PROTECTIVE VALUE OF NICKEL AND CHROMIUM PLATING ON STEEL

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ABSTRACT

Exposure tests of plated steel were conducted in cooperation with the American Electroplaters' Society and the American Society for Testing Materials, in rural, suburban, industrial, and marine locations. It was found that the thickness of the nickel layer is more important than any other factor. An intermediate layer of copper decreases the protective value of thin deposits but is not detrimental in thick coatings, especially if they are chromium plated. The customary thin chromium coatings (0.00002 in. or 0.0005 mm) increase the resistance to tarnish, but not the protection against corrosion.

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I. INTRODUCTION

In order to determine the relative protective values of different electroplated coatings on steel, exposure tests were conducted during the past 2 years through cooperation of the American Electroplaters' Society and American Society for Testing Materials with the National Bureau of Standards. The details of the experiments and inspections were arranged by a joint committee. The experimental work was conducted at the Bureau by the Research Associate of the American Electroplaters' Society with the assistance of various members of the Bureau staff.

This report is confined to those coatings in which the outer layer was nickel or chromium, sometimes with intermediate layers of copper, and occasionally of zinc or cadmium. Specimens plated only with zinc or cadmium were exposed simultaneously, but as these have thus far shown failure in only three locations, the results will be reserved for later publication.

As part of this investigation, accelerated tests and their relation to the results of atmospheric corrosion were studied. A study was also made of methods for stripping electro-deposited coatings to determine their weight and average thickness. The results of these investigations will be published in later papers.

II. PREPARATION OF SPECIMENS

1. BASE METAL

The base metal was cold-rolled strip steel with a selected good finish, which required no polishing. It was 4 in. (10 cm) wide [2] and 0.031 in. (0.78 mm) thick (U.S. Gage no. 22). The steel was SAE. no. 1010 which contains approximately 0.1 percent of carbon. The specimens were each 4 by 6 in. (10 by 15 cm). Microscopical examinations of the steel before and after plating, and after exposure, failed to detect any inclusions or structural defects that might affect the quality or protective value of the plated coatings. A few strips were rejected that showed, after pickling or plating, some rolling lines with slag inclusions.

Each specimen was numbered near one corner with a steel die, and a narrow strip was cut half-way across the top edge and turned over at a right angle to serve as a hanger. Six specimens were mounted in the same plane in a steel rack so that there was about 0.25 in. space between each edge and the adjoining plate or portion of the rack. Tests showed that with this spacing the maximum variation from the average weight of coatings on the 12 specimens plated on 2 racks in one operation was less than 5 percent, and the mean variation was

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[2] 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

about 2 percent. Microscopical examination of cross sections showed that close to the edge the thickness of the coatings was about 50 percent greater than the nominal thickness, but that on over 90 percent of the area the variations were less than 10 percent from the average thickness.

2. PREPARATION FOR PLATING

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 that it served as a basis of comparison.

The preparation consisted essentially in the removal of grease, which process is designated by platers as "cleaning", and treatment with acid, that is, pickling. Although there was no need for pickling to remove visible oxide or scale from this steel, preliminary tests showed that definite etching of the steel was necessary to insure good adherence of the deposits, as measured in tests that involved bending, elongation, and extrusion in the Erichsen test.

Standard cleaning "A".[3] Each plate was subjected to the following treatments.

"1". The bulk of the grease was removed with either carbon tetrachloride or amyl acetate. The plates were then:

"2". Cleaned electrolytically as cathodes at about 90 C (194 F) and 5 amp/dm² (47 amp/ft²) for 5 minutes in a solution with the composition shown below.

Alkaline cleaning solution	Approx. N	g/l	oz/gal
Sodium carbonate, Na_2CO_3	0.6	30	4
Trisodium phosphate, $Na_3PO_4.12H_2O$	0.25	30	4
Sodium hydroxide, $NaOH$	0.2	7.3	1

"3". Scrubbed with a bristle brush that was wet with the same cleaning solution;

"4". Rinsed in hot water;

"5". Pickled for 2 minutes in 2 N sulphuric acid (98 g/l or 13 avdp oz/gal or 7.5 fl oz/gal of H_2SO_4) at 50 C (122 F); and

"6". Rinsed in cold water.

Cathode pickling "B". The procedure was the same as in "A", except that *instead* of step "5" the steel was pickled *cathodically* in 2 N sulphuric acid at 50 C (122 F) for 2 minutes at 2 amp/dm² (19 amp/ft²), with lead anodes.

Anode pickling "C". The procedure was the same as in "A", except that *after* step "5" the steel was pickled as anode in 96 percent sulphuric acid at room temperature. Lead cathodes were used, and a potential of 12 volts was applied until the high initial current dropped nearly to zero (usually in about 2 minutes). The plates were then rinsed quickly in cold water.

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[3] The quoted numbers, capital letters, and sub-numerals used to identify the specimens, solutions, and conditions are the same as those employed in preliminary reports, and have been retained (with some omissions) for convenience of reference.

3. CONDITIONS USED IN PLATING

All 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) NICKEL PLATING

Rolled nickel anodes containing over 99 percent of nickel were used. The conditions of operation are summarized in table 1.   The pH values there given were determined with a quinhydrone electrode, and are equivalent to "colorimetric corrected values", that is they are about 0.5 pH below the uncorrected colorimetric results.[4]

TABLE 1.—*Conditions in nickel plating*

Method[1]	Composition of solution												pH	Temperature		Current density		Variation
	$NiSO_4.7H_2O$			$NiCl_2.6H_2O$			Na_2SO_4			H_3BO_3								
	N	g/l	oz/gal	N	g/l	oz/gal	N	g/l	oz/gal	M	g/l	oz/gal		C	F	amp/dm²	amp/ft²	
E	1.4	200	27	0.4	45	6	---	---	---	0.5	30	4	5.3	35	95	2	19	Standard.
E₁	1.4	200	27	.4	45	6	---	---	---	.5	30	4	5.3	60	140	4	37	Temp. and c.d.
F	1.4	200	27	.4	45	6	---	---	---	.5	30	4	2.5	60	140	4	37	Low pH.
				NH_4Cl														
G	1.0	140	19	.25	15	2	2.0	140	19	.25	15	2	5.7	22	70	2	19	High SO₄.

[1] See footnote 3, p. 333.

(b) COPPER PLATING

Rolled copper anodes were used.   The conditions employed in the copper baths were as follows:

Cyanide copper solution "L"	Approx. N	g/l	oz/gal
Copper cyanide, CuCN	0.25	22.5	3
Total sodium cyanide, NaCN	.65	34	4.5
Free sodium cyanide, NaCN	.15	7.5	1
Sodium carbonate. Na₂CO₃	.30	15	2
Temperature=50 C (122 F).			
Current density=1.5 amp/dm² (14 amp/ft²).			

[4] W. Blum and N. Bekkedahl, Trans. Am. Electrochem., Soc. 56,291(1929).

Acid copper solution "M"	N	g/l	oz/gal
Copper sulphate, $CuSO_4 5H_2O$ -------------------------------	2	250	33
Sulphuric acid, H_2SO_4 -------------------------------	1.5	75	10
Temperature=35 C (95 F).			
Current density=2.5 amp/dm² (23 amp/ft²).			

(c) CHROMIUM PLATING

An alloy of lead with 6 percent of antimony was used for the anodes. The different baths and conditions of operation are summarized in table 2.

TABLE 2.—*Conditions in chromium plating*

Method [1]	Composition of solution								Temperature		Current density		Variation
	CrO_3			H_2SO_4			Ratio $\dfrac{g\ CrO_3}{g\ SO_4}$		C	F	amp/ dm²	amp/ ft²	
	M	g/l	oz/gal	N	g/l	oz/gal							
I	2.5	250	33	0.05	2.5	0.33	100		45	113	16	150	Standard.
I₁	2.5	250	33	.05	2.5	.33	100		35	95	8	75	Temp. c.d.
I₂	2.5	250	33	.05	2.5	.33	100		55	131	27	250	Do.
I₃	2.5	250	33	.05	2.5	.33	100		65	149	38	350	Do.
I₄	2.5	250	33	.05	2.5	.33	100		45	113	8	75	C.d.
J	2.5	250	33	.025	1.25	.17	200		45	113	16	150	SO₄.
K	4.0	400	53	.08	4	.53	100		45	113	16	150	CrO₃.
K₁	4.0	400	53	.08	4	.53	100		55	131	27	250	Temp. c.d.
K₂	4.0	400	53	.08	4	.53	100		65	149	50	470	Do.

