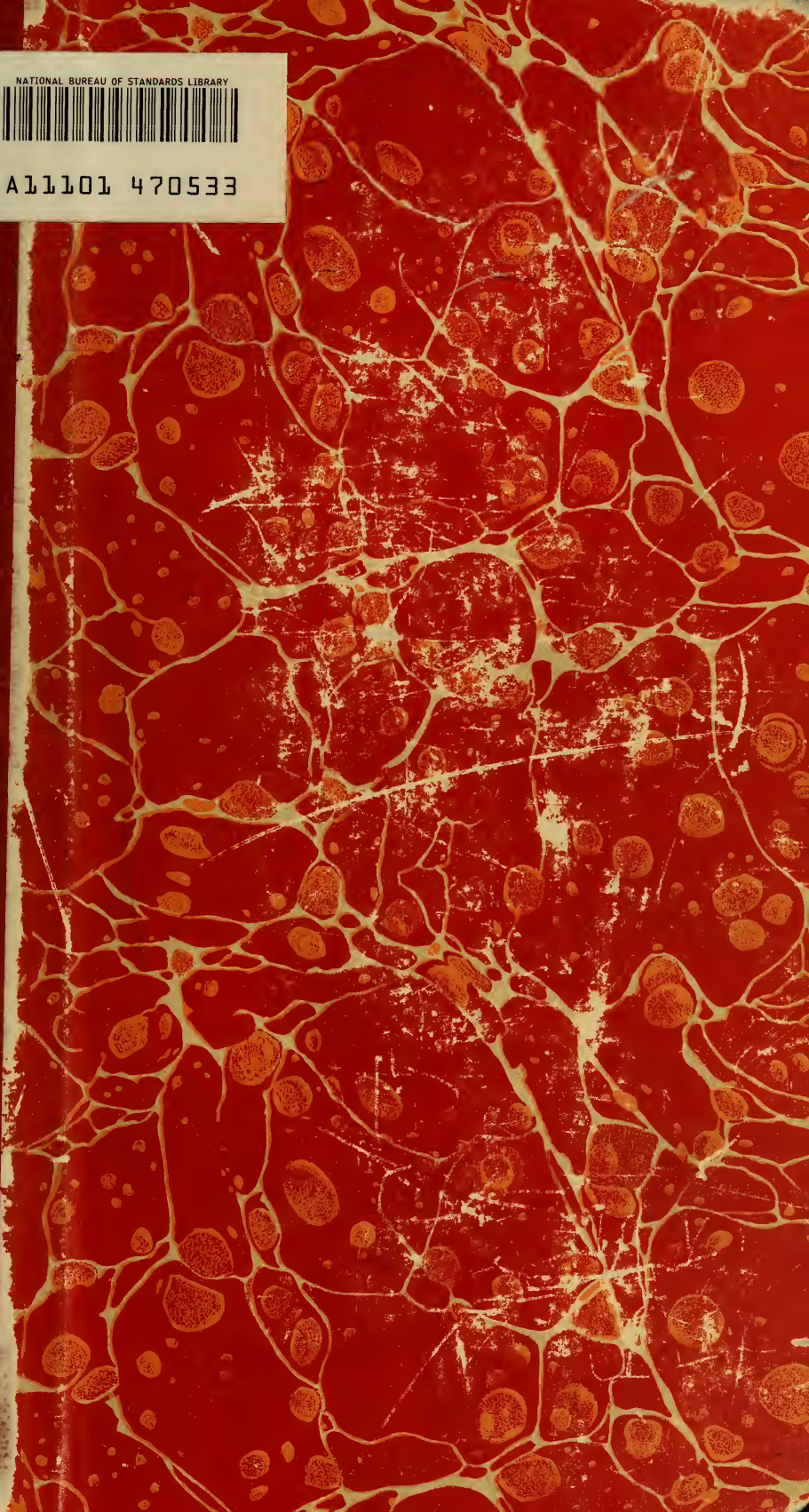


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## ACCELERATED TESTS OF NICKEL AND CHROMIUM PLATING ON STEEL

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### ABSTRACT

Plated specimens similar to those used in atmospheric exposure tests were subjected to accelerated tests, especially by means of a salt spray and by intermittent immersion in a salt solution. The time required for the first appearance of slight rust in these tests was not consistent and had no direct relation to the protective value of the coatings. When the extent of rust at the end of a definite period, for example 100 hours, was recorded, the results were approximately parallel to those of atmospheric exposure. The protective value of a metallic coating of this type depends principally upon its freedom from porosity. The latter can be determined in a few minutes by the ferroxy test.

