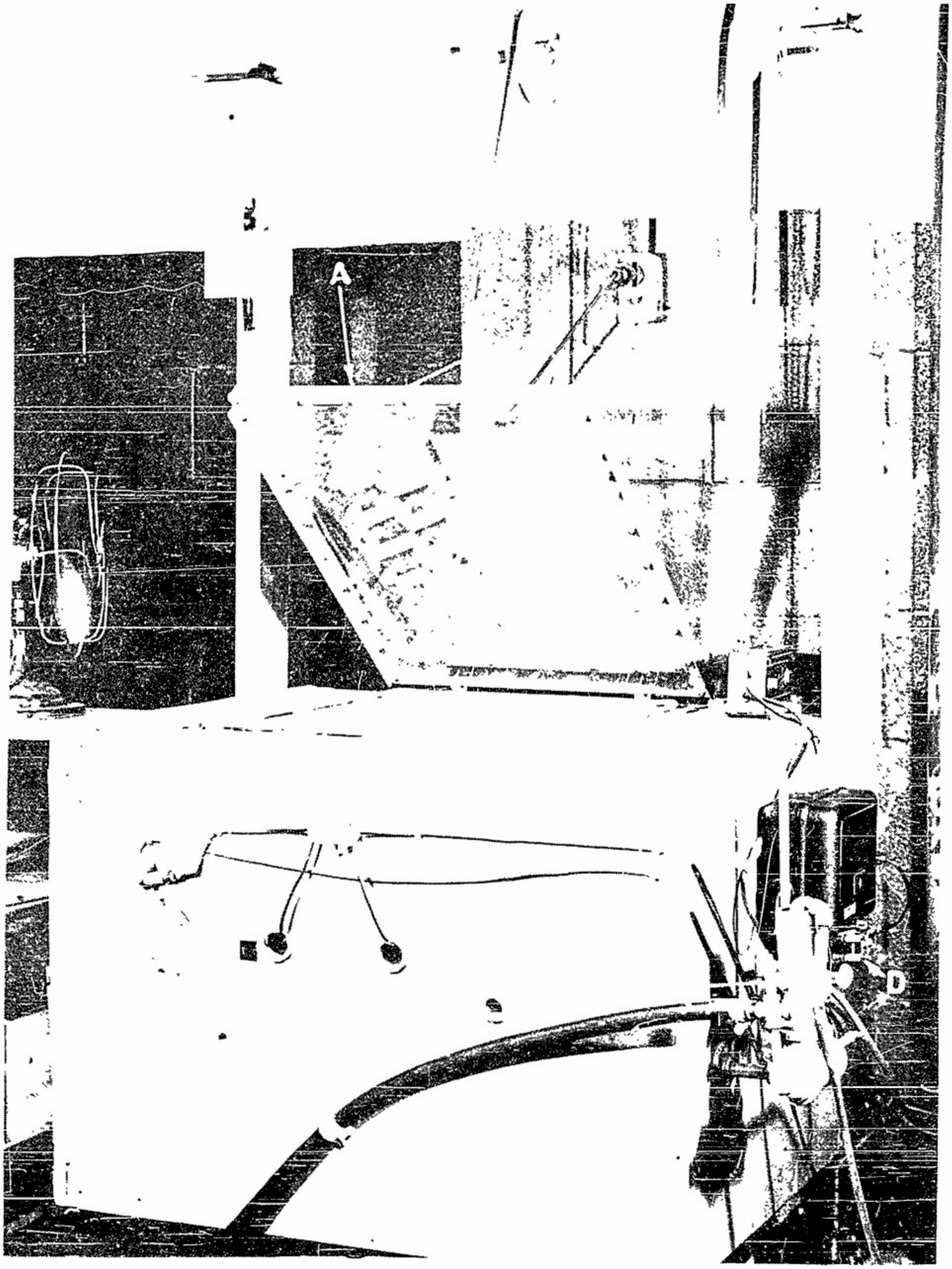

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Figure 13. "Wet-Dry Program" Cabinet, Showing Door Open and Corroding Specimens in Place

To provide high humidity when the door is closed, water in a copper pan is warmed by an immersion heater. The pan measures 16 inches x 16 inches x 5 inches. The heater (electrical leads at F) is regulated by a thermostatic control (hidden by plate G), and operates only when the door is closed. A constant-level device (E) is connected to the copper pan and maintains the water at a 4-inch depth. The electric fan operates when the door is opened, cooling and drying the specimens. When the door is closed again, the fan stops, and in the humid atmosphere, moisture readily condenses on the chilled specimens. A schematic drawing of the electrical circuit is given in Figure 14.