[1] See footnote 3, p. 333.

(d) ZINC PLATING (as an intermediate layer)

Cast zinc anodes were used in the following solution:

Cyanide zinc bath "N"	N	g/l	oz/gal
Zinc cyanide, $Zn(CN)_2$ -------------------------	1.0	60	8
Sodium cyanide, NaCN -------------------------	0.5	23	3
Sodium hydroxide, NaOH -------------------------	1.3	53	7
Temperature=22 C (70 F).			
Current density=2 amp/dm² (19 amp/ft²).			

(e) CADIUM PLATING (as an intermediate layer)

Cast cadmium anodes were used in the following solutions:

Cadmium bath (with gulac) "S"	N	g/l	oz/gal
Cadmium oxide, CdO -------------------------	0.7	45	6
Sodium cyanide, NaCN -------------------------	2.5	120	16
Gulac [1] -------------------------	----------	12	1.6
Temperature=22 C (70 F).			
Current density=2 amp/dm² (19 amp/ft²).			

[1] A by-product of the sulphite pulp industry.

Cadmium bath (with gulac and nickel) "T". The solution was the same as "S", with the addition of 1 g/l (0.13 oz/gal) of nickel sulphate, $NiSO_4.7H_2O$. The same temperature and current density were used.

4. BUFFING

Most of the nickel deposits were buffed, including those to be chromium plated. Allowance was made for the average loss in buffing similar specimens (usually from 10 to 20 percent), so that the final thicknesses were approximately those listed in tables 3 and 4. The chromium deposits were not buffed.

5. SCHEDULE OF DEPOSITS

The composition, thickness, and conditions used in depositing each coating are summarized in tables 3 and 4.

III. EXPOSURE TESTS

1. CONDITIONS OF EXPOSURE

(a) LOCATIONS

Five specimens of each set were exposed in the spring of 1932 in the following locations. In all except Washington and New York they were in enclosures used by the American Society for Testing Materials for other tests. In all places they were protected against unauthorized access.

At Key West (K.W.) Florida, at the United States naval station, they were frequently subjected to spray from the ocean. This represents a tropical marine exposure.

TABLE 3.—*Preparation of specimens with nickel finish*

[All thicknesses in inches, *=buffed]

Set no.	Cleaning[1]	Preliminary plating			Nickel plating		Variation
		Metal	Method[2]	Thickness	Method[3]	Thickness	
1	A				E	*0.001	Standard.
2	B				E	*.001	Cathode pickle.
3	C				E	*.001	Anode pickle.
4	A				E-1	*.001	High temp., high pH.
5	A				E	*.0005	Half thickness.
6	A				E	*.002	Double thickness.
7	A				F	*.001	Low pH.
9	A	Cu	L	0.0005	E	*.0005	Cu(CN), Ni.
10	A	Cu	L	*.0005	E	*.0005	Cu*(CN), Ni.
11	A	Cu / Cu	L / M	.0001 / .0004	E	*.0005	Cu(CN), Cu(acid), Ni.
12	A	Cu / Cu	L / M	.0001 / *.0004	E	*.0005	Cu (CN), Cu* (acid), Ni.
13	A	Cu	M	.0003	E	.0002 / *.0005	Ni, Cu(acid), Ni.
14	A	Cu	L	.0003	E	.0002 / *.0005	Ni, Cu(CN), Ni.
15	A	Cu	M	.00015	E	.0001 / *.00025	Set 13, half thickness.
16	A	Cu	M	.0006	E	.0004 / *.001	Set 13, double thickness.
17	A	Cu	M	.0003	F-1	.0002 / *.0005	Set 13, with Ni at low pH.
18	A	Cu	M	.0003	E	.0002 / *.0005	Set 13, heated 30 min to 200 C
19	A	Cu	M	.0003	F-1	.0002 / *.0005	Low pH and heated 30 min to 200 C.
21	A	Zn	N	.0005	G	*.0005	Zn, Ni.
23	A	Cd	T	.0005	G	*.0005	Cd, Ni.
24	A	Zn / Cu	N / L	.0002 / .0003	E	*.0005	Zn, Cu, Ni.
25	A	Cd / Cu	T / L	.0002 / .0003	E	*.0005	Cd, Cu, Ni.
51	A				E	.001	Standard, not.*
52	A				E	*.00025	Standard, ¼ thick.
53	A	Cu	M	.00008	E	.00005 / .00013	Set 13, ¼ thick.

[1] See p. 333.   [2] See p. 334.   [3] See table 1, p. 334.

TABLE 4.—*Preparation of specimens with chromium finish*

[All thicknesses in inches. *=buffed; **=heated after chromium plating]

1. ORIGINAL SETS

Set number	Clean-ing	Preliminary plating as in set no.[1]	Chromium plating		Variation
			Method[2]	Thick-ness	
101	A	1	I	0.00002	Ni-standard.
102	B	2	I	.00002	Ni-cathode pickle.
103	C	3	I	.00002	Ni-anode pickle.
104	A	4	I	.00002	Ni-high temp., high pH.
105	A	5	I	.00002	Ni, 0.0005.
106	A	6	I	.00002	Ni, 0.002.
107	A	7	I	.00002	Ni, low pH.
109	A	9	I	.00002	Cu (CN), Ni.
110	A	10	I	.00002	Cu* (CN), Ni.
111	A	11	I	.00002	Cu (CN), Cu (acid), Ni.
112	A	12	I	.00002	Cu (CN), Cu * (acid), Ni.
113	A	13	I	.00002	Ni, Cu (acid), Ni.
114	A	14	I	.00002	Ni, Cu (CN), Ni.
115	A	15	I	.00002	Ni, Cu (acid), Ni (0.0005).
116	A	16	I	.00002	Ni, Cu, Ni (0.002).
117	A	17	I	.00002	Ni, Cu, Ni, low pH.
118**	A	18	I	.00002	Ni, Cu, Ni, heated.
119**	A	19	I	.00002	Ni, Cu, Ni, low pH, heated.
121	A	21	I	.00002	Zn, Ni.
123	A	23	I	.00002	Cd, Ni.
124	A	24	I	.00002	Zn, Cu, Ni.
125	A	25	I	.00002	Cd, Cu, Ni.
126	A	13	I	.00001	Thickness of Cr.
127	A	13	I	.00003	Do.
128	A	13	I	.00005	Do.
129	A	13	I-1	.00002	Cr at 35 C.
130	A	13	I-2	.00002	Cr at 55 C.
131	A	13	I-3	.00002	Cr at 65 C.
132	A	13	J	.00002	CrO_3/SO_4 ratio=200.
133	A	13	K	.00002	400 g/l CrO_3.
134	A	none	I	.0002	Direct Cr thick.
135	A	none	I-2	.0002	Cr ar 55 C.
136	A	none	I-3	.0002	Cr at 65 C.
137	A	Cd *, S, 0.0005	I-1	*.00002	Cd, Cr.
138	A	Zn*, N, 0.0005	I-1	*.00002	Zn, Cr.
152	A	52	I	.00002	Ni (0.00025).
153	A	53	I	.00002	Ni, Cu, Ni (0.00025).
154	A	13	I	.0001	Thickness of Cr.
155	A	13	K-1	.00002	400 g/l CrO_3, 55 C.
156	A	13	K-2	.00002	400 g/l CrO_3, 65 C.

2. SUPPLEMENTAL SETS

Set number	Clean-ing	Preliminary plating as in set no.[1]	Chromium plating		Variation
			Method[2]	Thick-ness	
157	A	5	I	0.00001	Thickness of Cr.
158	A	5	I	.00003	Do.
159	A	5	I	.00005	Do.
160	A	15	I	.00001	Do.
161	A	15	I	.00003	Do.
162	A	15	I	.00005	Do.
163	A	5	J	.00002	Sulphate ratio.
164	A	15	J	.00002	Do.
165	A	5	I-4	.00002	Current density.
166	A	15	I-4	.00002	Do.
167	A	5	I-1	.00002	Temperature.
168	A	15	I-1	.00002	Do.
169	A	1	I	.00001	Thickness of Cr.
170	A	1	I	.00003	Do.