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### I. INTRODUCTION

In a previous paper<sup>2</sup>, the results of extensive exposure tests of nickel and chromium plating on steel were reported. That information is valuable in the selection and specification of the kind and thickness of plating for any given type of service. With adequate control and supervision, any given requirements for thickness can usually be met by a manufacturer or plater in his own plant. In such cases, however, it is desirable to have rapid methods of test to check the quality of the plating. Such tests are even more useful when parts are sent out to be plated, or plated parts are purchased, as then it

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<sup>2</sup> W. Blum, P. W. C. Strausser, and A. Brenner, *J. Research NBS* **13**, 357 (1934);RP712.



is not usually practicable for the purchaser or user to check the time and current density employed in the plating operations.

The above exposure tests furnished a good opportunity to determine the relation between various accelerated tests and the behavior of the coatings under various atmospheric conditions. The specimens used in this investigation were a part of those plated for the exposure tests. They will be referred to by number, with sufficient description for their identification. For details of their preparation the previous paper should be consulted.

## II. ACCELERATED CORROSION TESTS

The purpose of an accelerated corrosion test is to determine, in a short time, at least the relative value of different coatings under conditions likely to be encountered in service. The latter are, however, so varied that it is practically impossible to introduce all factors into an accelerated test, much less to control their relative effects. In general, therefore, it is preferable and customary to employ a simple test such as (a) exposure to a fine spray of sodium chloride, commonly known as a salt spray test, or (b) immersion in a corrosive solution, for example, intermittent immersion in a sodium chloride solution.

The principal substances that are likely to cause or accelerate corrosion of steel in the atmosphere are oxygen, water, carbon dioxide, sulphur dioxide and trioxide, and sodium chloride. The first three substances are always present, but generally their effects are slow and not directly susceptible of great acceleration. The sulphur compounds are found in urban and industrial atmospheres, and sodium chloride is present in marine exposures.

Various efforts have been made to introduce sulphur dioxide into simulated but accelerated atmospheric tests. The results here and elsewhere have shown that low concentrations of sulphur dioxide (0.1 to 1 percent), especially when continuously present, exert solvent effects on the coatings that are entirely unlike the effects of industrial atmospheres that contain fluctuating and much smaller concentrations of sulphur compounds. Sodium chloride has therefore been most extensively used in accelerated tests. It might be predicted, and has been approximately confirmed, that the results are at least similar to those obtained in a strictly marine exposure. The increased rate of corrosion is obtained partly by the use of high concentrations of sodium chloride and partly by the more severe conditions under which it is applied.

Another factor that can be varied to accelerate the corrosion is the temperature, which, however, should not be so high as to change the nature of the corrosion processes. As a temperature of 35° C (95° F) is often reached naturally, even in temperate climates, it was selected for use in the salt spray and intermittent immersion tests, which were carried out in a room with thermostatic control. Tests made at "room temperature" are subject to uncertainty through the fact that in uncontrolled rooms the extreme temperature at various seasons may range from 10° C (50° F) to 35° C (95° F). The latter temperature was selected because it is about the lowest that can be maintained throughout the year without artificial cooling.

Before applying any accelerated test to plated metals, the surface should be thoroughly cleaned in order to permit uniform access of the reagent to the surface. A simple test for cleanness is that the surface shall be uniformly wet with water, that is, there shall be no "water-break." The cleaning was accomplished in these tests by rubbing with cotton or cloth moistened with a thin paste of pure, fine magnesium oxide. Vapor cleaning with a suitable solvent is effective, but less convenient for laboratory testing.

## 1. METHODS

The salt spray and intermittent immersion were applied to most of the nickel and chromium finishes under the following conditions.

### (a) SALT SPRAY

The salt spray test was conducted with a 20 percent solution of pure sodium chloride in a room kept at 35° C (95° 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 placed at an angle of 45° from horizontal. The solution that was condensed from the spray was drained off and not used again. The specimens with buffed nickel and chromium coatings were painted on the edges with a bituminous paint to prevent formation of rust there, which might run over the surface.