Two minor changes in the electrical circuit have been made since Figures 13 and 14 were prepared. A new time control has been installed which allows greater latitude in cycling, and the original thermostatic control has been replaced by two controls connected in series and operating through a relay. The additional control serves as a "safety". The relay is necessary because the controls will not handle the high current drawn by the heater.

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

Motor - 110-volt A.C. Crise Electric Mfg. Co., Columbus, Ohio.

Time Control - Two #303 controllers. Paragon Electric Co., 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

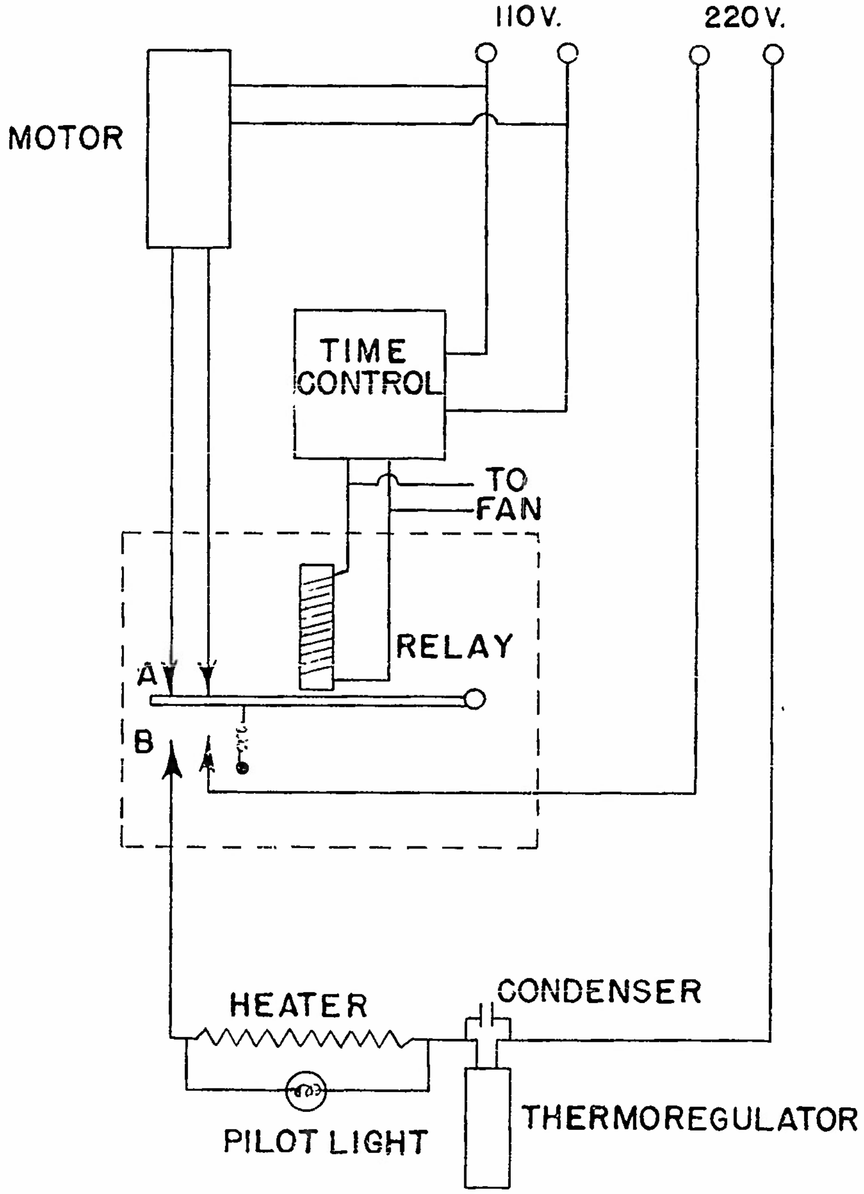

FIGURE 14. SCHEMATIC DIAGRAM OF ELECTRICAL CIRCUIT FOR "WET-DRY PROGRAM" CABINET.

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tabs on the circular time-setting plate could not be set for an interval as small as one hour.

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

Relay - Double-pole, double-throw relay. Struthers-Dunn, Inc., Philadelphia, Pennsylvania. (Note: In Figure 14, the relay was not represented as being of the DPDT type for reasons of simplicity.