[1] See table 3.
[2] See p. 334.

At New York (N.Y.), on the sixth story roof of the Bell Laboratories, considerable smoke from adjacent buildings and vessels produced an industrial urban atmosphere.

At Pittsburgh (P.), Pa., on Brunot's Island in the Ohio River, there was much smoke and fog, representing a severe industrial exposure.

At Sandy Hook (S.H.), N.J., on the Fort Hancock Reservation they were close to the ocean. In addition to the salt spray, representing a northern marine exposure, there was probably a slight industrial contamination from nearby vessels and locomotives and from cities surrounding New York harbor.

At State College (S.C.), Pa., they were in a field far removed from any buildings. This represents an uncontaminated rural atmosphere.

At Washington (W.), D.C., on the roof of a one-story building at the National Bureau of Standards, they were subject to only small concentrations of smoke from the heating plant and from nearby dwellings. This is a typical suburban atmosphere.

(b) RACKS

The specimens were supported on galvanized steel racks by means of porcelain insulators, which prevented contact with any metals. The racks were attached to supports so that the specimens were inclined 30 degrees from horizontal and faced south. The installation in Washington is illustrated in figure 1.

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. Over 100 inspections were made in the 6 locations in about 2 years.

(a) METHOD OF RATING

The approximate proportion of the surface rusted was expressed by the scale of ratings shown in table 5.

TABLE 5.—*Rating of specimens*

Surface rusted	Rating	Corresponding percentage score	Surface unrusted
Percent			*Percent*
0	5	100	100
0 to 5	4	80	95 to 100
5 to 10	3	60	90 to 95
10 to 20	2	40	80 to 90
20 to 50	1	20	50 to 80
50 to 100	0	0	0 to 50

Rust within 0.25 in. of an edge was disregarded, as on some specimens the coatings near the edge were reduced in thickness by the buffing. Each inspector assigned a numerical rating to each specimen, and the average of the ratings of all the inspectors for each set of specimens constituted the recorded rating for that set, location and inspection date. The mean of this and the rating at the preceding inspection, that is, the average rating for that period, was multiplied by the number of weeks intervening to obtain the "score" for the period. The total score for the entire period was compared with a perfect score for the same period to obtain the "percentage score." If, for example, the ratings for a set at intervals of 4 weeks were 4
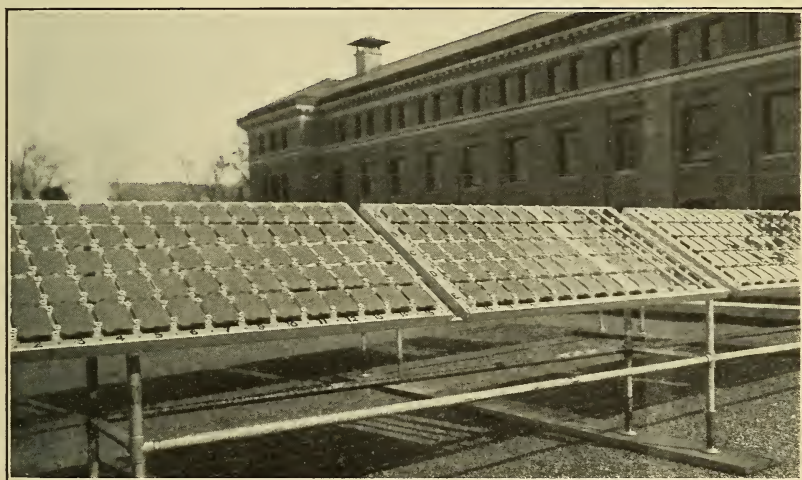
FIGURE 1.—*View of exposure tests at Washington, D.C.*

NOTE.—The dark areas on some specimens are the result of reflections and not of corrosion.

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 $24 \times 5 = 120$, and the percentage score was $\frac{90}{120} = 75$ percent.

The net result was to express the quality on a percentage basis, which, however, as shown in table 5, is not proportional to the percentage of unrusted surface. In other words, the quality score is not linear with respect to the proportion of rust, but is roughly logarithmic. This is an expression of the fact that a very small proportion of rust may indicate both in protection and appearance a relatively unsatisfactory coating. While this system appears to represent fairly the relative protective values of the coatings, it is important to note that a set with an average score of only 60 percent may have less than 10 percent of rusted area.

A detailed study of the data showed that when three or more experienced persons conducted successive inspections, the probable error of the average result for a set was about ± 0.2 unit on a scale of 5, corresponding to 4 percent. However, as the number and identity of the inspectors varied at different times and locations, it is doubtful whether differences of less than about 10 percent in the final scores are significant. No doubt the ratings would have been more consistent and more nearly comparable in different locations if all the inspections had been made by the same group, for example of three persons. This was not practicable.

(b) APPEARANCE

In addition to ratings based on rust, notations were made regarding the presence of other defects in the appearance, such as white or dark stains, blisters, cracks, and peeling. No attempt was made to assign numerical values to these defects, and it is difficult to decide upon the weight to be given them in the final evaluation of the data, which are discussed on p. 352.

3. SIGNIFICANCE OF EXPOSURE TESTS

(a) RELATION TO SERVICE

The most important question in the practical application of results of exposure tests is whether they represent fairly the conditions to which articles in service are actually subjected. This question cannot be answered exactly because the conditions under which plated articles are used are far more varied than are actual climatic conditions. Plated metals are subjected to three general classes of atmospheric exposure, (a) indoors, where the temperature and humidity do not vary greatly; (b) continuous outdoor exposure without cleaning, such as on pole-line hardware; and (c) intermittent outdoor exposure, which is usually accompanied by occasional cleaning operations, illustrated by the bright plating on automobiles. Of course, there are many other types of exposure that may cause corrosion, for example, exposure to soil, to washing materials, to specific chemicals, and to high temperatures. It is unsafe to apply to such corrosion the data obtained in simple atmospheric tests.

Without attempting to set an exact relation, it is probably fair to assume that any plated coatings that will furnish protection for a year or more outdoors in a noncorrosive atmosphere, such as at State College and Washington, will last almost indefinitely under normal household or office conditions. For class (b), for which zinc and cadmium are most commonly used, exposure tests that involve no cleaning during exposure represent actual conditions of service. For class (c), however, which is probably the most important use of plating, it is difficult to correlate the exposure tests with actual service. Most automobiles are washed frequently, and at the same time it is customary and desirable to rub the polished plated parts with grease or wax such as is applied to the body finish. These treatments undoubtedly prolong the protective value of the plating, (1) by removing the surface films which are likely to retain moisture and other corrosive constituents of the atmosphere, (2) by filling pores with grease, and (3) by reducing the tendency of the surface to be wet by water.

Any attempt to introduce these treatments into exposure tests would lead to complications that might obscure entirely the protective value of the metal coatings themselves. Serious consideration was given to the possibility of washing all the specimens at regular intervals. The objections which prevented the adoption of this course are as follows: (1) The physical task of bringing an ample supply of clean water would be very great, as many of the racks were in isolated spots, far removed from a supply of fresh water. (2) The time and labor required to clean over 500 specimens in each locality would be great. (3) It would be difficult to have the cleaning done uniformly at different times or in different locations, and to avoid variations in the technic of cleaning, such as the stiffness of the brush, the pressure applied, and the thoroughness of rinsing. (4) The cleaning would probably remove some of the rust, so that it would be necessary to rate the specimens either before cleaning on that day, or a definite short period such as one or two weeks after cleaning. This would increase the time and expense required for the inspections.

As the specimens were not cleaned during the first 18 months' exposure, the results represent only the relative and not the actual life of each coating when in service. In New York and Pittsburgh, removal of the dark films after 18 months had very little effect on the appearance of the specimens after a few weeks' subsequent exposure, because these specimens had already failed badly. In marine locations, where the rust was distinct, it was usually so thin during the early stages of failure that light rubbing would have almost completely restored the original appearance. It is probable that 1 year's exposure in any of the severe locations was equivalent to at least a few years of normal usage in the same climate.

