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## CORROSION-PROTECTIVE VALUE OF ELECTRODEPOSITED ZINC AND CADMIUM COATINGS ON STEEL

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### ABSTRACT

Atmospheric exposure of plated specimens in six locations showed that in a rural or purely marine climate, both zinc and cadmium coatings furnished better protection against the corrosion of steel than did nickel or chromium coatings of the same thickness, although the zinc and cadmium rapidly lost their luster. In an industrial atmosphere, where sulphurous and sulphuric acids are present, both zinc and cadmium were attacked rather rapidly, and the life was about proportional to the thickness. Under these conditions the cadmium coatings failed in about two-thirds of the time required for failure of zinc coatings of the same thickness. Zinc-cadmium alloys containing about 10 percent of cadmium were superior to either zinc or cadmium. Variations in the conditions selected for depositing the coatings did not have a marked effect on their protective value. Hot-dipped zinc coatings gave about the same protection as plated zinc coatings of the same thickness.

In accelerated tests, such as the salt spray or intermittent immersion in a solution of sodium chloride, the time required for failure of a zinc coating is about proportional to its thickness. Cadmium coatings last much longer than those of zinc in a salt spray, which is not, therefore, a true measure of their relative value in an industrial atmosphere.

The protective value of a zinc or cadmium coating depends principally upon its minimum thickness, which can be determined by dropping tests, microscopic measurements, and the chord method.

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## I. INTRODUCTION

During the past few years, exposure tests and accelerated tests of electroplated steel have been conducted through cooperation of the American Electroplaters' Society and the American Society for Testing Materials with the National Bureau of Standards. The results obtained with nickel and chromium finishes have been published [1], [2].<sup>2</sup> The purpose of this paper is to describe and discuss the results obtained in about 3.5 years' atmospheric exposure of zinc and cadmium coatings, and of a few deposits consisting of alloys of zinc and cadmium. As conclusive results have thus far been obtained only in severe industrial locations, this report is subject to revision in the light of longer exposures in marine or rural locations. However, as the specifications for commercial coatings are determined largely by the most severe conditions that are likely to be encountered, it is improbable that the results of longer exposures will materially change the practical application of the data. Accelerated tests and measurements of thickness were also made on these deposits.

Many of the procedures in this investigation were identical with those used for the nickel and chromium finishes. Full details of such operations are contained in Research Papers RP712 and RP724 [1], [2].

## II. PREPARATION OF SPECIMENS

## 1. BASE METAL

The base metal was cold-rolled strip steel SAE 1010, of the same lot that was used for the nickel and chromium finishes. It had a good finish and received no polishing prior to plating. Each specimen was 4 by 6 in. (10 by 15 cm).

<sup>2</sup> The numbers in brackets here and throughout the text refer to the references at the end of this paper.

## 2. PREPARATION FOR PLATING

In general, the methods used in cleaning and pickling the steel were the same as those used previously in nickel and chromium plating, though a few minor variations were applied. In both the cleaning and plating processes, a certain convenient procedure was arbitrarily selected as a "standard." This designation does not imply that it was superior, but merely shows that it served as a basis of comparison.

The procedures may be summarized as follows:

Standard cleaning "A."

"1." Most of the grease was removed with carbon tetrachloride. The plates were then:

"2." Cleaned cathodically in a hot solution containing sodium carbonate (30 g/liter or 4 oz/gal), trisodium phosphate (30 g/liter or 4 oz/gal), and sodium hydroxide (7.5 g/liter or 1 oz/gal);

"3." Scrubbed with a bristle brush;

"4." Rinsed in hot water;

"5." Pickled in warm dilute sulphuric acid (98 g/liter or 13 oz/gal);

"6." Rinsed in cold water.

Cleaning followed by hydrogen expulsion "A-1."

The procedure was exactly as in "A", except that after step "6", the plates were hung for 5 minutes in the hot cleaning solution without current; and were again scrubbed and rinsed. This procedure was found most effective to overcome blistering of zinc coatings produced in cyanide solutions, although it was also used for some of the acid-zinc deposits. Without this treatment, many of the zinc plated specimens developed large blisters on standing or on heating to 110° C. No such blisters were observed on specimens subjected to this "hydrogen expulsion." It is believed that the final heating in alkali eliminated much of the hydrogen absorbed during the pickling operation. This could no doubt have been accomplished by heating in boiling water, but the alkaline solution prevented the tarnishing that might have occurred in water. No reason can be given for the fact that, without this step, equally good adherence was obtained with some of the acid-zinc coatings and some of the cadmium coatings.

Cathode pickling "B."

The procedure was the same as in "A", except that instead of the direct pickling in step "5", cathode pickling was used.

Anode pickling "C."

The procedure was the same as in "A", except that after step "5" the steel was pickled anodically in 96 percent sulphuric acid, and was quickly rinsed in cold water.

## 3. CONDITIONS USED IN PLATING

Twelve specimens were plated simultaneously. Although the deposits were somewhat thicker near the edges than in the center, subsequent tests by the dropping method [3] showed that on at least 80 percent of the area the thickness varied less than 10 percent from that specified. The chemicals and anodes used in the plating were analyzed and found to be of good commercial quality. The solutions

were analyzed at intervals and were adjusted to within about 2 percent of their nominal compositions.

#### (a) ZINC PLATING

Cast-zinc anodes were used. The conditions of operation are summarized in table 1. Although the addition of mercuric oxide to the solution used in method "O" corresponds to about 1 percent as much mercury as zinc, some of the deposits were found to contain over 2 percent of mercury, which is somewhat higher than is commonly recommended.

The pH of the acid-zinc solutions was measured with a quinhydrone electrode. In the acid baths the zinc anodes were surrounded with muslin bags to prevent roughness of the deposits, and the cathodes were shaken occasionally to detach bubbles and thus prevent pitting.

TABLE 1.—*Conditions in zinc plating*

##### A. CYANIDE SOLUTIONS

Method	Composition of solution					Temperature		Current density		Variation <sup>1</sup>
	Zn(CN) <sub>2</sub>	NaCN	NaOH	HgO	pH					
N { g/liter oz/gal	1.0 60 8	0.5 23 3	1.3 53 7			22	70	2	19	Standard.
O { g/liter oz/gal	1.0 60 8	.5 23 3	1.3 53 7	0.0016 .35 .05		22	70	2	19	Mercury.

##### B. ACID SOLUTIONS

Method	ZnSO <sub>4</sub> ·7H <sub>2</sub> O	Na <sub>2</sub> SO <sub>4</sub>	AlCl <sub>3</sub> ·6H <sub>2</sub> O	Dextrin	pH	Temperature		Current density		Variation
P { g/liter oz/gal	3 410 54	1 75 10	0.25 20 3		3.5	35	95	5	47	High sulphate.
Q { g/liter oz/gal	3 410 54		.25 20 3	7.5 1	3.5	22	70	3	28	Dextrin.

<sup>1</sup> In this and succeeding tables, the term "variation" refers to the essential difference from the "standard" procedure.

#### (b) CADMIUM PLATING

Cast-cadmium anodes were used. The conditions of operation are summarized in table 2. Solution "S" contained "gulac", a waste product of the sulphite-pulp industry, which was selected as a typical organic addition agent. Solution "T" contained gulac and also a very small amount of nickel sulphate, an inorganic addition agent. The deposits from the plain solution "R" were dull and coarsely crystalline; those from "S" were smooth and fairly bright; and those from "T" contained about 0.015 percent of nickel and were still brighter.



TABLE 2.—Conditions in cadmium plating

Method	Composition of solution					Temperature		Current density		Variation
	CdO	NaCN	NaOH	Gulac <sup>1</sup>	NiSO <sub>4</sub> ·7H <sub>2</sub> O	°C.	°F.	amp/dm <sup>2</sup>	amp/dm <sup>2</sup>	
R {N----- g/liter... oz/gal...}	0.35 23 3	1.5 75 10	0.4 15 2	----- ----- -----	----- ----- -----	22	70	1	9	Standard
S {N----- g/liter... oz/gal...}	.7 45 6	2.5 120 16	----- ----- -----	----- 12 1.6	----- ----- -----					
T {N----- g/liter... oz/gal...}	.7 45 6	2.5 120 16	----- ----- -----	----- 12 1.6	0.007 1 0.13					

<sup>1</sup> A waste product of the sulphite-pulp industry.

## (c) DEPOSITION OF ZINC-CADMIUM ALLOYS

Deposits containing about 10 percent of cadmium and 90 percent of zinc were readily obtained by using anodes of that composition in bath "U", described in table 3. It was difficult to produce con-

TABLE 3.—Conditions for depositing zinc-cadmium alloys

Method	Composition of solution				Temperature		Current density		Variation
	(CN) <sub>2</sub> Zn	CdO	NaCN	NaOH	°C.	°F.	amp/dm <sup>2</sup>	amp/ft. <sup>2</sup>	
U {N----- g/liter... oz/gal...}	1.2 75 10	0.05 3 .4	0.75 38 5	2.25 90 12	35	95	2	19	10% of cadmium.
U-1 {N----- g/liter... oz/gal...}	1.2 75 10	.015 1 .13	.75 38 5	2.25 90 12					
U-2 {N----- g/liter... oz/gal...}	1.2 75 10	.10 6.5 .9	.75 38 5	2.25 90 12					

sistently deposits with 5 percent of cadmium, as planned. Even when the content of cadmium in the bath was greatly reduced, the deposits contained about 8 percent of cadmium. Coatings containing about 15 percent of cadmium (14 percent by actual analysis) were obtained by increasing the content of cadmium in the bath. Efforts to control the cadmium content by regulating the current density were not very successful, though in general the cadmium content was decreased by increasing the current density.