Thermoregulator - Two, 110-volt, 10-amp. thermoswitches connected in series. Fenwall, Inc., Ashland, Massachusetts.

Removal of Corrosion Products For Weight-Loss Tests

The corrosion products were removed from the zinc-antimony alloys, the zinc-silver alloys, and the pure cadmium and zinc specimens by immersing the test piece in 100 ml. of a 1% solution of sodium cyanide at 70°F. for 20 minutes. After 10 minutes had elapsed, the surfaces were brushed lightly for about one minute while the specimen was still immersed. A second 20-minute immersion in a fresh portion of solution with brushing was used to complete the removal of the corrosion products. It was found that this treatment removed only an insignificant amount of metal. Each specimen was examined at 20X magnification with a binocular microscope to be sure all nonmetallic material had been removed. The specimens were then reweighed and the weight-loss calculations made.

The manganese-nickel corrosion products were incompletely removed using a 15% solution of hydrogen peroxide, to which one drop of concentrated sulfuric acid was added for each one hundred milliliters. This solution attacked the underlying metal.

Preparation of Electrodeposited Specimens for Exposure in "Wet-Dry Program" Cabinet

SAE 4130 steel panels measuring 3 inches x 1 inch x 1/16 inch were given a 320-dry-grit finish on an abrasive belt. They were then numbered and stored in a desiccator until ready to be used. Just prior to plating, they were given the following pretreatment:

1. Wiped with clean cloth saturated with acetone or carbon tetrachloride.
2. Vapor degreased in trichlorethylene.
3. Cleaned electrolytically —

   Anodex 8-10 oz./gal., 180°F.

   Cathodic 1 min., 50 amp./sq. ft.

   Anodic 15 secs., 50 amp./sq. ft.
4. Rinsed in hot water.
5. Acid dipped —

   3N HCl, 70°-80°F., 5 secs.
6. Rinsed in cold water.
7. Plated (see below).

Zinc Plating

Bath (3393 - 22A)

$ZnSO_4 \cdot 7H_2O$	240 g./l.
NH_4Cl	15 g./l.
$Al_2(SO_4)_3 \cdot 18H_2O$	30 g./l.

Mg $SO_4 \cdot 7H_2O$	70 g./l.
Licorice	0.7 g./l.
Duponol ME	0.5 g./l.

pH: 4.5

Temperature: 84°F.

Current Density: 35 amp./sq. ft.

Voltage: 1.2 volts

Agitation: Work rod, 2 inch stroke, 32 r.p.m.

Anodes: Cast Zinc

Cadmium Plating

Bath (3393-22B)

Udylite Single Salt #1*	120 g./l.

Temperature: 90°F.

Current Density: 30 amp./sq.ft.

Voltage: 3.2 volts

Agitation: Work rod, 2 inch stroke, 32 r.p.m.

Anodes: Steel

Manganese Plating

The electropolishing procedure, necessary for uniform coverage of manganese plate on the SAE 4130 Steel, is covered by patents*, and

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* Udylite Corporation, Detroit 11, Michigan. This is a cyanide-type bath.

** Battelle Development Corporation, Columbus, Ohio conditions for its commercial use can be supplied, if the electropolishing should ultimately be required in practicing plating methods devised in the present research work.

Subsequent to electropolishing, the specimens were given the cleaning and acid-dip treatments recorded above. The plating-bath composition and conditions are as follows:

Bath (3363-85A)

$MnSO_4 \cdot H_2O$	37 g./l.
$(NH_4)_2\ SO_4$	132.5 g./l.
$Na_2SO_3 \cdot 7H_2O$	0.35 g./l.

pH: 7.8 (adjusted with NH_4OH)

Temperature: 100°F.

Current Density: 45 amp./sq. ft.

Anodes: Carbon rods enclosed in porous cups.

Anolyte: A solution containing 132.5 g./l. $(NH_4)_2\ SO_4$ is used in each of the porous cups.

Manganese with Tin Overlay

The manganese was deposited as described in the preceding section. On removing the plated specimen from the manganese bath, it was rinsed in cold water and immersed, while wet, in the tin-plating solution. To insure simultaneous and complete coverage, it is necessary to enter the tin solution with the current on. The tin-plating bath was as follows:

Bath (3363-62A)

$Na_2SnO_3 \cdot 3H_2O$	100 g./l.
$Na\ C_2H_3O_2$	22.5 g./l.