It is difficult to define "failure" in terms of the rating scale here used, or of any other arbitrary scale. As a rating of 4 may represent very few rust spots, one of 3, that is, from 5 to 10 percent of rust, really represents the first significant failure. If a coating does not go below 3 in the first year in a severe location, it has a good protective value. Practically, this is equivalent to a score of about 70 percent, which may then be used as an index of failure. As stated above, this is equivalent to an unrusted area of at least 90 percent.

Since the main purpose was to determine the relative protective values of the various coatings, and especially to learn the effect of each

of the factors upon the protective value, it is believed that differences of 10 percent or more in the scores are probably significant, while differences as low as 5 percent are significant only if they are consistent in different locations.

Another factor that must be considered in the application of these results is the distribution of the coatings on the plated surfaces. This was more uniform on these flat plates than it can be made on irregularly shaped articles. In plating the latter, the better throwing power of a particular solution may be significant, even though a given thickness of the deposit has no better protective value.

(b) RELATION TO PLATING OF OTHER BASE METALS

In any effort to estimate the protective value of plating from this investigation, it should be noted that the results apply only to the use of steel as the base metal. It is hoped to extend this study to include other base metals such as copper, brass, zinc, and aluminum. With the aid of the information thereby obtained, it should be possible to decide what base metal and what kind and thickness of plating would prove most suitable and most economical for any given application.

IV. RESULTS AND DISCUSSION

In the following discussion, reference will be made chiefly to the extent of rust, and the appearance will be referred to only when it seems to modify seriously the conclusions based on rust. Before discussing the results obtained with different coatings, the reproducibility of the data warrants consideration.

1. REPRODUCIBILITY

In at least 80 percent of all inspections, the ratings for the 5 specimens of a set were identical, and less than 2 percent of the specimens were distinctly erratic. Such uniform coatings can be produced only under conditions where each variable is under close control.

The ability to reproduce the coatings in an independent operation was determined in supplemental exposures in the 4 severe locations of 10 sets, each consisting of 2 of the original specimens that had been carefully preserved and 3 new specimens plated about a year later. The average difference in the two parts of each set was only 4.4 percent, which is just about the reproducibility of the observations. In only 2 sets was this difference greater than 5 percent, the old specimens of no. 113 being 14 percent inferior and of no. 126 being 10 percent inferior to the new specimens. Except for these discrepancies, which are not great, it is evident that specimens can be duplicated by following the same procedures.

2. SEASONS

The conclusions may be affected by the reproducibility of the weather at any location. This may be judged from the 10 sets used in the original and the supplemental exposures in 4 locations, by comparing the results obtained in 1932 with those for a similar period in 1933. In New York and Sandy Hook the results for the 2 years were about the same. In Key West the average score was about 30 percent less in 1932 than in 1933. This corresponds to a much heavier

rainfall in Key West in 1932 in 7 out of the 8 months considered in this comparison.   The 20 percent more severe corrosion in Pittsburgh in 1932 than in 1933 probably corresponds to a difference in industrial activity there, for which no exact figures are available.
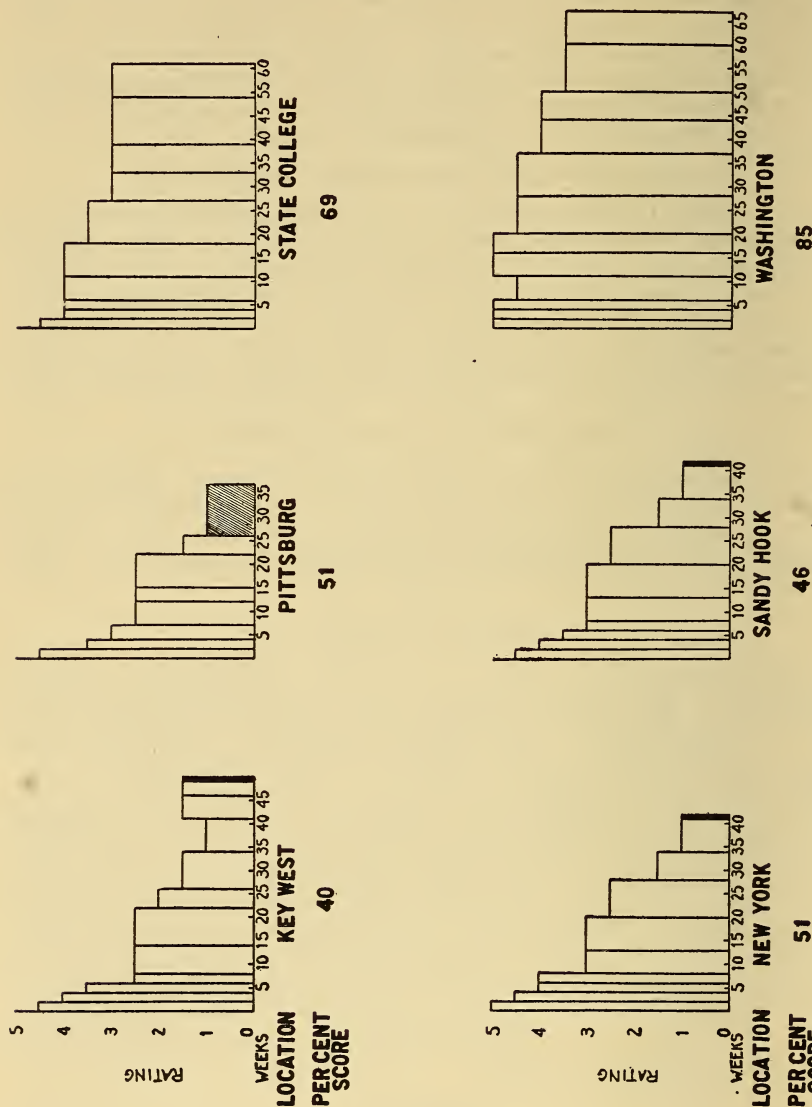
FIGURE 2.—*Ratings and scores of set 5 (0.0005 in. or 0.013 mm of nickel).*

3. LOCATION

The results for different locations are summarized in table 6 and illustrated in figure 2.   In this figure the behavior of set 5 (0.0005 in. of nickel) in the 6 locations is shown in a way that also illustrates the method of computing the scores.   Each narrow rectangle represents the product of an average rating and a number of weeks.   The total area under the horizontal lines represents the total score, and its ratio

to a rectangle with a height of 5, is the percentage score. The fact that ratings at one inspection were occasionally superior to those at a preceding inspection is illustrated in the diagrams for Key West and Washington. Such discrepancies may arise from personal errors in rating, or from an actual improvement in appearance caused by removal of rust by heavy rains.

TABLE 6.—*Effect of location on protective value of coatings*

[18 months exposure]

Nickel and chromium finishes. Total thickness—0.001 in. (0.025 mm)

Number of sets	Coating	Percent scores					
		K.W.	N.Y.	P.	S.H.	S.C.	W.
5	Ni	71	65	36	63	86	86
9	Cu and Ni	29	76	23	53	88	93
5	Ni, Cr	58	72	23	51	98	94
9	Cu and Ni, Cr	40	68	20	46	97	95
	Average	50	70	26	54	92	91

In the 2 marine locations the averages are very close and in each place the rust was distinct and easily rated. The detrimental effect of copper in the absence of chromium (to be discussed later) was more pronounced at Key West than at Sandy Hook. Another difference, not shown in table 6, is that more small blisters developed at Sandy Hook. This fact, and the more rapid failure of both zinc and cadmium coatings in Sandy Hook than in Key West (to be reported in a later paper), indicate that there is some industrial contamination at Sandy Hook in addition to the marine atmosphere.