The specimens were inspected at the end of the first 6 hours and of each 24-hour period. At each inspection, they were washed lightly with running water and the number of rust spots on each specimen was noted. In addition, a rating of from 5 to 0, on the same basis as the exposure ratings, was given to each specimen. If, at the end of a definite period such as 100 hours, the corrosion was so pronounced that rust spread over the surface, the latter was cleaned by light rubbing with magnesium oxide paste, rinsed, and returned to the salt spray for 4 hours. This served to bring out the spots clearly without much spreading of the rust.

### (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 air. The temperature was kept at 35° C (95° F) and the relative humidity at 60 ± 5 percent. This constant humidity insured a uniform tendency of the specimens to dry during the air exposures. Under these conditions they were visibly wet for about one-half the period in the air. The specimens were inspected at the same intervals as in the salt spray and the condition of each was similarly recorded.

## 2. RESULTS

The results of the accelerated tests may best be considered by comparing them with those of the atmospheric tests. The latter data in table 1 are based on 18 months' exposure. At Key West and Sandy Hook, the corrosion was more severe than at State College and Washington, and more easily rated than at New York and Pittsburgh.

TABLE 1.—Porosity and accelerated tests on nickel and chromium finishes

## (a) NICKEL

Set number	Total thickness	18 mo. atm ex. score			Ferroxyl Test Number of spots <sup>1</sup>	Salt spray				Intermittent immersion			
		KW SH	NY P	SC W		First rust	Spots at 100 hr <sup>1</sup>	Rating at 100 hr	Corresponding score	First rust	Spots at 100 hr	Rating at 100 hr	Corresponding score
	In.	Percent	Percent	Percent		Hr.			Percent	Hr.			Percent
52	0.00025	10	13	33	100	6	80	2	40	6	40	3	60
5	.0005	26	25	76	12	12	20	3.5	70	30	4	4	80
1	.001	65	52	87	3	20	5	4	80	30	2	4	80
6	.002	79	69	95	3	70	1	4.5	90	80	2	4.5	90

## (b) NICKEL, COPPER, NICKEL

53	.00025	4	13	15	200	6	100	1	20	6	100	1	20
15	.0005	13	3	81	40	6	70	2.5	50	25	35	3.5	70
13	.001	49	47	92	2	20	15	4	80	25	8	4	80
16	.002	69	65	99	0	6	10	4	80	75	2	4.5	90

## (c) NICKEL, CHROMIUM

152	.00025	9	20	51	80	15	100	2.5	50	50	35	3.5	70
105	.0005	10	20	72	20	25	25	3.7	70	65	2	4	80
101	.001	51	46	100	2	50	10	4	80	90	1	4.5	90
106	.002	80	84	96	0	55	1	4.5	90	85	0	4.5	90

## (d) NICKEL, COPPER, NICKEL, CHROMIUM

153	.00025	10	19	42	100	15	100	2	40	40	60	3	60
115	.0005	15	26	88	8	15	60	3	60	35	25	3.5	70
113	.001	36	39	98	2	15	20	4	80	40	25	3.5	70
116	.002	79	57	100	1	6	3	4.5	90	65	15	4.5	90

<sup>1</sup> Per specimen on 1 side, having an area of approximately 1.5 dm<sup>2</sup> or 1/6 ft<sup>2</sup>.

## (a) SALT SPRAY

The results of this test are most commonly reported in terms of the period required for the initial appearance of rust. There is, however, considerable latitude in judging the amount of rust that constitutes failure in this test. Some define it as rust plainly visible at a distance of 3 feet. Others simply disregard what they consider to be very small rust areas. In this study, any rust visible to the unaided eye at a distance of 12 to 18 inches was recorded. The number of rust spots was noted at intervals, and a rating was also given according to the scale used in the atmospheric tests.

The results in table 1 show that, as defined by us, the first appearance of rust has no direct relation to the quality of the coating. For example, in (b) and (d) a slight amount of rust appeared in 6 hours on very thick deposits (nos. 16 and 116), which were known to have good protective value in the atmosphere. The individual results are even more erratic than shown in table 1, which presents the averages of 3 specimens. It was not unusual for slight rust to appear on one specimen in 6 hours and on another of the same set in 50 or 100 hours.