4. SCHEDULE OF DEPOSITS <sup>3</sup>

The conditions used and the thickness of each deposit are summarized in tables 4, 5, and 6. None of the deposits were buffed. The corresponding total weights of the coatings on both sides of the sheet, expressed in oz/ft<sup>2</sup> of sheet metal, have been computed in table 4 for zinc coatings in order to facilitate their comparison with the hot-dipped coatings (such as set 219), for which the thickness of sheet metal is usually so expressed.

<sup>3</sup> Most of the experimental work was conducted with metric measurements. However, as the thickness of the coatings was specified in fractions of an inch, the English units of thickness have been used in this paper, in some cases with metric equivalents. The conversions are in all cases approximate, as no high precision was involved.

TABLE 4.—*Preparation of zinc coatings*

Set	Cleaning method	Plating			Variation
		Method	Thick-ness	Weight <sup>1</sup>	
			<i>Inch</i>	<i>Oz/ft<sup>2</sup></i>	
201.....	A-1.....	N.....	0.0005	0.59	Cyanide:
202.....	B, A-1.....	N.....	.0005	.59	Cathode pickle.
203.....	C.....	N.....	.0005	.59	Anode pickle.
205.....	A-1.....	N.....	.0002	.24	Thickness.
206.....	A-1.....	N.....	.0010	1.18	Thickness.
207.....	A-1.....	O.....	.0002	.24	Cyanide + mercury:
208.....	A-1.....	O.....	.0005	.59	Thickness.
209.....	A-1.....	O.....	.0010	1.18	Thickness.
210.....	A.....	P.....	.0005	.59	Acid, high sulphate:
214.....	A.....	P.....	.0002	.24	Thickness.
215.....	A.....	P.....	.0010	1.18	Thickness.
216.....	A-1.....	Q.....	.0002	.24	Acid dextrin:
217.....	A-1.....	Q.....	.0005	.59	Thickness.
218.....	A-1.....	Q.....	.0010	1.18	Thickness.
219.....		Hot galvanized.....	.0009	1.05	Hot dipped.

<sup>1</sup> The total weight of coating on both sides of the sheet.TABLE 5.—*Preparation of cadmium coatings*

Set	Cleaning	Plating		Variation
		Method	Thick-ness	
			<i>Inch</i>	
301.....	A.....	R.....	0.0005	Standard:
302.....	B.....	R.....	.0005	Cathode pickle.
303.....	C.....	R.....	.0005	Anode pickle.
304.....	A.....	R.....	.0002	Thickness.
305.....	A.....	R.....	.0010	Thickness.
307.....	A-1.....	S.....	.0002	Gulac brightener:
308.....	A-1.....	S.....	.0005	Thickness.
309.....	A-1.....	S.....	.0010	Thickness.
310.....	A-1.....	T.....	.0002	Gulac + nickel:
311.....	A-1.....	T.....	.0005	Thickness.
312.....	A-1.....	T.....	.0010	Thickness.

TABLE 6.—*Preparation of zinc-cadmium alloy coatings*

Set	Cleaning	Plating		Variation
		Method	Thick-ness	
			<i>Inch</i>	
401.....	A.....	U.....	0.0005	10% of cadmium:
402.....	A.....	U.....	.0002	Thickness.
403.....	A.....	U.....	.0010	Thickness.
404.....	A.....	U-1.....	.0005	8% of cadmium.
405.....	A.....	U-2.....	.0005	14% of cadmium.

## III. ATMOSPHERIC-EXPOSURE TESTS

## 1. CONDITIONS OF EXPOSURE

Five specimens of each set were exposed in the spring of 1932 in each of six locations, namely Key West (K.W.), Fla.; New York City (N.Y.), N. Y.; Pittsburgh (P.), Pa.; Sandy Hook (S.H.), N. J.; State College (S. C.), Pa.; and Washington (W), D. C. The specimens were supported on galvanized steel racks by means of porcelain insulators. They were inclined 30 degrees from horizontal and faced south.

## 2. INSPECTION

At specified intervals, at first of a few weeks and later of a few months, the specimens were examined by members of the joint inspection committee and other interested persons. The average number of persons at each inspection was three.

The approximate proportion of the surface rusted was expressed by the scale of ratings shown in table 7. As the specimens had not

TABLE 7.—System used for rating of specimens

Surface rusted		Rating	Corresponding score	Surface rusted		Rating	Corresponding score
Range	Average			Range	Average		
	<i>Percent</i>		<i>Percent</i>		<i>Percent</i>		<i>Percent</i>
0 percent.....		5	100	10 to 20 percent.....	15	2	40
0 to 5 percent.....	2.5	4	80	20 to 50 percent.....	35	1	20
5 to 10 percent.....	7.5	3	60	50 to 100 percent.....	75	0	0

## (a) METHOD OF RATING

been buffed, the entire surface of each plate was included in the inspections. (In the inspections of nickel and chromium finishes, rust near the edges was disregarded, because the thickness of the coatings there had been reduced by buffing.) The cut edges of the hot-dipped specimens (set 219) were protected with a black paint. Each inspector assigned a numerical rating on the above scale to each specimen, and the average of the ratings of all the inspectors for a set of specimens constituted the recorded "rating" (R) for that set, location, and inspection date. The mean of this and the rating at the preceding inspection, that is, the average rating for the period, was multiplied by the number of weeks intervening to obtain the "score" (S) for the period. The total score for the entire period of the tests was compared with a perfect score for the same period to obtain the "percentage" score (T%). If, for example, the ratings for a set at the end of 20 and 24 weeks were 4 and 3, respectively, the average rating for that period was 3.5, and the score was  $3.5 \times 4 = 14$ . If the total score for the 20 weeks previously elapsed was 76, the score for the entire 24 weeks was  $76 + 14 = 90$ , instead of the possible perfect score of  $24 \times 5 = 120$ , and the percentage score was  $90/120 = 75$  percent.

The net result was to express the quality on a percentage basis, which, however, as shown in table 7, is not proportional to the per-

centage of unrusted surface. It is possible, however, to approximately convert the scores to percentages of rust in order to compare the results with those of other investigations. This can be conveniently done by use of figure 1, based on the average percentage

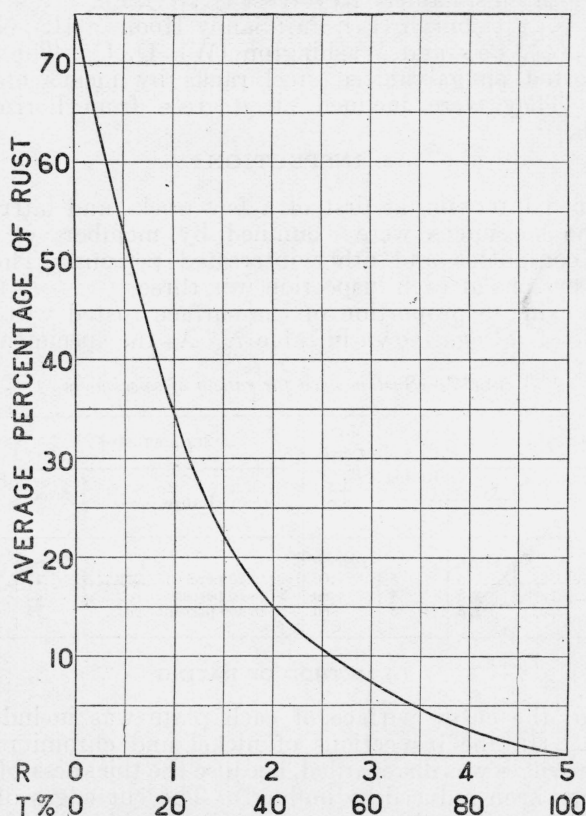


FIGURE 1.—Relation between rating (R), percentage score (T%) and average percent of rust.

of rust for each rating. (This conversion has been made in fig. 4.) The use of this roughly logarithmic scale is justified by the fact that for many purposes a small amount of rust is relatively more significant than a large amount. Another advantage is that a difference, for example of 10 percent, in the percentage score corresponds approximately to the same proportional difference in the extent of rust, whether this is small or large.

#### (b) APPEARANCE

As zinc and cadmium coatings are generally used outdoors only when appearance is at most a secondary factor, no effort was made to rate other defects on the specimens, such as loss of luster, or the presence of stains or white coatings. Incidental observations were made, however, that will be referred to later.