At New York and Pittsburgh the behavior was more similar than is indicated by the numerical values, though the failure was much more rapid in Pittsburgh, especially during the first 6 months (from April to October 1932) when there was industrial smoke in Pittsburgh but very little smoke in New York until heating was required in buildings. In these locations both buffed and unbuffed specimens became nearly black, so that it was difficult to determine whether rust was present. Microchemical examination showed that these black films contained very little carbon, but consisted largely of black magnetic oxide of iron, Fe_3O_4. The following tentative explanation for its formation is suggested. In each of these locations there was an appreciable concentration of sulphur dioxide (and possibly of sulphuric acid) in the atmosphere. This penetrated any pores and caused attack of the steel, to form ferrous sulphite, which was identified as a light green layer next to the steel. Further oxidation produced the more soluble ferrous sulphate, which exuded, spread over the surface, and, in the presence of sulphur dioxide was only partly oxidized, to form the black oxide. In addition, the sulphur compounds rapidly etched the nickel surfaces and no doubt increased the number and size of the pores. There was much less etching of the chromium-plated surfaces.

It is apparent, therefore, that these black films were just as much evidence of corrosion of base metal as was the appearance of red rust. However, as it was more difficult to define and evaluate the

extent of the dark films, the ratings in New York and Pittsburgh were less concordant than elsewhere, and the percentage scores are less reliable.

At State College and Washington there was very little rust on any coatings that were 0.001 in. or more in thickness, although the very thin coatings failed rapidly there and elsewhere. The slight extent of rust on thick coatings at State College and Washington, and the
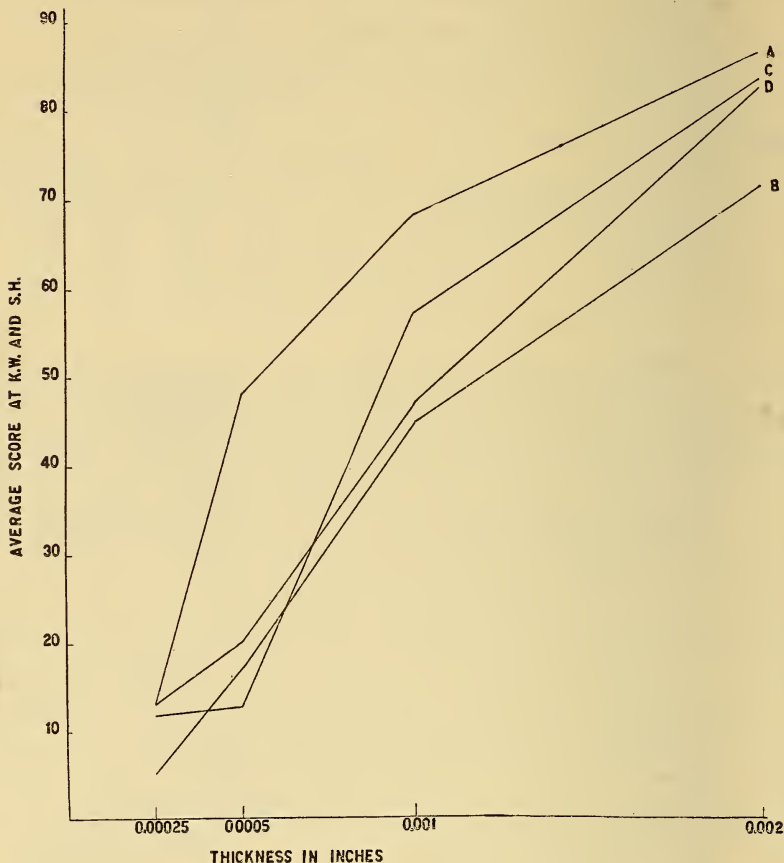
FIGURE 3.—*Effect of thickness on protective value during first 15 months exposure in marine locations.*

A, nickel; B, nickel, copper, nickel; C, nickel+0.00002 in. (0.0005 mm) of chromium; D, nickel, copper, nickel+0.00002 in. (0.0005 mm) of chromium. Plotted values for 0.001 in. are averages of 5 or more sets.

difficulty of rating the specimens at New York and Pittsburgh, make the results at Key West and Sandy Hook more conclusive than the others. Attention will be called, however, to those cases in which the results elsewhere appear to contradict those of marine exposure.

4. PROTECTION AGAINST CORROSION

The following conclusions are based on over 100,000 individual ratings of specimens. The data were assembled and summarized into extensive tables showing the effects of the different variables.

These tables are too long to warrant complete publication, but they were available to the joint committee and to about 25 other interested persons, who agreed to the following conclusions in all essential respects. Sufficient data and figures will be included to show the magnitudes involved. The effects of each important variable will be discussed separately. Unless otherwise specified, the conclusions are based on the original exposures for 18 months, from March 1932 to October 1933. When mention is made of the supplemental tests, the period of 14 months from January 1933 to March 1934 is referred to.

(a) NICKEL COATINGS

(1) *Thickness.*—The total thickness of nickel (or copper and nickel) coatings is the most important factor in their protective value, regardless of whether or not chromium is also applied. As shown in table 7 and figure 3, coatings with a thickness of only 0.00025 in. (0.006 mm) are practically worthless for outdoor exposure in any location, and those with a thickness of 0.0005 in. (0.013 mm) are valuable only in mild locations, S.C. and W. Except in Pittsburgh, fair protection was obtained with 0.001 in. (0.025 mm) and almost perfect protection with 0.002 in. (0.05 mm) of nickel. It is evident that the most practical way of increasing the protective value of nickel deposits is to increase their thickness.

TABLE 7.—*Effect of thickness of nickel and conditions of deposition on protective value of coatings*

Nickel finish.   18 months' exposure.   Percent scores

Set number	Procedure	Thickness	K.W.	N.Y.	P.	S.H.	S.C.	W.	Average (6)	Marine, average K.W., S.H.	Industry, average N.Y., P.	Suburban, average S.C., W.
		In.										
52	Standard	0.00025	10	17	8	10	31	35	19	10	13	33
5	do	.0005	25	30	20	27	70	82	42	26	25	76
1	do	.001	67	67	36	62	87	86	68	65	52	87
2	Cathode, pickling	.001	54	67	36	64	91	87	68	59	52	89
3	Anode, pickling	.001	76	66	36	68	89	87	70	72	51	88
4	High temperature, high pH	.001	79	62	36	61	86	87	69	70	49	87
7	High temperature, low pH	.001	54	61	34	62	77	83	62	58	48	80
51	Standard, not buffed	.001	31	61	37	56	87	91	61	44	49	89
	Average (with 0.001)	.001	60	64	36	62	86	87	66	61	50	87
6	Standard	.002	79	86	52	79	96	94	81	79	69	95

(2) *Conditions of deposition.*—The data in table 7 for sets with 0.001 in. (0.025 mm) of nickel, show that the maximum variation from the average of the 6 sets in 6 locations was only 5 percent. It is evident that none of the conditions used in the preparation of nickel plating had any marked effect on the protective value. That the apparent slight inferiority of the low pH nickel deposits "7", observed especially at Key West, was probably not significant, is shown by the fact that when the same nickel deposits were plated with 0.00002 in. (0.0005 mm) of chromium, the specimens plated at the low pH were correspondingly better than the average. The unbuffed nickel

deposit "51" behaved about the same as the average buffed deposit, except in Key West, where it was decidedly inferior.

(b) EFFECT OF COPPER LAYERS IN NICKEL DEPOSITS

Copper is sometimes applied to the steel as an initial layer, in which case cyanide solutions are used, and sometimes as an intermediate layer between two nickel deposits. In the latter application, either cyanide or acid copper solutions may be employed. In these tests, four sets consisting of nickel, acid copper and nickel, were prepared with different total thicknesses, and nine sets with a total thickness of 0.001 in. (0.025 mm) were prepared with different combinations of copper and nickel. (See table 3.) The results in table 8 and in curves *B* and *D* of figure 3 represent a comparison of these coatings with pure nickel deposits of the same total thickness, that is, they show the effects of substituting copper for part of the nickel. The use of the average of 9 sets is justified because the maximum deviation in these sets with the same thickness was only 10 percent; in other words, about the same protection was obtained with copper deposits of a given thickness from acid and from cyanide solutions.