NaOH	13 g./l.
H_2O_2 (30%)	1-2 drops/l.

Temperature: 180°F.

Current Density: 50 amp./sq. ft.

Voltage: 3.0-3.2 volts

Agitation: Work rod, 1-1/4 inch stroke, 32 r.p.m.

Zinc-Tin Alloy Plating

Bath (3363-65A)

$Na_2SnO_3 \cdot 3H_2O$	58 g./l.
$Zn(CN)_2$	14.5 g./l.
NaCN	33 g./l.
NaOH	5.5 g./l.

Temperature: 150°F.

Current Density: 20 amp./sq.ft.

Voltage: 3.8-4.0 volts

Anodes: 22% zinc - 78% tin cast alloy anodes

Analysis of Deposit: 79.5% tin

Cadmium-Silver Plating

Bath (3363-91A)

CdO	32 g./l.
AgCN	2.1 g./l.
NaCN	83 g./l.
Na_2CO_3	10 g./l.
NH_4OH (28%)	2 ml./l.

The "free-cyanide" content of this solution was 32 g./l.

Temperature: 90°F.

Current Density: 21 amp./sq. ft.

Voltage: 2.2 volts

Anodes: Steel

Analysis of Deposit: 7.4% silver

Experimental Electrodeposition

Zinc-Silver

The zinc-silver electrodeposition experiments were made using 50- to 100-ml. portions of solutions contained in electrolytic beakers. The cathode, a round, 1/4-inch-diameter, 18-8 stainless steel rod, was immersed to a depth of one or two inches. In the preliminary experiments, a soluble silver anode was used. Where the silver was added as the oxide, two 1/4-inch-diameter carbon rods, enclosed in porous cups, served as insoluble anodes. Temperatures were varied from 70° to 150°F., and the current densities from 4 to 72 amps./sq. ft. A 60-r.p.m. synchronous motor rotated the specimen in the experiments where agitation was used. Addition agents were first dissolved in a concentrated sodium iodide solution, which was added dropwise to the plating solution. The reason for doing this was to prevent precipitation of silver iodide, which would occur if a simple aqueous solution were added.

The following bath produces a deposit of approximately 50% silver:

Bath (3363-58A)

NaI	520 g./l.
Citric Acid	60 g./l.
ZnI_2	394 g./l.
Ag_2O	2.5 g./l.

The zinc iodide was prepared in solution by reacting ZnO with HI. The other reagents were then added. The preparation of Ag_2O is described elsewhere in this Appendix.

Manganese-Tin

The preliminary tests were made using 50-to 250-ml. portions of solutions. The details of representative experiments are given in Table 4.

Aluminum Plating

Details of the aluminum-plating solution and conditions will be found in the Battelle Institute Progress Reports to the Bureau of Aeronautics, U. S. Navy, Contract No. NOa(s)9409, dated May 10, 1948.

Chemical Analysis

The chemical analysis of the cast alloys was accomplished using methods described in the standard texts such as:

"Applied Inorganic Analysis," W. F. Hillebrand and G. E. F. Lundell, John Wiley and Sons.

"Scott's Standard Methods of Analysis," D. VanNostrand Company.