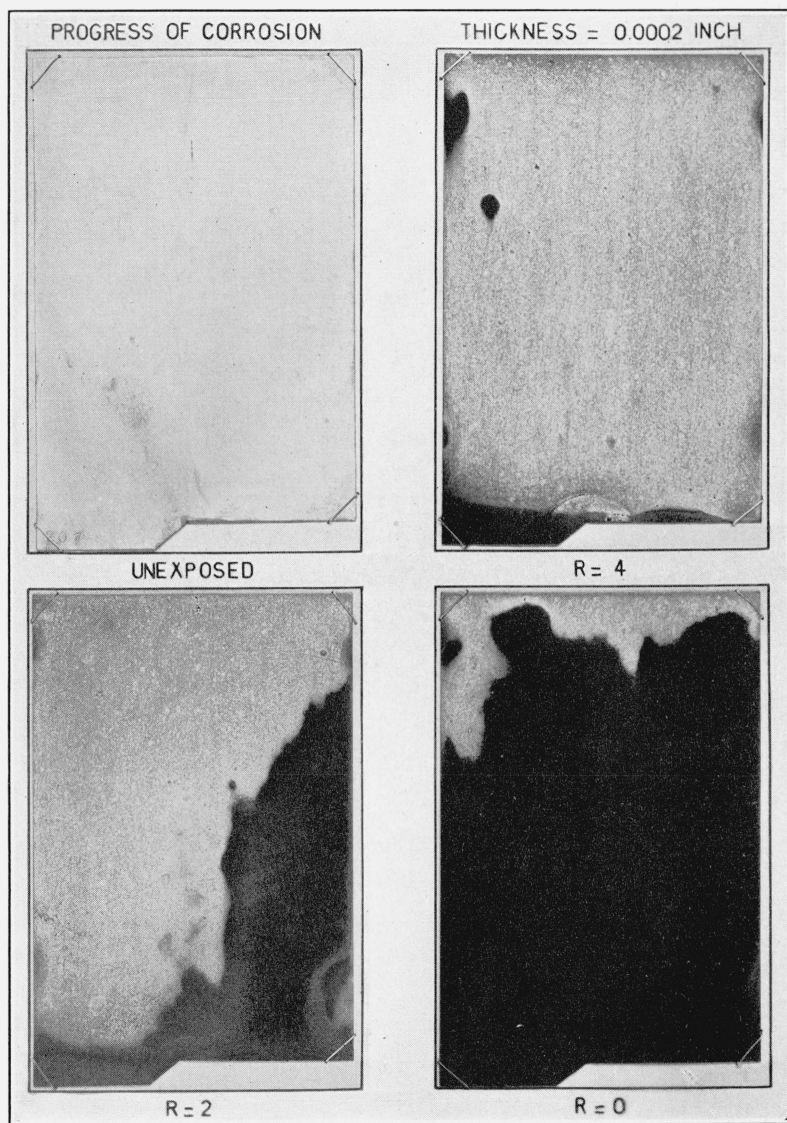


FIGURE 2.—Progress of corrosion of steel coated with 0.0002 inch of zinc at Washington after 180 weeks' (3.5 years) exposure.

None of these specimens showed appreciable corrosion at the end of 160 weeks. The dark areas represent red rust. Cadmium coated specimens behaved similarly.



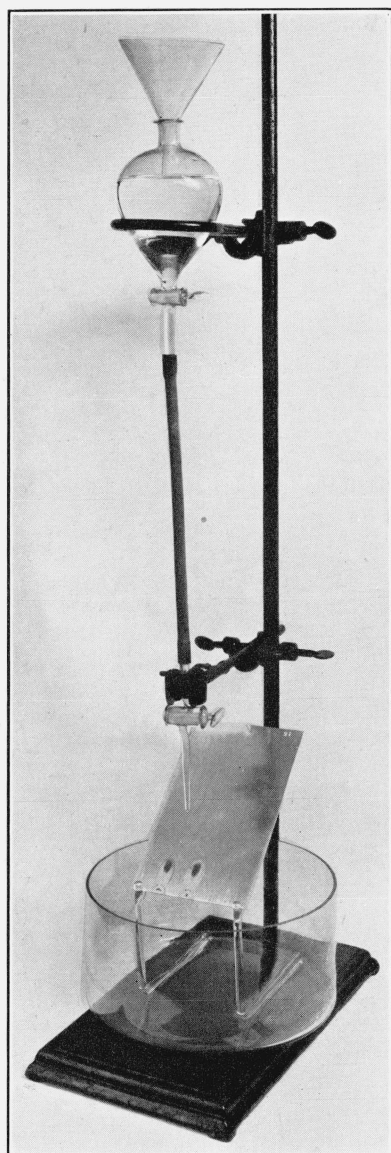


FIGURE 8.—Apparatus used in dropping tests for thickness of zinc and cadmium coatings.

### 3. SIGNIFICANCE OF EXPOSURE TESTS

In the report on nickel and chromium coatings it was pointed out that in actual service on automobiles, the finishes are usually washed at intervals and are often waxed, whereby their protective value may be increased. Consequently the results of continuous exposure tests without cleaning do not necessarily represent the behavior of such coatings in service. However, as zinc and cadmium coatings are rarely washed or waxed when used outdoors, the results of the exposure tests probably represent closely the behavior of such finishes in actual service in comparable atmospheres.

### 4. RESULTS OF EXPOSURE TESTS

The behavior and present status of all the sets are summarized in table 8.

#### (a) REPRODUCIBILITY

The data for the zinc and cadmium coatings show that, especially in industrial locations, there was even closer agreement in the reports of several inspectors than with the nickel and chromium finishes previously reported. This agreement was caused by the fact that although the latter more noble coatings usually fail by permitting rusting in pin holes, the coatings of less noble metals such as zinc and cadmium generally furnish complete protection of the steel until the coating is entirely dissolved from a relatively large part of the area, which then rusts. In almost every case the rusting started along the lower edge, where moisture adhered longest, and then spread up the sides and finally to the center, figure 2. This figure shows that the rate of solution of the zinc varied on different parts of the same specimen, which explains the failure of these relatively uniform coatings to dissolve simultaneously from the entire surface of each specimen. It is easier to estimate the proportional area of one or of a few large rust spots than of a large number of very small spots.

In the marine atmosphere at Key West, almost all the zinc- and cadmium-coated specimens (regardless of thickness), developed in one to two years a few very small rust spots, which did not materially increase in number or size during more prolonged exposure. This amount of rust, corresponding to a rating of 4, apparently does not represent an appreciable destruction or weakening of the base metal, which is very evident when failure occurs in an industrial climate. It is difficult to reconcile the presence of these small rust spots with the well-known tendency of zinc and cadmium to protect small exposed areas of steel against corrosion, especially as the adherent film of salt water is conducting. An explanation may be found in the fact that in a marine atmosphere the zinc and cadmium become coated with insoluble films, which may insulate the metal coatings, and thus prevent them from exercising their "sacrificial" effect on the adjacent small exposed areas of steel. If this explanation is correct, freedom from pores is more important in zinc and cadmium coatings that are exposed to a marine climate than in those exposed to industrial conditions, even though the pores may not result in structural damage.

TABLE 8.—Summary of exposure tests to November 1, 1935 (about 180 weeks' exposure)

## ZINC

Set	Description	Thick- ness	Key West 1	New York					Pittsburgh					Sandy Hook					State College					Washington					Set
				T 2	R 3	Rust	T	Weeks to R =		R	Rust	T	Weeks to R =		R	Rust	T	Weeks 4 to R =		R	Rust	T	Weeks to R =						
								3	0				3	0				3	0				3	0					
201	Cyanide.....	.0005	% 93	0	% 75	% 53	93	143	0	% 75	% 55	118	162	5	% 0	% 98			5	% 0	% 100			201					
202	Cathode pickle.....	.0005	98	0	75	41	83	93	0	75	54	118	132	4.6	1	99	-----	-----	5	0	100	-----	-----	202					
203	Anode pickle.....	.0005	96	0	75	43	93	100	0	75	51	118	118	4	3	97	-----	-----	5	0	100	-----	-----	203					
205	Cyanide.....	.0002	94	0	75	28	52	65	0	75	29	55	81	0	75	53	100	143	5	0	100	-----	-----	205					
206	do.....	.0010	92	0.4	55	74	143	175	1.2	28	91	173	-----	5	0	98	-----	-----	5	0	100	-----	-----	206					
207	Cyanide+Hg.....	.0002	90	0	75	30	57	75	0	75	22	45	55	0	75	55	108	121	5	0	100	-----	-----	207					
208	do.....	.0005	93	0	75	60	121	143	0	75	63	132	162	5	0	99	-----	-----	5	0	100	-----	-----	208					
209	do.....	.0010	88	4	3	93	181	-----	0.4	56	88	173	-----	5	0	99	-----	-----	5	0	100	-----	-----	209					
210	Acid+SO <sub>2</sub> .....	.0005	86	0	75	49	100	108	0	75	52	118	118	5	0	98	-----	-----	5	0	100	-----	-----	210					
214	do.....	.0002	85	0	75	27	52	57	0	75	23	50	50	0	75	50	93	108	5	0	100	-----	-----	214					
215	do.....	.0010	89	0	75	83	169	169	4.0	3	91	-----	-----	5	0	98	-----	-----	5	0	100	-----	-----	215					
216	Acid+dextrin.....	.0002	89	0	75	28	52	57	0	75	24	50	60	0	75	59	108	121	5	0	100	-----	-----	216					
217	do.....	.0005	87	0	75	52	100	103	0	75	55	118	118	4.8	1	97	-----	-----	5	0	100	-----	-----	217					
218	do.....	.0010	86	0.6	48	83	169	169	3.6	4	93	-----	-----	5	0	99	-----	-----	5	0	100	-----	-----	218					
219	Hot dip.....	.0009	85	0	75	76	121	169	0	75	86	173	183	4	3	98	-----	-----	4.8	1	100	-----	-----	219					