TABLE 8.—*Effect of a layer of copper on the protective value of coatings*

Percent variation in scores from those of pure nickel deposits of same total thickness

Thickness	K.W.	N.Y.	P.	S.H.	S.C.	W.	Average (6)	Marine, average, K.W., S.H.	Industrial, average N.Y., P.	Suburban, average S.C., W.
In.										
0.00025	−7	+2	−2	−5	−18	−18	−8	−6	0	−18
0.0005	−18	+15	−3	−8	+5	+4	0	−13	+6	+5
0.001 (avg. of 9)	−42	+11	−13	−10	+2	+6	−8	−25	0	+4
0.002	−19	+8	−17	−1	+4	+4	−3	−10	−4	+4
Average	−21	+9	−9	−6	−2	−1	−5	−14	0	1−

It is apparent from table 8 that in very thin coatings the presence of copper is practically always detrimental. This harmful effect of copper persists in thicker deposits in the two marine locations and in Pittsburgh, but not in New York, State College, or Washington. If this effect of copper is caused by electrolytic acceleration of the corrosion of any steel exposed in pores, we would expect it to be more pronounced when an electrolyte is present, such as the salt water in marine locations or the sulphurous acid in a severe industrial atmosphere.

In supplemental exposures, the copper was also detrimental in the two marine locations, but beneficial in both New York and Pittsburgh. The discrepancy in the last place is consistent with the fact that in 1933 the general corrosion was less severe in Pittsburgh than in 1932. The beneficial effect of copper in thick deposits in urban locations is consistent with the results previously obtained at the same site in Washington.[6] It illustrates the danger of drawing general conclusions on corrosion from results in a single location.

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[6] C.T. Thomas and W. Blum, Trans. Am. Electrochem. Soc., **48,**69(1925), and **52,**277(1927).

In all cases, those deposits in which the copper layer was buffed before the application of the final nickel layer were found to be slightly superior to those with unbuffed copper. It is probable that this advantage of buffing the copper would have been more noticeable if the steel had had more defects in the surface than did the steel used in this study.

As indicated in figure 3 the detrimental effect of copper in thick deposits in marine locations is nearly overcome by the application of chromium, or, more strictly speaking, the chromium has a somewhat detrimental effect on the pure nickel deposits but not on those containing copper. No explanation is offered for this curious counteracting of effects. The net result is that copper is not objectionable in thick deposits if chromium is applied.

(c) EFFECTS OF CHROMIUM

(1) *Chromium directly on steel.*—Three sets (134, 135, 136) were plated directly with 0.0002 in. (0.005 mm) of chromium, at temperatures respectively of 45, 55, and 65 C. In all locations they rusted badly within a few months and were generally inferior to specimens with 0.00025 in. (0.006 mm) of nickel or of copper and nickel. This result is consistent with the well-known porosity of chromium deposits. Although those produced at 65 C had a distinctly better protective value than those at 45 or 55 C, they were too poor to warrant consideration for outdoor exposure.

(2). *Effect of 0.00002 in. (0.0005 mm) over nickel.*—As the average commercial thickness of chromium for exposed metal parts is now about 0.00002 in., this thickness was applied (under "standard" conditions) to a large number of plates with deposits of nickel or of copper and nickel. The results show what effects may be expected under average conditions.

The addition of this thickness of chromium to nickel deposits had much the same effect as an intermediate layer of copper, that is it reduced by about 10 percent the protective value of the coatings in marine (K.W. and S.H.) and severe industrial (P.) atmospheres, but correspondingly improved the protection in the other three locations. In all locations, however, the chromium preserved the appearance, especially the luster, of those parts of the surface that were not rusted. It is evident therefore that in severe exposures the protection furnished by composite coatings is determined principally by the thickness and quality of the nickel deposits. This confirms the frequent statement that "the nickel protects the steel from rusting, and the chromium protects the nickel from tarnishing."

The application of this thickness of chromium over composite coatings of copper and nickel improved their protective value, especially at Key West. As shown in figure 3, when chromium is applied as the final finish over thick deposits, there is very little difference in the protection afforded by the pure nickel deposits and by those containing a copper layer. This result apparently justifies the use of a copper layer when it is otherwise expedient [7] to employ it.

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[7] Among the practical reasons for using a copper layer are (a) the greater ease of covering slight defects in the steel, especially if the copper is buffed, (b) the more ready detection of copper than of steel if the final nickel layer is accidentally cut through in the final buffing operation, and (c) the lower cost of copper.

(3) *Variations in thickness.*—It was shown by E. M. Baker and A. M. Rente [8] and confirmed by others [9] that as the thickness of chromium deposits is increased, their porosity decreases to a minimum and then increases. The latter effect is caused principally by the development of fine cracks in the chromium deposits. On this basis it has been predicted that there is a certain optimum thickness of chromium (usually about 0.00002 to 0.00003 in.), and that thinner or thicker deposits furnish less protection. It was therefore important to determine whether these predictions would be confirmed in actual atmospheric tests.

In the first exposures, only one series of specimens was used to determine the effect of the thickness of chromium, which was applied
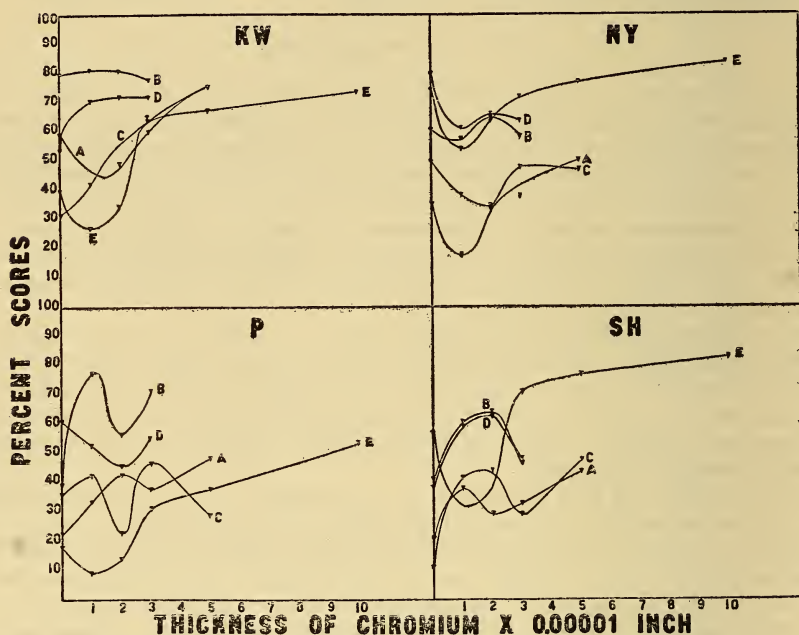
FIGURE 4.—*Effect of thickness of chromium on protective value.*

Chromium applied over

Coating	Thickness	Exposure	Months
	In.		
A—nickel	0.0005	Supplemental	14
B—nickel	.001	____do____	14
C—nickel, copper, nickel	.0005	____do____	14
D—nickel, copper, nickel	.001	____do____	14
E—nickel, copper, nickel	.001	Original	18

over nickel, copper, nickel coatings with a total thickness of 0.001 in. The results, shown in curves E in figure 4 were consistent in all locations. They showed a decided detrimental effect of a very thin chromium coating (0.00001 in.) followed by a marked and continuous increase in protective value as the thickness of the chromium was

[8] E. M. Baker and A. M. Rente, Trans. Am. Electrochem. Soc., **54**, 337 (1928).
[9] W. Blum, W. P. Barrows, and A. Brenner, BS J. Research **7**, 697, (1931); RP 368.

increased. As the latter effect was unexpected, four new series were included in supplemental tests, which yielded the results shown in curves A, B, C, and D, of figure 4.

While there is considerable variety in the shapes and positions of these curves, it is evident that there is no consistent detrimental effect of 0.00001 in. of chromium. Between 0 and 0.00003 in. of chromium there is almost always a minimum protective value. The positions of these minima differ, so that it is practically impossible to select a definite thickness of chromium that gives either minimum or maximum protection. Perhaps the most significant conclusion is that from 0.00001 to 0.00003 in. of chromium is a critical range, in which a slight variation in thickness (or perhaps in the conditions of deposition) may either increase or decrease the protective value.