TABLE 4. PRELIMINARY MANGANESE-TIN ELECTRODEPOSITION EXPERIMENTS

Bath Type	Bath Number	Bath Composition	Temp. (°F.)	Current Density (Amps./Sq.Ft.)	Volts	Time (Mins.)	Anode	Cathode	Results
Fluoborate	3363-74B	$Mn(BF_4)_2$ soln.* 100 ml. $Sn(BF_4)_2$ soln.** 1 ml. Duponol ME 0.1 g.	140	35	3	-	Carbon	Steel	Soft spongy deposit. Qualitative test shows high tin, low manganese.
	3363-75B	$Mn(BF_4)_2$ soln. 100 ml. $Sn(BF_4)_2$ soln. 1 ml. Glue 0.5 g. Beta-naphthol 0.1 g.	120	20	2.6	22	Carbon	Stainless steel	Gray, mat, compact plate. Negative test for tin, positive test for manganese.
		Add 1 ml. $Sn(BF_4)_2$ soln. to 75B	120	20	2.6	30	Carbon	Stainless steel	Positive test for tin, trace of manganese.
	3363-76A	$Mn(BF_4)_2$ soln. 250 ml. $Sn(BF_4)_2$ soln. 2.5 ml. Glue 0.25 g. Beta-naphthol 0.25 g.	120	20	2.5	10	Carbon	Stainless steel	Spongy, dark gray deposit. Tin present, trace of manganese.
		Add 0.25 g. glue to 76A	120	20	2.5	10	Carbon	Stainless steel	Improved deposit but still not acceptable. Tin present, no manganese.
Tartrate	3363-77A	$MnSO_4 \cdot H_2O$ 12.5 g. $(NH_4)_2 SO_4$ 12.5 g. $(NH_4)_2 C_4H_4O_5$ 75 g. $SnCl_4 \cdot 5H_2O$ 2.5 g. Diluted to 250 ml.; pH adjusted to 8.5 with NH_4OH	130	30	-	5	Platinum	Steel	No deposit.
			130	30	-	10	Platinum	Steel	No deposit.
			175	60	3.4	15	Platinum	Copper	Smooth adherent deposit, but could not be built up. No analysis.
			175	60	3.4	15	Platinum	Stainless steel	Manganese present but no tin.
			175	120	-	15	Platinum	Stainless steel	Black deposit, partially soluble in conc. HNO_3. Manganese present, no tin.
		Add 10 g. $SnCl_4 \cdot 5H_2O$ to 77A	175	60	-	15	Platinum	Stainless steel	Gray deposit. Turned black on addition of conc. HNO_3. Manganese present, no tin.

* General Chemical Co., Lot No. 1, $Mn(BF_4)_2$ 47%, Free Boric Acid 4.86%, Free Fluoboric Acid 0.71%.
** General Chemical Co., Lot No. C244, $Sn(BF_4)_2$ 46.1%, Free Boric Acid 2.3%, Free Fluoboric Acid 3.6%.

With one exception, the compositions of the electrodeposits were determined by plating duplicate cathodes of stainless steel and stripping the electrodeposit with nitric acid. The resulting solution was then analysed, using standard methods. The compositions of the zinc-tin alloys were determined by depositing the alloys on SAE 1010 steel, dissolving the entire, weighed specimen in strong hydrochloric acid, and then following the standard procedure for the determination of tin.

Electroplating solution analysis followed the methods given in "Modern Electroplating", published by The Electrochemical Society, Inc., in 1942.

Preparation of Silver Oxide and Silver Sulfate

Silver Oxide

C. P. silver nitrate was dissolved in distilled water. A second aqueous solution containing a stoichiometric quantity of C. P. sodium hydroxide was then added to the silver nitrate solution with rapid stirring. After the silver oxide precipitate had coagulated, it was washed 20 times by decantation, using 100-ml. portions of hot distilled water. The product was dried at 105°C. for 12 hours.

Silver Sulfate

C. P. silver nitrate was dissolved in distilled water, and the solution was cooled to approximately 50°F. An equivalent amount of dilute sulfuric acid was added to the silver nitrate solution and the solution stirred. The precipitate was washed twice by decantation using 100-ml. portions of cold distilled water. The resulting salt was dried at 105°C.

for 12 hours. Since silver sulfate is appreciably soluble in water and the solubility increases with temperature, it is necessary to conduct the precipitation and washings in cold water and to wash only a few times.

APPENDIX II

APPENDIX II

This Appendix contains tabulated data relative to potential and corrosion current-density measurements.

CLF:gs/esl/cla

June 23, 1949

TABLE 5. STATUS OF INDIVIDUAL ALLOY SYSTEMS AND PURE METALS IN THE TESTING PROGRAM: "X" DENOTES TEST HAS BEEN COMPLETED, "O" DENOTES TEST HAS NOT BEEN MADE

Alloy System	Composition Range Investigated, %	Static Potential Measurements			Dynamic Measurements in 3% NaCl Solution	"Wet-Dry" Test (Visual Examination)	"Wet-Dry" Test (Weight Loss)
		3% NaCl Solution	CO_2-Saturated Water	Distilled Water			
Zinc-Copper (cast)	0-28 Cu	X	X	X	X	0	0
Zinc-Copper (plated)	0-28 Cu	X	0	0	X	0	0
Zinc-Silver (cast	0-44 Ag	X	X	X	X	X	X
Zinc-Indium (cast)	0-40 In	X	X	X	X	0	0
Zinc-Tin (cast)	Complete	X	X	X	X	X	0
Zinc-Tin (plated)	0-85 Sn	X	0	0	0	X	0
Zinc-Nickel (cast)	0-47 Ni	X	X	X	X	X	0
Zinc-Lead (cast)	0-1 Pb	X	X	X	X	X	0
	99 Pb	X	X	X	0	0	0
Zinc-Chromium (cast)	0-5 Cr	X	X	X	X	X	0
Zinc-Manganese (cast)	0-10 Mn	X	X	X	X	X	0
Zinc-Antimony (cast)	0-80 Sb	X	X	X	X	X	X