## CADMIUM

301	Cyanide.....	0.0005	81	0	75	26	57	65	0	75	43	98	118	4	3	94	-----	5	0	100	-----	4	3	97	-----	301		
302	Cathode pickle..	.0005	81	0	75	25	57	65	0	75	42	89	118	3.4	5	94	-----	5	0	100	-----	4.3	2	97	-----	302		
303	Anode pickle....	.0005	81	0	75	25	52	65	0	75	41	81	118	3.8	4	95	-----	5	0	100	-----	3.8	4	94	-----	303		
304	Cyanide.....	.0002	81	0	75	16	33	40	0	75	17	36	50	0	75	43	93	108	3.6	4	94	-----	0	75	59	112	148	304
305	do.....	.0010	81	0	75	44	93	121	0.2	65	81	162	183	5	0	94	-----	4.8	1	100	-----	4.3	2	96	-----	305		
307	Gulac.....	.0002	81	0	75	16	33	40	0	75	17	36	42	0	75	47	100	121	3	8	85	178	0	75	58	112	148	307
308	do.....	.0005	81	0	75	27	57	65	0	75	37	81	118	4	3	88	-----	5	0	100	-----	4.3	2	97	-----	308		
309	do.....	.0010	81	0	75	46	100	121	0	75	71	132	173	5	0	96	-----	5	0	100	-----	5	0	100	-----	309		
310	Gulac+Ni.....	.0002	81	0	75	14	33	40	0	75	18	36	45	0	75	46	83	108	3	8	87	159	0	75	78	126	159	310
311	do.....	.0005	82	0	75	28	57	75	0	75	34	60	98	3.2	6	90	-----	5	0	100	-----	4.4	2	96	-----	311		
312	do.....	.0010	82	0	75	44	93	108	0	75	81	162	183	5	0	97	-----	5	0	100	-----	4.8	1	99	-----	312		

## ZINC-CADMIUM ALLOY

401	10% of cadmium..	0.0005	87	0	75	58	108	143	0	75	69	132	162	5	0	98	-----	5	0	100	-----	4.8	1	99	-----	401		
402	do.....	.0002	86	0	75	28	57	57	0	75	25	50	60	0	75	53	100	108	5	0	100	-----	0	75	76	148	159	402
403	do.....	.0010	85	4	3	94	-----	5	0	97	-----	5	0	99	-----	5	0	100	-----	4.9	1	99	-----	-----	-----	403		
404	8% of cadmium..	.0005	89	0	75	62	121	143	0	75	60	118	162	5	0	99	-----	5	0	100	-----	4.9	1	99	-----	404		
405	14% of cadmium..	.0005	87	0	75	60	121	143	0	75	58	118	162	5	0	98	-----	5	0	100	-----	5	0	100	-----	405		

<sup>1</sup> All sets at Key West have a rating of 4, corresponding to 3 percent of rust.<sup>2</sup> T=total score, in percent.<sup>3</sup> R=Rating.<sup>4</sup> No sets at State College have reached a rating of 0.

## (b) EFFECT OF LOCATION

The prevailing atmosphere has a very marked effect upon the rate of failure of zinc and cadmium coatings. The behavior of thin coatings (0.0002 in.) is illustrated in figure 3. This shows complete failure of both zinc and cadmium in industrial locations (New York and Pittsburgh) in about a year; in Sandy Hook, a combined marine and industrial atmosphere, in about 2 years; and in Washington, a mild urban location, in about 3 years. On the other hand, neither metal showed decided failure in 3 years in either a marine location (Key West) or a rural exposure (State College). As thick coatings have failed severely only at New York and Pittsburgh, detailed comparisons of the coatings must be confined to these two locations.

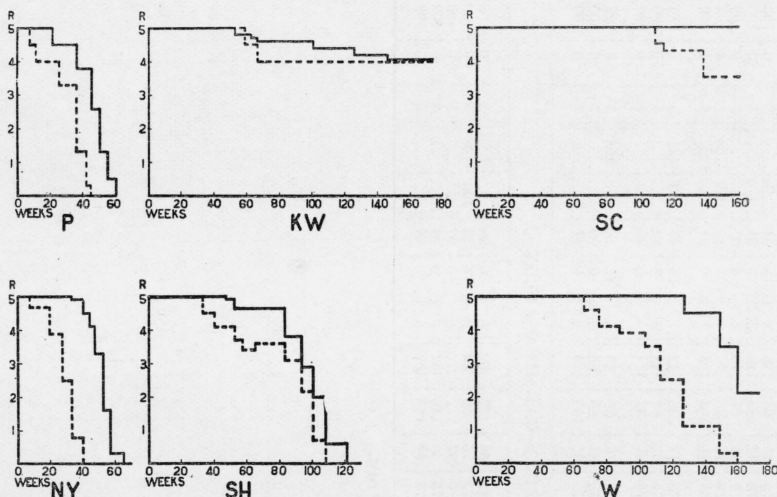


FIGURE 3.—Rates of corrosion of steel plated with 0.0002 in. of zinc or cadmium, expressed as ratings *R*.

The data represent the averages of four sets (20 specimens) of zinc and three sets (15 specimens) of cadmium in each location. P=Pittsburgh; KW=Key West; SC=State College; NY=New York; SH=Sandy Hook; W=Washington. Zinc ——— Cadmium - - - -

The more rapid failure of zinc and cadmium in industrial locations is undoubtedly caused by the higher concentrations of sulphur dioxide (and possibly of sulphur trioxide) in the atmosphere of such places. These sulphur compounds produce soluble salts of zinc and cadmium, which are readily removed by rain, the amount of which is therefore a secondary factor in the corrosion. That the rainfall is not a primary factor, as suggested by H. Figour and P. Jacquet [4], is evident from the very slow failure of these coatings at Key West, where the rainfall is relatively high.

In the absence of sulphur dioxide, it is probable that both metals are protected by thin films of basic carbonate. These are sometimes visible, especially on zinc coatings in a marine atmosphere. Sulphur acids dissolve these films, and hence permit more rapid solution of the coating.



## (c) COMPARISON OF ZINC AND CADMIUM

The data in figure 3 show conclusively that in industrial locations cadmium coatings fail more rapidly than do zinc coatings of equal thickness. As the specific gravity of cadmium (8.6) is about 20 percent greater than that of zinc (7.1), the comparison would be still less favorable to cadmium if coatings of equal weight per unit area were considered. These results fully confirm the conclusions of other investigators, based on loss of weight of zinc and cadmium coatings in New York [5], [6], in London [8], and in Paris [4].

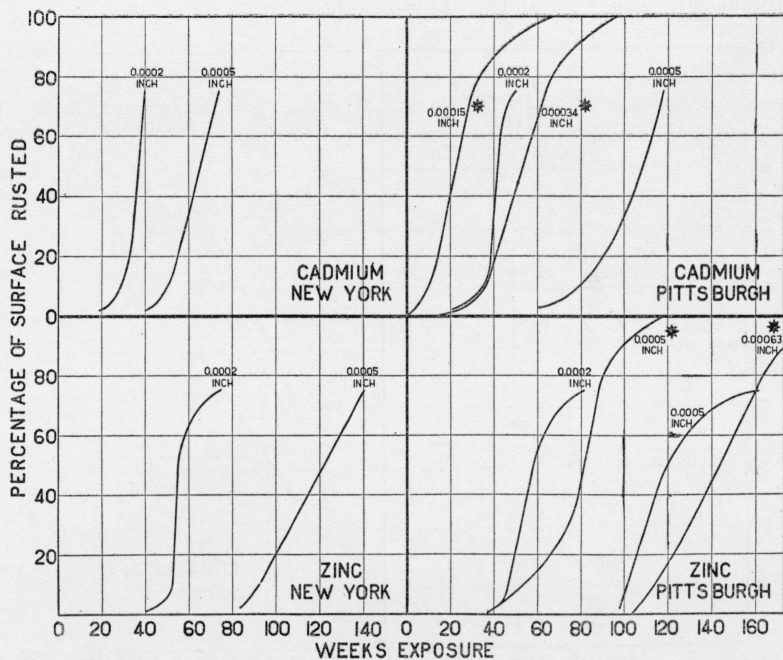


FIGURE 4.—Average rates of corrosion of steel plated with different thicknesses of zinc or cadmium, expressed as percentage of surface rusted.

Curves marked \* are from figure 1 of the paper by Passano [reference 7], whose curve for 0.0005 in. of zinc is for a sherardized zinc coating, and for 0.00063 in. is for hot-dipped sheets.