The practical significance of this conclusion is increased by the fact that on irregularly shaped articles that are plated with an average of, for example, 0.00002 in. of chromium, some portions of the surface may have either 0.00001 or 0.00003 in. of chromium. Even if it were possible to define closely an optimum thickness of chromium, it would be practically impossible to apply it uniformly to many articles. It is therefore fortunate that the total protective value of the coatings is determined much more by the thickness of nickel (or of copper plus nickel) than by that of the chromium. This is shown by the fact that in figure 4, curves B and D (for 0.001 in. undercoat) are above curves A and C (for 0.0005 in. undercoat).

The greater protective value in most locations of the relatively thick chromium coatings (0.00005 and 0.0001 in.) is surprising in view of the previously reported greater porosity of such coatings, which was confirmed by tests with the copper-deposition method on specimens similar to those used in the exposure tests. The value of thick chromium deposits is illustrated by the fact that, after 2 years' exposure, set 154 (consisting of 0.001 in. of Ni, Cu, Ni and 0.0001 in. of chromium) is superior to any other sets with this same thickness of nickel or of copper plus nickel, and is about equal to sets 106 and 116, which have 0.002-in. undercoats and 0.00002 in. of chromium. No entirely satisfactory explanation is known for the greater protective value of these thick chromium coatings, that undoubtedly contain many cracks. It is tentatively suggested that it may be caused by the greater tendency for the initial products of corrosion to seal the narrow cracks in a thick coating than in a thin coating. From a practical standpoint the result suggests the use of relatively thick chromium deposits for very severe conditions, and especially in an industrial atmosphere containing sulphur dioxide, which rapidly attacks nickel but not chromium.

(4) *Conditions of deposition.*—In chromium deposition both the temperature and current density must be controlled to yield bright deposits. In preparing specimens for the original exposures, the temperature of deposition was varied from 35 to 65 C (95 to 149 F) and the current densities (see table 2) were selected to yield bright deposits with about 12 percent cathode efficiency. It was found that the deposits produced at 35 C were consistently about 15 percent superior to those produced at 45, 55, or 65 C. The latter three sets were about equal. This small but definite improvement contradicts the results of porosity tests which showed that the deposits made at

35 C were more porous than those made at higher temperatures. Changes in temperature at a constant current density, or in current density at a constant temperature (within the bright plating range) showed very little effect on the protective values of the coatings.

Changes in the concentration of chromic acid from 250 to 400 g/l (33 to 53 oz/gal) had no definite effect on the value of the coatings. A decrease in sulphate content, that is an increase in the ratio, $\dfrac{g\ CrO_3}{g\ SO_4}$, from 100 to 200 (at 45 C and 16 amp/dm² or 150 amp/ft²), made a consistent improvement of about 20 percent in the scores, both in the original and the supplemental tests. This beneficial effect of a high "sulphate ratio" corresponds with the lower porosity of such deposits, previously reported from this Bureau [10] and also confirmed by tests of these deposits.

Heating the chromium plated specimens to 200 C (392 F) for 30 minutes had no effect on their protective value in the atmosphere, though R. J. Wirshing [11] reported that it improved their resistance to calcium chloride.

(d) EFFECTS OF INTERMEDIATE ZINC OR CADMIUM LAYERS

As both zinc and cadmium coatings furnish electrolytic protection against corrosion of steel but tend to tarnish quickly in the atmosphere, it has often been suggested that such metals should be used as initial layers to be followed by coatings of nickel or chromium. It was early shown,[12] however, that the application of a more noble metal, such as nickel, over zinc reduced the protective value of the latter, as the corrosion of any zinc exposed through pores in the nickel was thereby accelerated.

The results of the exposure tests of these coatings are given in detail in table 9. A comparison of the scores for sets 1 and 21, shows that in all localities the substitution of zinc for part of the nickel reduced the protective value below that of either metal alone. This effect was most marked for the mild exposures (in S.C. and W.).

TABLE 9.—*Effects of zinc and cadmium under nickel and chromium*

1. NICKEL FINISH—18 months exposure—Total thickness=0.001 in.

Set number.	Undercoat [1]	K.W.	N.Y.	P.	S.H.	S.C.	W.	Average (6)	Marine av-erage K.W. S.H.	Industrial av-erage N.Y. P.	Suburban av-erage S.C. W.
1	(Ni 0.001)	67	67	36	62	87	86	68	65	52	87
21	Zn 0.0005	59	48	31	49	60	59	51	54	40	60
23	Cd 0.0005	48	63	36	64	90	88	65	56	50	89
24	{Zn 0.0002 {Cu 0.0003	67	74	40	86	93	92	76	77	57	93
25	{Cd 0.0002 {Cu 0.0003	42	75	46	78	96	91	71	60	61	94

[1] Followed by 0.0005 in. of nickel except in sets 137 and 138.

[10] See footnote 9.
[11] Trans. Am. Electrochem. Soc. 58, 89 (1930).
[12] O. P. Watts and P. L. Derverter, Trans. Am. Electrochem. Soc. 30, 145 (1916).

TABLE 9.—*Effects of zinc and cadmium under nickel and chromium*—Continued

II. CHROMIUM FINISH (0.00002 Cr)—Total thickness 0.001 in.

(1) Over Nickel

Set number	Undercoat	K.W.	N.Y.	P.	S.H.	S.C.	W.	Average (6)	Marine av- erage K.W. S.H.	Industrial av- erage N.Y. P.	Suburban av- erage S.C. W.
101	(Ni 0.001)	54	69	23	47	100	99	65	51	46	100
121	Zn 0.0005	81	47	20	65	85	80	63	73	34	83
123	Cd 0.0005	71	63	22	79	97	93	71	75	43	95
124	{Zn 0.0002 {Cu 0.0003	75	60	24	81	87	97	71	78	42	92
125	{Cd 0.0002 {Cu 0.0003	63	59	29	77	99	95	70	70	44	97

(2) Over Zinc or Cadmium (No Nickel)

Set number	Undercoat	K.W.	N.Y.	P.	S.H.	S.C.	W.	Average (6)	Marine av- erage K.W. S.H.	Industrial av- erage N.Y. P.	Suburban av- erage S.C. W.
137	Cd 0.0005	38	67	64	78	93	87	71	58	66	90
138	Zn 0.0005	38	79	77	88	95	79	76	63	78	87

During the first few months of exposure, white spots appeared over the surface, and a few months later decided rust appeared. It appears therefore that the nickel accelerated not only the corrosion of exposed zinc, but also of iron that was exposed when the zinc was penetrated, even though some zinc was still adjacent to the iron. The specimens with 0.0005 in. each of zinc and nickel rusted much more rapidly than those in the parallel tests with 0.0005 in. of zinc and no nickel.

When chromium was applied (121) over the zinc-nickel coatings, the results were less consistent. At Pittsburgh, State College, and Washington, the effect of the zinc layer was detrimental while at Key West and Sandy Hook it was beneficial. It is difficult to explain why the chromium coating (which had very little if any effect on the porosity of the coatings) should counteract the detrimental effect of zinc in marine locations. The results in table 9 show that the introduction of a cadmium layer under the nickel had very little effect on the protective value. When chromium was also present, the cadmium was beneficial in marine locations.

The difference in the behavior of zinc and cadmium as undercoats is consistent with the fact that the standard potential of cadmium is closer to that of nickel than is the potential of zinc, and hence the corrosion of the cadmium is less accelerated by contact with nickel.

The application of a layer of copper between the zinc and nickel overcame the detrimental effect of the zinc. No explanation is offered for the fact that one noble metal (copper) counteracted the accelerating effect of another noble metal (nickel). The copper had no marked effect on the protective value of composite coatings containing cadmium.

Coatings with a layer of chromium over cadmium, "137", or over zinc, "138", became dull after a few months' exposure. Later, numerous very fine rust spots appeared. While the scores based on the percentage of rust are relatively high, these composite coatings are not desirable where appearance is an important consideration.

5. APPEARANCE

As previously noted, a record was kept of all significant changes in appearance. It was impracticable to devise any numerical system of rating to cover all the defects that might appear, such as light or dark stains, large or small blisters, cracking and peeling. It is difficult to decide how much weight to attach to appearance apart from corrosion, even though it is one of the most important factors in the choice and value of plated coatings. A coating which furnishes very little protection against corrosion of the steel is practically useless whether other defects develop or not. The consideration of appearance may therefore be confined principally to those coatings which furnish at least fair protection against corrosion.