If, however, the number of rust spots is recorded at the end of a definite period such as 100 hours, the results in the salt spray



are very similar to those of the ferroxyl test to be described later. Apparently, the salt spray merely detects pores, but requires 24 to 100 hours, instead of the 5 or 10 minutes required for the ferroxyl test. In general, the ratings at the end of 100 hours correspond inversely to the number of spots at that time. It is therefore suggested that in the salt-spray test greater attention be paid to the number and size of the spots after a definite interval than to the time of their initial appearance.

As the salt spray test is sometimes conducted with a dilute salt solution, and is almost always conducted without control of temperature, a few tests were made to determine the effects of concentration and temperature. The results, not recorded in table 1, may be summarized as follows:

With a *N* solution of sodium chloride (about 5.5 percent NaCl), the rate of failure of nickel and chromium plated steel was much slower than in a 20 percent solution. In general at 22° C (72° F) it required about 72 hours in the dilute solution to produce the same corrosion as appeared in 24 hours in the 20-percent solution.

The effect of temperature was more marked during the first part of the test period than during longer periods. For example at approximately 22° C (72° F) it required about 48 hours to produce the same corrosion as appeared in 24 hours at 35° C (95° F). However, at the end of 100 hours there was not much difference in the amount of rust produced at the 2 temperatures. It is apparent therefore that the customary definition of failure in terms of the time required for the first appearance of rust requires even closer control of temperature than when the extent of rust at the end of a longer period is estimated.

Any ratios based on the above tests are only approximate, and are useful merely for showing the direction and magnitudes involved, and not for making corrections for variations in temperature or concentration. Consistent results can be obtained only at a controlled temperature, for which 35° C (95° F) is the lowest practicable without artificial cooling.

#### (b) INTERMITTENT IMMERSION

The results of the intermittent immersion are very similar to those of exposure to salt spray and are subject to the same limitations. The periods for the first appearance of rust are somewhat longer, but more consistent than in the salt spray. The number of spots developed in 100 hours is usually less than in the salt spray. There does not appear to be any marked advantage in using the intermittent immersion test instead of the salt-spray test for nickel and chromium finishes.

#### (c) RELATION TO ATMOSPHERIC EXPOSURE

When the rating or number of spots after 100 hours is noted, both the salt spray and intermittent immersion tests place the sets of each group in the order of thickness, that is, in the same order of quality as in the atmosphere. They are therefore useful in distinguishing between good and poor coatings, even though the size, color, and distribution of the rust spots are not very similar to those in even a marine atmosphere, much less in an industrial atmosphere.

These two tests do not generally serve to detect small differences in protective value, which in turn are not usually consistent in different types of exposure. However, they both showed (in tests not recorded

in table 1) the superiority of nickel finishes applied over a buffed copper layer to those over unbuffed copper, which difference was also reported in the atmospheric tests. This effect was not observed when chromium was also present.

An example of misleading results in the salt spray and intermittent immersion tests is the fact that composite coatings of cadmium, copper, and nickel (set no. 25) failed very rapidly in both tests, but not in either a marine or an industrial atmosphere. When chromium was applied over the nickel (set no. 125), no marked failure of the composite coating was observed in either the accelerated or atmospheric tests.

### III. POROSITY TESTS

Both the exposure tests and the accelerated tests showed clearly that the protective value on steel of coatings consisting of the more noble metals, such as copper, nickel, or chromium, depends almost entirely on their freedom from porosity, while that of less noble metals such as zinc and cadmium is approximately proportional to the minimum thickness. If it were possible to produce absolutely impervious coatings of the first group, especially of chromium, they would furnish permanent protection in most climates. Apparently the only practical method of approaching this goal is to make the deposits thicker, and even this method is not certain for chromium. Reliable tests for porosity may therefore be very useful for inspection, as they require much less time than the usual accelerated corrosion tests.

#### 1. IN NICKEL COATINGS

##### (a) ON STEEL

*Ferroxyl test.*—This well-known test is applicable for detecting pores in any metallic coating on steel that is more noble than the steel. It depends upon treating the surface with a solution containing an agent, usually sodium chloride, that will attack steel but not the coating, and a substance that will react visibly with iron compounds. A ferricyanide solution is used, as it produces blue spots with any ferrous salt formed by the action of the sodium chloride on exposed steel. The mixed reagent may be applied as an aqueous solution, or one containing a gel (such as agar) that will form a congealed film, or in paper saturated with the reagent.<sup>3</sup> As the latter method yields a permanent record, it was employed in this investigation.