The same conclusion may be reached from figure 4, in which the data for New York and Pittsburgh have been plotted in terms of the percentage of surface rusted, in order to make these results directly comparable with those of the ASTM tests on hardware [7]. (A few curves for coated hardware from the ASTM tests in Pittsburgh are included for comparison.) As indicated in figure 1 total failure (a rating of 0) may represent from 50 to 100 percent of rust, and has therefore been plotted as 75 percent. That complete failure of the plated flat specimens is more sharply defined than of the hardware specimens is caused partly by this method of rating, and partly by the fact that the latter are of irregular shape and hence the coatings are less uniform in thickness. It is evident, however, that the periods required for the major part of the rusting are consistent for coatings of similar thickness.

Consideration of the atomic weights of zinc and cadmium shows that electrochemically equivalent corrosion of the two metals would dissolve 1.72 times (by weight) as much cadmium as zinc. Hence, at any specified current density a given *weight* of cadmium would dissolve in 58 percent of the time required for the same weight of zinc. As, however, the specific gravity of cadmium is greater than that of zinc, it requires 71 percent as many ampere hours to dissolve the same *thickness* of cadmium as of zinc. As this ratio is about the same as that observed with the two metals in an industrial atmosphere, it is apparent that they are corroding at about the same electrochemical rates, that is, at the same anode current densities.

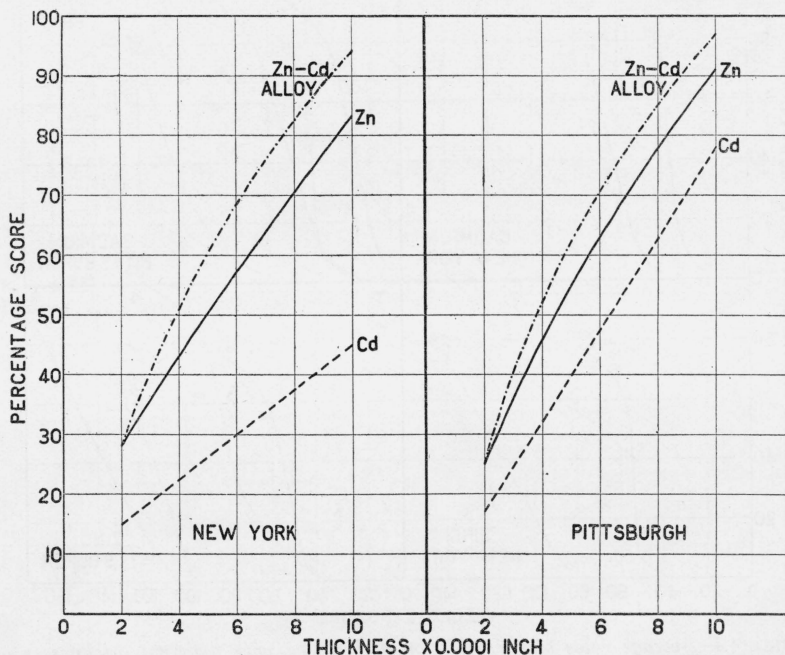


FIGURE 5.—Relation between thickness of zinc, cadmium, or zinc-cadmium alloy, and percentage scores in New York and Pittsburgh, after 3.5 years' exposure.

In mild locations, such as State College and Washington, thin coatings of both zinc and cadmium lasted a few years, but coatings of cadmium failed somewhat sooner than those of zinc. In marine locations the difference is not very significant. At Key West, the two coatings are in practically identical condition after 3 years, with only the few small rust spots referred to previously. It is evident that thin coatings of either of these metals furnish good protection for at least a few years against rural or marine exposures.

The curves in figure 5 show that deposits 0.0005 and 0.001 in. thick, that contain about 10 percent of cadmium and 90 percent of zinc, furnish somewhat better protection in industrial regions than do zinc coatings of the same thickness, although the scores for thinner coatings are practically identical. Similarly, Hippensteel and Borgman [6] found that alloy deposits containing 5 percent of cadmium corroded less rapidly than pure zinc deposits from cyanide baths.

## (d) EFFECT OF THICKNESS

If, as is generally agreed, zinc and cadmium protect steel against corrosion by "sacrificial" action, their protective value should be proportional to their thickness, as has been frequently reported. [5], [6], [7], [9]. The curves of figure 5 show that, when expressed in terms of the percentage score, the protective value of either zinc or cadmium is practically a linear function of its thickness.

With zinc-cadmium alloys, the protective value does not increase quite linearly with the thickness, although the departure is not great. The same behavior is illustrated in figure 6, where are shown the

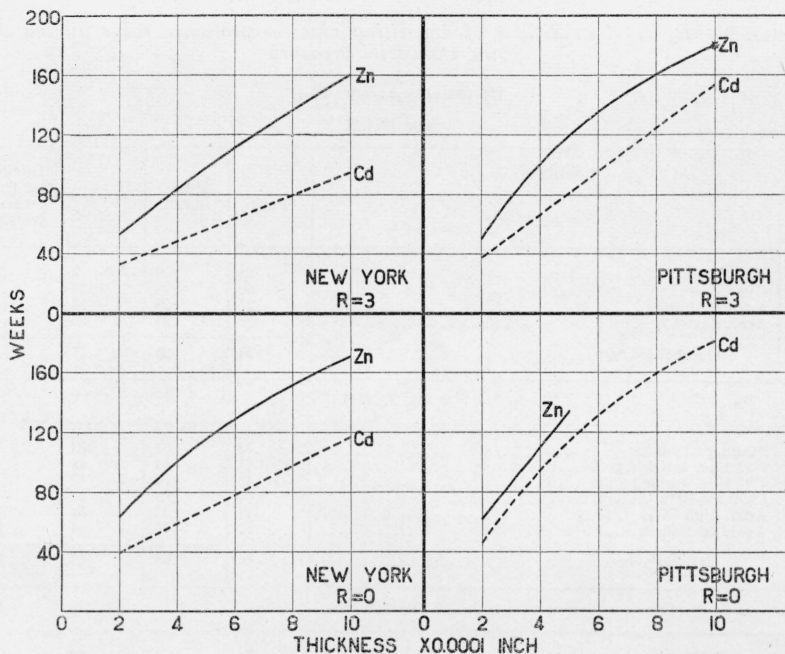


FIGURE 6.—Time required on zinc and cadmium coated steel for first decided failure ( $R=3$ , i.e., (5 to 10 percent of rust), and for complete failure ( $R=0$ , i.e., over 50 percent of rust).

The curve marked \* is a minimum value as only two of the four sets have reached a rating of 3.

periods required to reach (a) a rating of 3, that is, from 5 to 10 percent of rust, and (b) a rating of 0, that is, over 50 percent of rust. While the data for failure of thick coatings in Pittsburgh are incomplete, the available results are consistent with those for New York. For practical purposes we may consider that the life of a zinc or a cadmium coating in an industrial atmosphere is proportional to its thickness. No evidence was found in these tests in support of the "critical thickness" mentioned by W. S. Patterson [8] for zinc coatings and by S. Wernick [9] for cadmium coatings. These authors found that in accelerated tests very thin coatings of these metals dissolved relatively much more rapidly than thicker deposits; and designated the point of inflection in the thickness-corrosion rate curve as a "critical thickness." In most of their experiments this was found to be about

0.0002 in. of either zinc or cadmium. They attributed the more rapid attack of thin coatings to their porosity. As the minimum thickness used in this investigation (0.0002 in.) was about equal to the reported critical thickness, no evidence was afforded as to the behavior of thinner coatings, or as to the existence of a critical thickness.

(e) EFFECT OF CONDITIONS OF DEPOSITION

(1) *Zinc*.—The data in table 9 show that the method of preparing this particular steel (such as anodic or cathodic pickling) had no marked effect upon the protective value of the coatings in industrial

TABLE 9.—*Effect of conditions of depositing zinc on protective value during 3.5 years' industrial exposure*

[In percentage score (T%)]

0.0002 INCH					
Set	Coatings Description	New York	Pitts- burgh	Average	Devia- tion from general average
205	Standard cyanide.....	28	29	29	+2
207	Cyanide+Hg.....	30	22	26	-1
214	Acid, high SO <sub>4</sub> .....	27	23	25	-2
216	Acid, dextrin.....	28	24	26	-1
	General average.....	28	25	27	-----
0.0005 INCH					
201	Standard cyanide.....	53	55	54	+1
202	Cyanide, cathode pickle.....	41	54	48	-5
203	Cyanide, anode pickle.....	43	51	47	-6
208	Cyanide+Hg.....	60	63	62	+9
210	Acid, high SO <sub>4</sub> .....	49	52	51	-2
217	Acid, dextrin.....	52	55	54	+1
	General average.....	50	55	53	-----
0.001 INCH					
206	Standard cyanide.....	74	91	82	-5
209	Cyanide+Hg.....	93	88	91	+4
215	Acid, high SO <sub>4</sub> .....	83	91	87	0
218	Acid, dextrin.....	83	93	88	+1
	General average.....	83	91	87	-----
219	Hot dipped.....	76	86	81	-6

locations. There was no consistent difference in the behavior of deposits from cyanide and acid-zinc baths, though Hippensteel and Borgman [6] reported that zinc deposited from acid baths corroded more rapidly than that from cyanide baths. Observations, not included in the table, showed that the zinc deposits from cyanide solutions darkened more rapidly in the atmosphere than did those from acid baths, which was also reported by Hippensteel and Borgman. The common belief that better protection is obtained with zinc deposits from cyanide than from acid baths, is no doubt based partly on the fact that the throwing power of the cyanide solutions is superior to that of acid solutions, and that the coatings from cyanide baths are more uniformly distributed on irregularly shaped articles,



which therefore have a longer life. The results of this study simply show that if a given minimum thickness of zinc can be applied to an article there is no great difference in protective value, whether this is accomplished from a cyanide or an acid bath.