(a) BLISTERS AND PEELING

Two distinct types of blisters were observed: (a) Small blisters from which products of corrosion exuded, and (b) large blisters from which there was no exudation. As these occurred under entirely different conditions, they will be considered separately.

Blisters of the first type (fig. 5) appeared chiefly on the chromium-plated specimens, and were most common in marine locations, especially Sandy Hook. Initially, they were very fine and barely discernible to the naked eye. In time, they increased in size, and rust appeared at the apex of each. Microscopical examination showed that rust was always present. When some of these blisters were dissected under the microscope, rust was plainly evident on the underlying steel.

These facts indicate that these blisters were the result and not the cause of rusting. Apparently a fine pore in the coating permitted the exposed steel to corrode. If the pore were sufficiently fine, the initial products of corrosion might seal the opening. Any corrosion that followed would then develop pressure and tend to lift the coating to form a small blister. Continued corrosion would subsequently cause the products of corrosion to exude from the pore.

This explanation of the formation of these blisters raises several questions, namely, (a) the conditions that cause pores in a plated coating, (b) the effect of adherence of the coatings on their tendency to blister, and (c) the climatic factors that may foster blistering. It is well known that pores in the coating may be caused by defects in the base metal, by the methods of cleaning, by suspended particles in the plating bath, or by the liberation of gas on the cathode, in the latter case with the formation of visible pits. There is good reason to believe that these deposits were less porous than average commercial deposits of the same thickness. The steel was of high quality, with a good finish. It required very little cleaning or pickling to remove scale, but it was pickled to etch the surface. The solutions were made from relatively pure chemicals and were filtered. Hydrogen peroxide was added to the nickel baths so as to practically eliminate visible pits. There is no known way of completely preventing porosity, which is apparently characteristic of all plated coatings of the usual thickness.

The conditions of preparation and plating were adjusted so as to produce "perfect" adherence, that is, it was impossible to detach the coatings by any mechanical test. It is recognized that these tests

FIGURE 5.—*Small blisters observed after long exposure of many chromium-plated specimens, especially in marine locations.*   ×5.

The bright spots are blisters, while the dark spots are rust that usually followed the blistering.

FIGURE 6.—*Large blisters that formed on storage of many of the specimens with a zinc or cadmium layer under the nickel.* Natural size.

are of limited value, and that there may have been undetectable differences in the degree of adhesion of the coatings.

The fact that these blisters occurred most frequently in marine locations indicates that they are characteristic of very rapid corrosion of the steel, which is more likely to fill up minute pores than is slower corrosion. Their more common occurrence at Sandy Hook suggests that they form most readily in a combined marine and industrial atmosphere. Their more frequent occurrence on chromium-plated specimens suggests that the adherence of the nickel coatings may have been decreased by the process of applying the chromium. The fact that they were more pronounced on specimens "102" that had been cathodically pickled (which was the only set that blistered badly in New York and Pittsburgh) suggests that their formation was fostered by hydrogen absorbed in the steel.

Another evidence that these blisters were the result of rust, is that in severe locations they finally merged to form large areas. When the coating was peeled from these a mass of rust was exposed.

Consideration has been given to these small blisters, because they were more pronounced than on most commercial plating that has rusted in service, though they have since been observed on several automobile radiators and bumpers. It is probable that their marked occurrence on these test specimens was caused by the more severe conditions of continuous exposure.

Blisters of the second type (fig. 6) appeared only on specimens that had zinc or cadmium under the nickel, and especially if copper was also present. These large blisters sometimes formed in storage before exposure, and showed no enlargement or corrosion on subsequent long exposure. When these were opened, it was found that part of the zinc or cadmium adhered to both the steel and the nickel, and there was no evidence of corrosion within the blister. It appears probable that these blisters were formed by the escape from the steel of hydrogen that was absorbed during the pickling or plating operations. While no exact data are available, it is probable that hydrogen penetrates less readily through zinc or cadmium than through steel, nickel, or chromium. The pressure developed by the hydrogen trying to escape through the zinc or cadmium was apparently sufficient actually to split the coating of soft metal. (This is an illustration of "perfect" adherence, that is, adherence equal to the strength of the weakest member of the combination.) This type of blistering was neither a cause nor effect of corrosion, though it is of course objectionable. It is a least possible that it might be eliminated by changes in the procedure that would reduce the hydrogen content of the steel.

(b) STAINS

As previously noted, black films were observed in New York and Pittsburgh. Apparently these were simply the result of rust which took the form of black magnetic oxide of iron.

White stains were observed to some extent on all the coatings that contained a layer of either zinc or cadmium. They were probably carbonates or basic sulphates of these metals, produced by their corrosion through pores in the outer layers. In general, more white stains were produced with zinc than with cadmium.

(c) CRACKS

The presence of very fine cracks in chromium deposits has been frequently reported. On exposure, these cracks sometimes became distinctly visible, but only occasionally and after long exposure did rust appear in the cracks. There was no evident relation between the development of these cracks and the conditions of chromium deposition or the protective value of the coatings.

V. SUMMARY OF EXPOSURE TESTS

1. CONCLUSIONS

(1) The protective value of nickel coatings depends almost entirely on their thickness. At least 0.0005 in. (0.013 mm) is required for good protection under mild conditions, and at least 0.001 in. (0.025 mm) for severe conditions.

(2) The conditions of nickel deposition and of the cleaning and pickling have no marked effects on the protective value.

(3) The presence of a layer of copper reduces the protective value of thin nickel deposits under all conditions, and of thick deposits under severe conditions. If chromium is also present, the copper has very little harmful effect in thick deposits. If the copper layer is buffed, the protective value of the composite coating is increased.

(4) A very thin deposit of chromium, such as 0.00001 in. (0.00025 mm), sometimes reduces the protective value, especially of pure nickel deposits. Chromium coatings about 0.00002 to 0.00003 in. (0.0005 to 0.0008 mm) add very little to the protective value, but maintain their bright appearance owing to their resistance to tarnish. Relatively thick chromium coatings, from 0.00005 to 0.0001 in. (0.0013 to 0.0025 mm), improve the protection against corrosion, especially in an industrial atmosphere.

(5) The protective value of chromium over nickel or composite coatings is somewhat improved by using a bath with a high ratio, $\frac{\text{g/l } CrO_3}{\text{g/l } SO_4}$, such as 200. Deposits produced at 35 C (95 F) are slightly superior to those made at somewhat higher temperatures.

(6) The use of zinc under nickel makes the protective value less than that of either metal alone. Cadmium has very little effect under nickel.

(7) The use of zinc or cadmium under nickel tends to produce white stains and blisters.

2. RELATION TO OTHER INVESTIGATIONS

There have been very few comparable exposure tests of metals plated with known thicknesses of copper, nickel, or chromium. The conclusions of E. M. Baker [13] regarding effects of thickness and of multiple coatings were based largely on accelerated tests such as the salt spray. The reported [14] superiority of nickel deposits produced at a low pH was based on specimens that were all plated with chromium and exposed at one location (inland near Miami, Fla.). The results of the present study also show a slight superiority of the plates

[13] J. Soc. Automotive Eng. 15,127(1924).
[14] W. M. Phillips, Trans. Am. Electrochem. Soc. 59,393(1931).

with nickel deposited at a low pH when coated with chromium, but not without the chromium.

Pierre Jacquet [15] made exposure tests of numerous plated steel specimens on the roof of a building in Paris. In general his conclusions are consistent with those of this study. He found that no appreciable protection was furnished by nickel deposits less than 0.008 mm (0.0003 in.), and that the conditions of nickel deposition had little effect. He reported that very thin chromium deposits decreased the protective value and he advised the use of not less than 0.00067 mm (0.000027 in.) of chromium. He found that the presence of cadmium as an intermediate layer led to peeling of the final layers. He advised the use of coatings consisting of Ni, Cu, Ni, Cr, though he did not include any in his tests.

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[15] Bul. Soc. Française Electriciens [5]2,631(1932).