A study of this method showed that the concentration of the sodium chloride is not critical, though stronger solutions accelerate the attack of exposed steel. The concentration of ferricyanide should, however, be kept as low as possible and still yield blue spots. In high concentrations, the ferricyanide attacks nickel appreciably, especially in the presence of sodium chloride, and may therefore produce pores where the nickel is originally thin but not porous.

The most consistent results were obtained under the following conditions. The liquid reagent contained 60 g/l of sodium chloride and 0.5 g/l of potassium ferricyanide. For making the ferroxyl paper, 10 g/l of agar was dissolved in this warm reagent, and a 50 percent white rag bond paper was soaked in it and allowed to dry. The plated surface was cleaned by rubbing with fine magnesium oxide

<sup>3</sup> Pitschner, K., *Proc. Am. Soc. Testing Materials* [II], 27 304(1927).



and water, and rinsed, after which it was immersed in the ferroxyl solution without agar for 5 minutes. The paper was then moistened, pressed on the surface, and removed after 5 minutes. The number of blue spots, excluding those within 0.25 in. of the edge, was recorded.

As shown in table 1, when the ferroxyl test is applied to coatings consisting of copper, nickel, or chromium on steel, the porosity roughly corresponds (though inversely) to the thickness of the coatings and to their percentage scores in the exposure tests. The method serves to detect marked differences in porosity, such as are commonly observed on coatings of different thicknesses, but cannot be used to predict the small differences in behavior of specimens with the same thickness but with different composition. Just as with the above-described accelerated tests, it is difficult to incorporate the ferroxyl test into a specification because the value of the coating depends on the size of the pores as well as their number. The method is therefore chiefly of value for factory inspection of similar coatings and articles.

#### (b) ON COPPER

In most cases it is necessary to detect only those pores which extend through to the steel, which can usually be done with the ferroxyl test. Occasionally, however, it may be desirable to study the porosity of the separate layers, and especially of the outer nickel layer, in composite coatings that include a layer of copper.

Sometimes when the ferroxyl test is applied to composite coatings with an intermediate copper layer, red spots appear. These are caused by copper ferrocyanide, and their detection can be facilitated by adding a small amount, such as 1 g/l, of ferro-cyanide to the ferroxyl reagent.

Another method that yields fair results is to immerse the specimen in hydrogen sulphide water. Black spots appear where any appreciable area of copper is exposed, but fine pores are not readily detected.

#### (c) ON ZINC OR CADMIUM

It was found that by treating the surface for about 30 seconds with a solution that contained sulphuric acid ( $N$ , 49 g/l  $H_2SO_4$ ) and copper sulphate (0.08  $N$ , 10 g/l  $CuSO_4 \cdot 5H_2O$ ), copper deposited wherever zinc or cadmium was exposed. The presence of the copper was more readily detected by subsequently immersing the specimen in water saturated with hydrogen sulphide, which produced black spots. Any large pores or unplated areas were readily revealed, but the detection of fine pores was uncertain.

## 2. IN CHROMIUM

The methods for detecting pores or cracks in chromium coatings were fully described in a previous publication.<sup>4</sup> The copper deposition test, which depends upon the fact that copper is deposited only in pores or cracks in the chromium, was then found to be most reliable. When applied to various deposits used in this investigation, the results were consistent with those previously reported. This is important in view of the fact that some of the results of the exposure

<sup>4</sup>The porosity of electroplated chromium coatings, W. Blum, W. P. Barrows, and A. Brenner, BS J. Research 7, 697(1931);RP368.

tests did not correspond with the predictions made on the basis of the porosity of the chromium coatings.

#### IV. CONCLUSIONS

Both the salt spray and intermittent immersion tests are useful for determining the relative quality, and especially the porosity, of coatings consisting of copper, nickel, and chromium. The results are more significant and more closely related to those of atmospheric exposure if the number and size of the rust spots at the end of a specified period, such as 100 hours, are recorded, rather than the time for the first appearance of rust. These methods do not, however, closely reproduce the types of corrosion produced in the atmosphere, and do not serve to detect small differences in protective value. The ferroxyl test is a rapid, reliable method for determining the relative porosity of the coatings.

WASHINGTON, August 4, 1934.