The presence of a small amount of mercury in the zinc coatings appears advantageous, as it produced an improvement of 9 percent in the score of set 208 (0.0005 in.). It remains to be seen whether thicker coatings (set 209) will show a similar relative improvement on longer exposure. Attention should be called to the fact that such deposits may not be desirable in contact with brass or aluminum, the corrosion of which is accelerated by mercury.

The results for the hot-dipped coatings (set 219) in table 9, are practically identical with the average of the electroplated coatings having a comparable thickness. As the average thickness of these hot galvanized specimens was found by analysis to be approximately 0.0009 in., their scores are practically equivalent to those of the plated coatings of the same thickness. However, the hot-dipped zinc has failed severely only in industrial locations, and further observations will be needed to establish more certainly the relative value of the two types of coating.

TABLE 10.—Effect of conditions of depositing cadmium on protective value during 3.5 years' industrial exposure

[In percentage score (T%)]

0.0002 INCH

Coating		New York	Pittsburgh	Average	Deviation from general average
Set	Description				
304	Standard cyanide.....	16	17	17	0
307	Cyanide+gulac.....	16	17	17	0
310	Cyanide+gulac+Ni.....	14	18	16	-1
	General average.....	15	17	17	-----

0.0005 INCH

301	Standard cyanide.....	26	43	35	+2
302	Cyanide, cathode pickle.....	25	42	34	+1
303	Cyanide, anode pickle.....	25	41	33	0
308	Cyanide+gulac.....	27	37	32	-1
311	Cyanide+gulac+Ni.....	28	34	31	-2
	General average.....	26	39	33	-----

0.001 INCH

305	Standard cyanide.....	44	81	63	+1
309	Cyanide+gulac.....	46	71	59	-3
312	Cyanide+gulac+Ni.....	44	81	63	+1
	General average.....	45	78	62	-----

(2) *Cadmium*.—The data in table 10 show that the differences in the protective value of cadmium coatings produced under various conditions or from different cyanide baths are very small. As there was a marked difference in the initial appearance and probably in



the crystal structure of the three types of cadmium deposits, these results show that no advantage in protective value is *necessarily* obtained by making the deposits brighter or finer-grained. The use of a specific addition agent must therefore be justified by a demonstrated increase in protective value, by an improvement in the initial appearance of the coating or in the throwing power, or by some operating advantage. After a moderate period in a severe industrial location all the cadmium deposits turned dull and had about the same appearance. In a marine atmosphere the cadmium coatings had less white film and preserved a better appearance than did the zinc coatings.

(3). *Zinc-Cadmium Alloys*.—From a practical standpoint, it is important to know whether a small variation in the cadmium content of the alloy deposits has an appreciable effect on their behavior. It was found difficult to control closely the cadmium content of these deposits on flat plates, and it is reasonably certain that on irregularly shaped articles, where the current density is less uniform, the composition as well as the thickness may vary considerably. The results in table 11 show that moderate variations in the cadmium content, for example from 8 to 15 percent, have no significant effect on the protective value.

TABLE 11.—*Effect of composition of zinc-cadmium alloys on protective value during 3.5 years' industrial exposure*

[In percentage score (T%)]  
0.0005-INCH COATING

Coating		New York	Pittsburgh	Average	Deviation from general average
Set	Cadmium content				
	<i>Percent</i>				
401.....	10	58	69	64	+3
404.....	8	62	60	61	0
405.....	14	60	58	59	-2
General average.....	-----	60	62	61	-----

#### IV. ACCELERATED TESTS

In the accelerated tests that have been most frequently used to evaluate zinc and cadmium coatings, sodium chloride is the principal corroding agent. It might be predicted and has been approximately confirmed, that the results of such tests are at least similar to those in a marine atmosphere. In view of the fact, however, that both zinc and cadmium coatings fail much more rapidly in an industrial than in a marine location, it would be more logical to apply, in accelerated tests, the substances that are most significant in an industrial atmosphere, that is sulphurous and sulphuric acid. Although numerous efforts [10], [11], [12], [13] have been made to develop tests in which sulphurous acid is used, such tests have never been standardized or extensively applied. Unsuccessful efforts were made in this investigation to develop a sulphur dioxide test that can be conveniently operated and that will yield reproducible and significant results. There is a need for more study of such tests, especially for zinc and cadmium coatings.

In the salt spray and intermittent immersion tests the temperature was maintained at  $35 \pm 2^\circ \text{C}$  ( $95 \pm 4^\circ \text{F}$ ) in order to obtain reproducible results. This temperature was selected because it is about the lowest that can be maintained in the United States throughout the year without artificial cooling. The rate of the failure at this temperature is somewhat more rapid than at the lower temperatures that usually prevail in laboratories, but it is not feasible to fix any exact ratio of the results at different temperatures.

Before applying an accelerated test, the surface of each specimen was rubbed with a thin paste of very finely divided magnesium oxide and was rinsed. This produced a clean surface that was free from "water-break", that is, remained uniformly wet, which is a condition essential for reproducible results.

## 1. METHODS EMPLOYED

### (a) SALT SPRAY

The salt-spray test was conducted with a 20-percent solution of pure, neutral, sodium chloride in a room kept at  $35^\circ \text{C}$  ( $95^\circ \text{F}$ ). The nozzle, air pressure and baffle were so adjusted as to keep a uniform fine mist throughout the box and to wet uniformly the specimens, which were supported on glass at an angle of  $45^\circ$  from horizontal. The solution that was condensed from the spray was drained off and not used again.

The specimens were inspected at the end of the first 6 hours and of each succeeding 24-hour period. (The elapsed intervals have been rounded off to multiples of 5 for convenience of reference.) At each inspection, the specimens were washed with running water and allowed to dry, because then the amount of rust could be more accurately estimated than when they were wet. With some coatings, especially zinc deposits that had been in the salt spray or intermittent immersion for a considerable period, the white coating (probably basic zinc carbonate) was so adherent that light scrubbing with a bristle brush was required to remove it. It was found that such specimens failed somewhat sooner than unscrubbed specimens. Complete removal of the white coating evidently permitted more rapid subsequent corrosion of the zinc.

Just as in the exposure tests, the zinc- and cadmium-coated specimens tended to corrode in relatively large areas, instead of in the fine rust spots that usually appear on nickel and chromium finishes. As a consequence, it was easier to estimate the extent of the corroded area and to assign a rating from 5 to 0, on the same basis as in the atmospheric-exposure tests.

### (b) INTERMITTENT IMMERSION

The intermittent immersion tests were also conducted with a 20-percent solution of sodium chloride. Each cycle included 1 minute in the solution and 14 minutes in the air. The temperature was kept at  $35^\circ \text{C}$  ( $95^\circ \text{F}$ ) and the relative humidity at  $60 \pm 5$  percent. Under these conditions the specimens were visibly wet for about one-half of each period in the air. The specimens were inspected at the same intervals as those in the salt spray and the condition of each was similarly recorded.

TABLE 12.—Accelerated tests on zinc and cadmium coatings

## A. ZINC—0.0002 INCH

Set	Coating Description	Atmos- pheric average score NY+P	Salt spray			Intermittent immersion		
			Initial rust		Rating 100 hours R	Initial rust		Rating 100 hours R
			To R=4	To R=0		To R=4	To R=0	
		Percent	hr	hr		hr	hr	
205	Standard cyanide.....	29	80	120	1.3	25	50	0
207	Cyanide+Hg.....	26	80	120	1.3	25	55	0
214	Acid, high SO <sub>4</sub> .....	25	60	110	.3	25	55	0
216	Acid, dextrin.....	26	60	110	1.0	25	55	0
	Average.....	27	70	115	1.0	25	55	0

## 0.0005 INCH

201	Standard cyanide.....	54	140	410	4.0	60	120	1.0
202	Cyanide, cath. pickle.....	48	110	390	4.5	70	140	2.0
203	Cyanide, anode pickle.....	47	120	240	3.5	60	100	1.0
208	Cyanide+Hg.....	62	140	390	4.0	70	120	2.0
210	Acid, high SO <sub>4</sub> .....	51	100	320	2.5	60	120	1.0
217	Acid, dextrin.....	54	110	390	3.0	70	120	2.0
	Average.....	53	120	360	3.6	65	120	1.5

## 0.001 INCH

206	Standard cyanide.....	82	220	720	5.0	110	170	4.5
209	Cyanide+Hg.....	91	160	720+	4.5	110	190	4.5
215	Acid, high SO <sub>4</sub> .....	87	340	720	5.0	120	250	4.0
218	Acid, dextrin.....	88	270	720	5.0	110	250	4.5
	Average.....	87	250	720	4.9	110	220	4.5
219	Hot dip.....	81	80	360	3.5	90	250	4.0