TABLE 5. (Continued)

Alloy System	Composition Range Investigated, %	Static Potential Measurements 3% NaCl Solution	Static Potential Measurements CO$_2$-Saturated Water	Static Potential Measurements Distilled Water	Dynamic Measurements in 3% NaCl Solution	"Wet-Dry" Test (Visual Examination)	"Wet-Dry" Test (Weight Loss)
Cadmium-Zinc (cast)	Complete	X	X	X	X	X	0
Cadmium-Silver (cast)	0-32 Ag	X	X	X	X	X	X(1)
Cadmium-Silver (plated)	0-8 Ag	X	0	0	0	X(1)	0
Cadmium-Indium (cast)	0-40 In	X	X	X	X	0	0
Cadmium-Tin (cast)	Complete	X	X	X	X	X	0
Cadmium-Nickel (cast)	0-3 Ni	X	X	X	X	X	0
Cadmium-Lead (cast)	0-13 Pb	X	X	X	X	0	0
Manganese (plated)	—	X	X	X	X	X	0
Manganese-Nickel (cast)	Complete	X	X	X	X	X	0
Manganese (plated) Plus Electro-Tin Overlay	—	0	0	0	0	X(1)	0
Porous Zinc Plus Chromate	—	X	0	0	0	X	0

(1) These tests are under way at present

TABLE 6. WEIGHT LOSSES IN MILLIGRAMS PER SQUARE DECIMETER PER DAY FOR CAST ZINC-ANTIMONY SPECIMENS AFTER 50 DAYS' EXPOSURE IN THE "WET-DRY PROGRAM" TEST

% Sb.	Specimen No.	Weight Loss (mdd)	Specimen No.	Weight Loss (mdd)	Average Weight Loss (mdd)
1.15	3942-26A1	6.82	3942-26A3	6.89	6.86
5.22	-26B1	7.44	-26B3	6.74	7.09
10.4	-26C1	6.68	-26C3	6.32	6.50
25.5	-26D1	5.75	-26D2	6.94	6.35

TABLE 7. WEIGHT LOSSES IN MILLIGRAMS PER SQUARE DECIMETER PER DAY FOR CAST ZINC AND CADMIUM SPECIMENS AFTER 50 DAYS' EXPOSURE IN THE "WET-DRY PROGRAM" TEST

Metal	Specimen No.	Weight Loss (mdd)	Specimen No.	Weight Loss (mdd)	Average Weight Loss (mdd)
Zinc	3180-5B	7.35	3180-16C	7.13	7.24
Cadmium	3180-19?	1.40	3180-19C	1.37	1.39

TABLE 8. WEIGHT LOSSES IN MILLIGRAMS PER SQUARE DECIMETER PER DAY FOR CAST ZINC-SILVER ALLOYS AFTER 50 DAYS' EXPOSURE IN THE "WET-DRY EXPOSURE" TEST

% Ag	Specimen No.	Weight Loss (mdd)	Specimen No.	Weight Loss (mdd)	Average Weight Loss (mdd)
1.02	2875-62A2	8.82	2875-62A3	8.35	8.59
5.14	-62B1	8.87	-62B3	8.35	8.61
17.8	-62C1	1.05	-62C3	1.68	1.37
24.8	-62D1	*	-62D3	*	*

* Actually, in the case of these specimens, there was a very slight weight gain, but this is within the limits of experimental error

TABLE 9. POTENTIAL-TIME DATA FOR CAST ZINC-ANTIMONY ALLOYS, MEASURED AT 90°F., IN 3 PER CENT SODIUM CHLORIDE SOLUTION AND DISTILLED WATER SATURATED WITH CARBON DIOXIDE. SATURATED CALOMEL SCALE, VALUES IN VOLTS*