## B. CADMIUM—0.0002 INCH

304	Standard cyanide.....	17	720	720+	5	530	690+	2.5
307	Cyanide+gulac.....	17	340	560	5	680+	720+	4.5
310	Cyanide+gulac+Ni.....	16	720	720+	5	300	590	0
	Average.....	17	590	670+	5	500+	670+	2.3

## 0.0005 INCH

301	Standard cyanide.....	35	720+	720+	5	530+	720+	4.5
302	Cyanide, cath. pickle.....	34	720+	720+	5	600+	720+	4.5
303	Cyanide, anode pickle.....	33	720+	720+	5	660+	720+	4.5
308	Cyanide+gulac.....	32	720+	720+	5	600+	720+	4.5
311	Cyanide+gulac+Ni.....	31	720+	720+	5	520+	720+	3.0
	Average.....	33	720+	720+	5	580+	720+	4.2

## 0.001 INCH

305	Standard cyanide.....	63	720+	720+	5	540	720+	4.5
309	Cyanide+gulac.....	59	720+	720+	5	620+	720+	4.5
312	Cyanide+gulac+Ni.....	63	720+	720+	5	530	720+	4.0
	Average.....	62	720+	720+	5	560+	720+	4.3

## C. ZINC-CADMIUM ALLOY—0.0002 INCH

402	10% of Cd.....	27	50	150	3	30	70	0
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TABLE 12.—Accelerated tests on zinc and cadmium coatings—Continued

C. Zinc-Cadmium Alloy—0.0005 INCH

Set	Coating Description	Atmos- pheric average score NY+P	Salt spray			Intermittent immersion		
			Initial rust		Rating 100 hours R	Initial rust		Rating 100 hours R
			To R=4	To R=0		To R=4	To R=0	
		Percent	hr	hr		hr	hr	
401	10% of Cd.....	64	200	600	5	90	160	1.5
404	8% of Cd.....	61	200	650	5	90	130	2.0
405	14% of Cd.....	59	150	460	5	90	120	1.5
	Average.....	61	180	570	5	90	140	1.7

0.001 INCH

403	10% of Cd.....	96	270	720+	5	100	110	3
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## 2. RESULTS

Each result in table 12 represents the average of four similar specimens tested at different times. In general, the reproducibility in these tests was somewhat better than with nickel and chromium finishes, though there were appreciable variations in the periods required for initial rust to appear. The periods required for complete

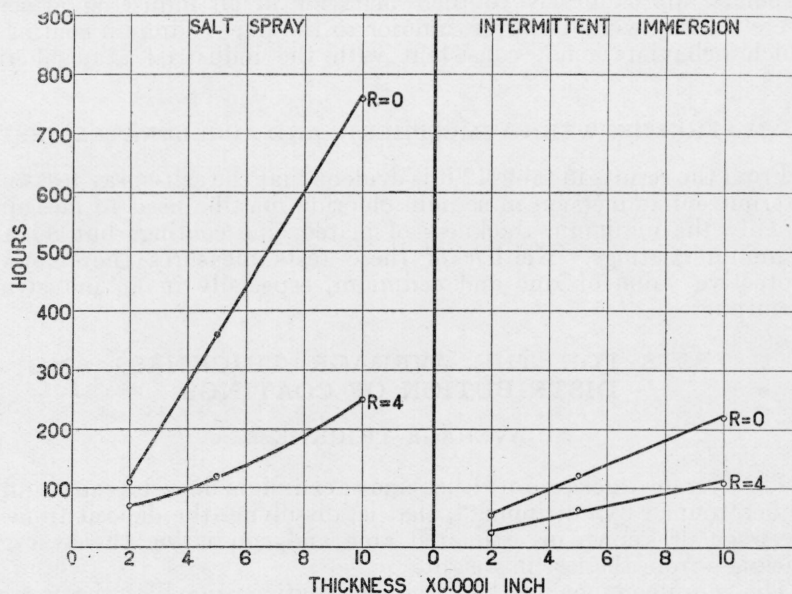


FIGURE 7.—Rate of failure of zinc plated steel in accelerated tests, to R=4 (1 to 5 percent rust) and to R=0 (over 50 percent of rust).

failure (that is, to a rating of 0, representing 50 percent or more of rust) were generally more consistent.

The results for zinc coatings, shown in table 12 and in figure 7, indicate that in both salt spray and intermittent immersion the time



of failure is a rough measure of the thickness. As the latter can be more conveniently measured by the dropping test [3], to be described, there is no advantage in using these accelerated tests, especially on thick coatings, for which long periods are required. In general, the tests were run continuously for one month (720 hours). Absence of rust at the end of that time is indicated in table 12 by "720+." Values such as 690+, which may represent an average of 660, and 720+ indicate that only part of the specimens of that set withstood the test for over 720 hours. In a few cases the test was continued for as much as 1,440 hours (2 months), but the results were no more conclusive. Changes in the method of plating produced no consistent differences in the results.

With intermittent immersion, electroplated zinc coatings failed in about half the time that was required in the salt spray. On the other hand, the hot-dipped coatings (set 219) failed in about the same time in both the spray and the immersion tests. Groesbeck and Tucker [13, p. 273] reported that electroplated zinc coatings failed more rapidly in a salt spray than in continuous immersion.

The results in table 12 fully confirm the well known high resistance of cadmium coatings to sodium chloride solutions in both the spray and immersion tests. Neither test is a reliable measure of the thickness of cadmium, as the 0.001-in. coatings showed initial failure in about the same time as did the 0.0005- or 0.0002-in. coatings.

In both of the accelerated tests, the zinc-cadmium alloys showed somewhat greater resistance than pure zinc coatings, which corresponds approximately to their behavior in an industrial atmosphere. They were, however, inferior to the pure cadmium coatings, which behavior is not consistent with the industrial atmospheric tests.

### 3. RELATION BETWEEN ATMOSPHERIC AND ACCELERATED TESTS

From the results in table 12 it is evident that the salt-spray test and intermittent immersion in sodium chloride may be used to measure roughly the minimum thickness of plated zinc coatings but not of cadmium coatings. Neither of these tests measures the relative protective value of zinc and cadmium, especially in an industrial atmosphere.

## V. TESTS FOR THE AVERAGE THICKNESS AND DISTRIBUTION OF COATINGS

### 1. AVERAGE THICKNESS

The average thickness of either zinc or cadmium deposits can readily be determined by "stripping", that is, dissolving the deposit from a specimen of known or estimated area and computing the average thickness from the loss in weight.

The most common method for zinc coatings involves the use of hydrochloric acid containing antimony chloride. The same method and conditions are applicable to cadmium coatings. The solutions specified by the ASTM have the following composition [14]:



*Solution a.*—Antimony Chloride. Dissolve 20 g of antimony trioxide ( $\text{Sb}_2\text{O}_3$ ) or 32 g of antimony trichloride ( $\text{SbCl}_3$ ) in 1,000 ml of chemically pure concentrated hydrochloric acid (sp gr 1.19).<sup>4</sup>

*Solution b.*—Hydrochloric Acid (HCl). Chemically pure concentrated hydrochloric acid (sp gr 1.19).<sup>5</sup>

*Solution c.*—Test Solution. This consists of 5 ml of solution a and 100 ml of solution b.

The specimen with a measured area is cleaned with an organic solvent, followed if necessary by light rubbing with magnesium oxide paste and thorough rinsing. It is dried and weighed, and then immersed in a suitable volume of the test solution until evolution of hydrogen practically ceases (usually in 15 to 30 seconds). The temperature of the solution should not exceed 38° C (100° F) during the test. The specimen is then rinsed and scrubbed under running water, rinsed with alcohol, wiped dry, dried at 100° C (212° F), and cooled. It is reweighed and the loss in weight is taken as the weight of zinc or cadmium on the specimen. The average thickness may be computed from the area stripped and the specific gravity of zinc (7.1), or of cadmium (8.6).

For stripping cadmium coatings a solution containing 120 g/liter of ammonium nitrate is sometimes used at a temperature slightly above room temperature, for example, 40° C (104° F). About 10 minutes is required to dissolve 0.001 in. of cadmium.

Another stripping solution for cadmium deposits contains 50 g/liter of ammonium persulphate and 100 ml/liter of concentrated ammonium hydroxide (sp gr 0.90), which should be freshly prepared before use. At room temperature about an hour is required to dissolve 0.001 in. of cadmium.

The average results obtained by applying these methods to duplicate weighed deposits on steel are shown in table 13. It is evident that the errors in these methods are almost never over 1 percent, which is sufficiently accurate for commercial testing.

## 2. DISTRIBUTION AND LOCAL THICKNESS

The present tendency to specify the minimum rather than the average thickness of zinc and cadmium coatings on steel necessitates the development of simple methods for measuring the thickness of the deposit on any small selected area.

### (a) PREECE TEST

The Preece test (immersion in neutral copper sulphate) is a measure of the variations in the thickness of zinc coatings, which is used in spite of its admitted shortcomings [15]. Many of these objections do not apply to plated coatings, which are practically pure zinc, with no layer of zinc-iron alloy.

A practical difficulty in the use of the Preece test for zinc-plated coatings is that they are usually thinner than hot-dipped coatings. If, then, for example, only two 60-second dips are required, the precision of the method is only about 50 percent. This difficulty can be

<sup>4</sup> Chemically pure concentrated hydrochloric acid usually has a specific gravity of approximately 1.18, which is satisfactory for this test.

<sup>5</sup> See footnote 4.

TABLE 13.—Accuracy of methods for stripping zinc and cadmium

## A. ZINC

Set	Description	Average thickness <sup>1</sup>	Average error (%)		
			SbCl <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub>	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>
205	Standard cyanide.....	<i>Inch</i> 0.0002	—0.9	-----	-----
202	do.....	.0005	+0.5	-----	-----
208	Cyanide+Hg.....	.0005	—0.2	-----	-----
210	Acid, high SO <sub>4</sub> .....	.0005	+0.4	-----	-----
217	Acid, dextrin.....	.0005	+1.2	-----	-----
206	Standard cyanide.....	.001	+0.1	-----	-----
	Average.....	-----	+0.2	-----	-----

## B. CADMIUM

304	Standard.....	0.0002	+0.7	+0.1	+0.8
302	do.....	.0005	+0.1	+0.5	+0.9
308	Gulac.....	.0005	+1.2	+1.9	+0.9
311	Ni+gulac.....	.0005	+0.1	+0.3	+0.3
305	Standard.....	.001	+0.1	+0.2	+0.2
	Average.....	-----	+0.4	+0.6	+0.6

## C. ZINC-CADMIUM ALLOY

402	10% of Cd.....	0.0002	+2.6	-----	-----
401	10% of Cd.....	.0005	+0.3	-----	-----
404	8% of Cd.....	.0005	+0.8	-----	-----
405	14% of Cd.....	.0005	+1.0	-----	-----
403	10% of Cd.....	.001	+0.4	-----	-----
	Average.....	-----	+1.0	-----	-----

<sup>1</sup> Based on the actual weights of metal deposited.

partly overcome by using shorter immersion periods, such as 15 seconds. Under these conditions the results are more reproducible, but are not directly comparable with those obtained in 1-minute dips; as four 15-second dips are not exactly equivalent to one 1-minute dip.

A more serious objection to the use of the Preece test for relatively thin electrodeposits is that if the coating on a given article is nearly uniform in thickness, an endpoint of adherent copper is not always obtained, even when the entire surface of the steel is exposed. This behavior results from the fact that the adherent copper is ordinarily deposited because the adjacent residual zinc acts as an anode with respect to the bare steel, which serves as the cathode. If, however, a thin uniform coating is removed in one immersion, no zinc is left to serve as the anode. This difficulty can be overcome by attaching to the test specimen a piece of zinc gauze or thin strips of zinc, whose presence will then cause deposition of adherent copper on exposed steel. This modification makes the method cumbersome. Therefore the Preece test is not recommended for testing plated zinc coatings having a minimum thickness of less than 0.0005 in.

It was found that it requires approximately four 1-minute dips for 0.001 in., two 1-minute dips for 0.0005 in., and three 15-second dips for 0.0002 in. As the individual values were not very concordant, no high accuracy should be attached to these values. They show that the time is approximately proportional to the thickness.

## (b) DROPPING TESTS

Recent experience has shown that the rate of solution of a zinc or cadmium coating is more constant if the reagent is applied to the surface in successive drops than if the specimen is immersed in the solution. S. G. Clark [16] described such a method, in which an aqueous solution containing 100 g/liter of iodine and 200 g/liter of potassium iodide was allowed to fall at the rate of one drop per second upon the surface to be tested, until the steel was exposed. Under these conditions, 18 drops were required for 0.0001 in. of cadmium. This rate for cadmium was confirmed at this Bureau, and it was also found that with this solution 22 drops were required for 0.0001 in. of zinc.

This method was modified by Hull and Strausser [3], who substituted acidified ammonium nitrate solutions for the iodine. They found that with more rapid dropping (90 to 110 drops per minute), the rate of solution was practically independent of the rate of dropping. They therefore expressed their results in terms of the time required to dissolve the coatings. To simplify the calculations, they adjusted the composition of the various reagents so that a specified coating was dissolved at the rate of 0.000 01 in. per second. The tests were made at room temperature (20 to 30° C or 70 to 90° F). Temperature changes within this range had a negligible effect on the rate of solution. Simple apparatus for this test is shown in figure 8 (facing p. 193). Experiments made here subsequent to those reported by Hull and Strausser have shown that hot-dipped zinc coatings can be similarly tested with an appropriate reagent. On weighed specimens the following solutions yielded results that were accurate to  $\pm 15$  percent, which is a higher precision than is usual with the Preece test.

*For zinc—*

(1) Plated coatings (including those that contain small amounts of mercury):

Ammonium nitrate.....	100 g/liter.
Nitric acid (sp gr 1.42).....	55 ml/liter.

(2) Hot-dipped coatings:

Ammonium nitrate.....	100 g/liter.
Hydrochloric acid (sp gr 1.180).....	75 ml/liter.

*For cadmium—*

Ammonium nitrate.....	110 g/liter.
Hydrochloric acid (sp gr 1.180).....	10 ml/liter.

The specimen to be tested is cleaned so that it is free from "water-break", and is then supported under the outlet tip so that the solution hits the spot to be tested and runs off quickly. The time required to expose the steel is measured with a stop-watch. In applying this and other tests to determine the minimum thickness, consideration should be given to those portions where the minimum thickness is most likely to occur.

## (c) MICROSCOPIC MEASUREMENTS

For relatively hard metals such as copper and nickel, the measurement of metallographic cross sections at selected points is a very satisfactory method for determining the distribution and local thickness.

With soft metals like zinc and cadmium it is very difficult to avoid flow of the coating during the polishing of a cross section, even when a harder metal is deposited upon or clamped against the deposit to be examined. Results of numerous tests on coatings of known average thickness, whose distribution had been checked by dropping methods, were erratic. Considerable skill is required to obtain reliable microscopic measurements of either zinc or cadmium coatings.

#### (d) CHORD METHOD

F. C. Mesle [17] recently described a method for testing the thickness of plated coatings, which depends upon just cutting through the coating on a curved surface with a flat file, or on a plane surface with a precision grinding wheel of known radius. In either case the thickness of the coating,  $T$ , may be computed from the width of the chord,  $C$  (measured with a lens and scale) and the radius  $R$  of the object or grinding wheel, in accordance with the equation

$$T = \frac{C^2}{8R}$$

In effect, the method results in a mechanical instead of an optical magnification of the cross section of the deposits.

A detailed study of this method [18] was recently made at the National Bureau of Standards. It showed that under favorable conditions the accuracy of the method for various coatings, including zinc and cadmium on steel, is about 10 percent, which is at least equal to that obtained for zinc and cadmium by other methods. This method is not satisfactory for coatings less than 0.0002 in. thick.

### VI. CONCLUSIONS

1. Thin coatings of either zinc or cadmium furnish better protection against corrosion of steel in most normal climates than do equally thin coatings of nickel or chromium [1].

2. In uncontaminated marine or rural atmospheres either zinc or cadmium coatings with a minimum thickness of 0.0005 in. furnish protection against corrosion for at least a few years.

3. In industrial locations both zinc and cadmium coatings fail in a comparatively short time. (Most of the following conclusions regarding atmospheric exposure are based on industrial exposure.)

4. In an industrial atmosphere cadmium coatings fail in from 65 to 75 percent of the time that is required for failure of zinc coatings of the same thickness.

5. In an industrial atmosphere alloy deposits that contain about 10 percent of cadmium and 90 percent of zinc have a slightly longer life than zinc and considerably longer than cadmium deposits.

6. In industrial locations the protective value of either zinc or cadmium coatings is practically proportional to their thickness.

7. Neither the methods used for preparing the steel employed in this investigation nor the variations made in the composition of the zinc-or cadmium-plating solutions had any effect on the protective value of the coating that was comparable with the effect of thickness.

8. Plated zinc coatings furnish about the same protection as hot-dipped zinc coatings of the same thickness.



9. In the salt-spray and intermittent-immersion tests, the time required for failure of zinc coatings is approximately proportional to the thickness.

10. Plated zinc coatings fail more rapidly in the intermittent immersion than in the salt spray test.

11. Neither the salt spray nor intermittent immersion furnishes a reliable criterion of thickness of cadmium coatings or of their protective value relative to that of zinc in an industrial atmosphere.

12. The average thickness of either zinc or cadmium coatings can be determined reliably from the loss in weight in the antimony chloride-hydrochloric acid stripping test; and of cadmium coatings by stripping in ammonium nitrate or ammonium persulphate.

13. The Preece test is a fairly reliable measure of the distribution (but not of the actual thickness) of plated zinc coatings over 0.0005 in. thick. It is not satisfactory for thinner coatings.

14. The dropping methods with an iodine solution or an ammonium-nitrate solution measure the local thickness and distribution of zinc and cadmium coatings with an accuracy of about 15 percent.

15. The "chord" method may be used to measure the local thickness of zinc and cadmium coatings with an accuracy of about 10 percent.

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