Specimen No.	% Sb.	Volts at Elapsed Time of: 1 Min.	30 Mins.	50 Mins.	60 Mins.**
		(3 Per Cent Sodium Chloride Solution)			
3942-26A2	1.15	1.043	1.053	1.057	1.058
-26B2	5.22	1.031	1.046	1.049	1.051
-26C2	10.4	1.029	1.044	1.048	1.050
-26D1	25.5	1.026	1.043	1.045	1.047
-26E1	51.5	1.037	1.041	1.043	1.044
-26F1	78.6	0.488	0.478	0.468	0.465
		(Distilled Water Saturated With Carbon Dioxide)			
3942-26A2	1.15	1.068	1.078	1.081	1.083
-26B2	5.22	1.064	1.075	1.077	1.079
-26C2	10.4	1.062	1.077	1.080	1.081
-26D1	25.5	1.047	1.062	1.068	1.071
-26E1	51.5	1.054	1.077	1.080	1.081
-26F1	78.6	0.363	0.285	0.285	0.285

* All values are negative
** 60-minute values plotted in Figure 2

TABLE 10. POTENTIAL-TIME DATA FOR CAST ZINC-ANTIMONY ALLOYS, MEASURED AT 90°F., IN DISTILLED WATER. SATURATED CALOMEL SCALE, VALUES IN VOLTS*

Specimen No.	% Sb.	Volts at Elapsed Time of: 60 Mins.**	75 Mins.	90 Mins.
3942-26A2	1.15	0.788	0.762	0.785
-26B2	5.22	0.862	0.836	0.828
-26C2	10.4	0.856	0.830	0.810
-26D1	25.5	0.802	0.796	0.820
-26E1	51.5	0.859	0.854	0.892
-26F1	78.6	0.430	0.426	0.426

* All values are negative

** 60-minute values plotted in Figure 2

TABLE 11. INITIAL AND 24-HOUR DYNAMIC POTENTIAL AND CORROSION CURRENT-DENSITY DATA FOR CAST ZINC-ANTIMONY ALLOYS COUPLED WITH STEEL. COUPLES IMMERSED IN 3 PER CENT SODIUM CHLORIDE SOLUTION AT 90°F., FOR THE 24-HOUR PERIOD. SATURATED CALOMEL SCALE.

		Initial Measurements		24-Hour Measurements	
Specimen No.	% Sb.	Coupled Alloy (Volts)*	Corrosion Current Density (Ma./In.^{2})	Coupled Alloy (Volts)*	Corrosion Current Density (Ma./In.^{2})
3942-26A2	1.15	1.022	0.85	1.052	0.54
-26B2	5.22	1.038	0.68	1.051	0.53
-26C2	10.4	1.038	0.76	1.030	0.50
-26D1	25.5	1.039	0.74	1.025	0.54
-26E1	51.5	1.030	0.73	1.017	0.40

* All voltage values are negative

TABLE 12. POTENTIAL-TIME DATA FOR CAST MANGANESE-NICKEL ALLOYS, MEASURED AT 90°F., IN 3 PER CENT SODIUM CHLORIDE SOLUTION. SATURATED CALOMEL SCALE, VALUES IN VOLTS*

Specimen No.	% Ni	Volts at Elapsed Time of: 1 Min.	30 Mins.	60** Mins.	120 Mins.
Electroplated manganese	0.0	1.389	1.312	1.292	-
Commercial electro-manganese	0.0	1.390	1.317	1.316	1.307
3942-71A	7.6	1.095	0.924	0.912	0.882
3942-71B	9.4	-	0.935	0.907	0.879
3942-71C	11.9	-	0.916	0.915	0.891
3942-35A1	13.7	0.892	0.865	0.857	0.851
3942-35B1	29.5	0.974	0.744	0.738	0.735
3942-35C1	51.0	0.379	0.473	0.484	0.496
3942-35D2	80.7	0.364	0.256	0.268	0.272
3942-35E2	91.0	-	0.242	0.254	0.264
Electrolytic nickel	100.0	0.303	0.187	0.179	0.182

* All values are negative
** 60-minute values plotted in Figure 5

TABLE 13. POTENTIAL-TIME DATA FOR CAST MANGANESE-NICKEL ALLOYS, MEASURED AT 90°F., IN DISTILLED WATER SATURATED WITH CARBON DIOXIDE. SATURATED CALOMEL SCALE, VALUES IN VOLTS*

		Volts at Elapsed Time of:				
	% Ni	1 Min.	30 Mins.	60** Mins.	120 Mins.	180 Mins.
Electroplated manganese	0.0	1.354	1.181	1.186	1.171	1.164
Commercial electro-manganese	0.0	1.346	1.233	1.218	1.201	1.192
3942-71A	7.6	1.025	0.748	0.730	0.703	0.686
3942-71B	9.4	1.015	0.767	0.717	0.672	0.661
3942-71C	11.9	0.990	0.740	0.701	0.659	0.642
3942-35A1	13.7	0.989 0.991	0.776 0.733	0.726 0.696	0.675 0.655	0.650 0.638
3942-35B1	29.5	0.867 0.883	0.785 0.789	0.752 0.755	0.724 0.726	0.713 0.713
3942-35C1	51.0	0.560 0.632	0.496 0.533	0.497 0.517	0.504 0.511	0.513 0.518
3942-35D2	80.7	0.565 0.579	0.530 0.536	0.522 0.526	0.503 0.521	0.500 0.515
3942-35E2	91.0	0.497	0.455	0.457	0.463	0.469
Electrolytic nickel	100.0	0.288	0.405	0.413	0.426	0.430

* All values are negative

** 60-minute values plotted in Figure 5

TABLE 14. POTENTIAL-TIME DATA FOR CAST MANGANESE-NICKEL ALLOYS, MEASURED AT 90°F., IN DISTILLED WATER. SATURATED CALOMEL SCALE, VALUES IN VOLTS*

Specimen No.	% Ni	Volts at Elapsed Time of: 60** Mins.	75 Mins.	90 Mins.	180 Mins.
Electroplated manganese	0.0	1.251	1.222	1.201	1.158
Commercial electro-manganese	0.0	1.215	1.189	1.189	1.151
3942-71A	7.6	0.500	0.462	0.440	0.376
3942-71B	9.4	0.483	0.437	0.378	0.297
3942-71C	11.9	0.484	0.454	0.418	0.266
3942-35A1	13.7	0.406	0.415	0.373	0.166
3942-35B1	29.5	0.128	0.189	0.240	0.225
3942-35C1	51.0	0.083	0.086	0.077	0.077
3942-35D2	80.7	0.039	0.034	0.036	0.031
3942-35E2	91.0	0.034	0.028	0.023	0.014
Electrolytic nickel	100.0	0.024	0.018	0.020	0.006

* All values are negative
** 60-minute values plotted in Figure 5

TABLE 15. INITIAL AND 24-HOUR DYNAMIC POTENTIAL AND CORROSION CURRENT DATA FOR CAST MANGANESE-NICKEL ALLOYS COUPLED WITH STEEL. COUPLES IMMERSED IN 3 PER CENT SODIUM CHLORIDE SOLUTION AT 90°F., FOR THE 24-HOUR PERIOD. SATURATED CALOMEL SCALE.

Specimen No.	% Ni	Initial Measurements		24-Hour Measurements	
		Coupled Alloy (Volts)*	Corrosion Current Density (Ma./In.^{2})	Coupled Alloy (Volts)*	Corrosion Current Density (Ma./In.^{2})
Electroplated manganese	0.0	>1.307	2.4	1.201	1.48
3942-71A	7.6	0.927	0.41	0.808	0.2
3942-71B	9.4	0.896	0.41	0.767	0.34
3942-71C	11.9	0.894	0.31	0.747	0.13
3942-35A1	13.7	0.856	0.44	0.732	<0.001
3942-35B1	29.5	0.788	0.38	0.716	<0.001

* All voltage values are negative

TABLE 16. CURRENT-DENSITY AND AVERAGE CATHODE POTENTIAL VALUES* FOR ZINC AND SILVER IN SULFATE SOLUTIONS**. POTENTIAL VALUES ARE RELATIVE TO THE SATURATED CALOMEL ELECTRODE. TEMPERATURE 77°F.

Zinc		Silver	
Current Density (Amps./Sq.Ft.)	Cathode Potential (Volts)	Current Density (Amps./Sq.Ft.)	Cathode Potential (Volts)
0	-1.001	0	
0.32	-1.029	0.17	+0.429
0.575	-1.104	0.34	+0.428
0.99	-1.111	0.64	+0.425
1.6	-1.118	0.85	+0.419
4.7	-1.124	1.23	+0.404
13.8	-1.206	1.7	+0.394
22.4	-1.179	2.54	+0.404
29.4	-1.156	4.25	+0.395

* These data are plotted in Figure 8.

** The compositions of these solutions are given on pp. 44-45, Appendix I.