U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP975

Part of Journal of Research of the National Bureau of Standards, Volume 18, March 1937

ANODIZING OF ALUMINUM ALLOYS IN CHROMIC ACID SOLUTIONS OF DIFFERENT CONCENTRATIONS

By Robert W. Buzzard

ABSTRACT

Investigation of the 3-percent chromic acid anodizing bath showed that the recommended voltage cycle was essential for formation of the best coatings. It was shown that not only could the corrosion-inhibiting properties of the coatings be improved by an increase in concentration of the electrolyte to 5 to 10 percent of chromic acid, but that the cycle could be eliminated, the time decreased, and the anodizing range of voltage and temperature broadened.

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I. INTRODUCTION

The practical advantage of the so-called "anodic" coatings on aluminum alloys to increase the adhesion of paint [8] [1] has been well established and accepted for a number of years. Coatings of this kind are produced electrolytically by making the specimen the anode in a suitable electrolytic bath. The outstanding coating used for the above purpose for a number of years is that produced in an electrolyte of chromic acid. The only concentration of chromic acid used previous to the present investigation was that recommended by Bengough [3] in 1926. In this method a 3-percent (0.3 *M*) chromic acid solution was used for the electrolyte and a definite empirical voltage cycle was specified, a requirement that made the method an intermittent process. This requirement was a decided limitation in mass production and has been cited by proponents of other methods as the outstanding objection to the use of the chromic acid method. This limitation, coupled with the relatively early "break-down" of the bath, and the very narrow "anodizing" range of voltage and temperature, prompted the study here reported. The purpose of the investigation was to improve the method, both with respect to the stability of the solution and to the technique of the anodizing process.

II. PROCEDURE

Practical tests with the 3-percent chromic acid electrolyte demonstrated the necessity of close adherence to the recommended voltage cycle [2] and temperature (40° C) [3]. Sheet duralumin specimens were

[1] The numbers in brackets refer to the literature references at the end of this paper.

[2] 0 to 40 volts in 15 minutes, 35 minutes at 40 volts, 5 minutes from 40 to 50 volts, and 5 minutes at 50 volts.

anodized in this solution under the recommended conditions. Comparison specimens were anodized in the same bath at a constant potential of 40 volts at 40° C for 1 hour. Visual examination of the resultant coatings showed only slight differences in surface characteristics, for example, the coating produced at a constant voltage was darker in color and had a softer surface, which adhered slightly to the fingers on rubbing. The specimens coated by the recommended voltage cycle showed superior corrosion-resistance in laboratory salt-spray tests,[3] as is shown in figure 1. Both coatings complied with the

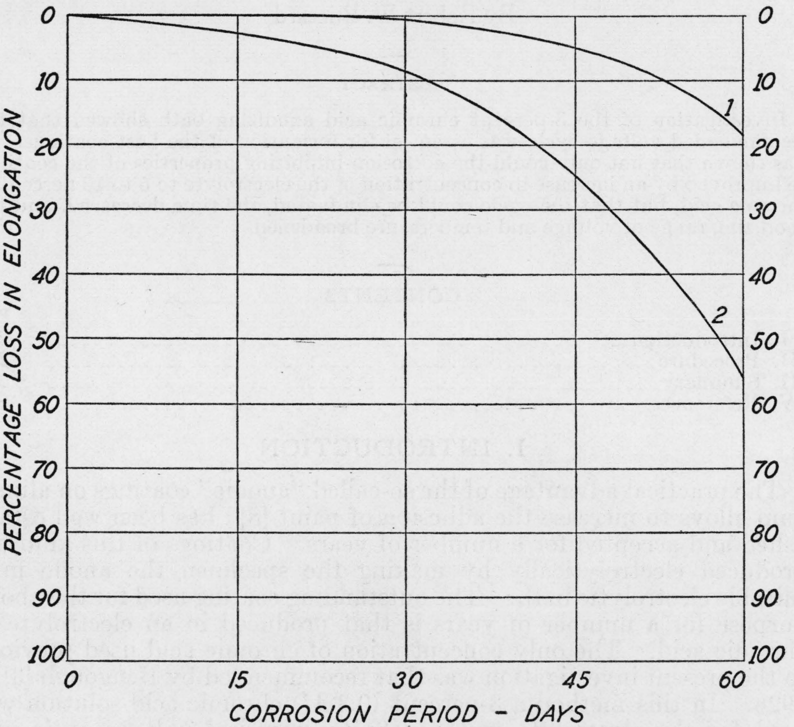

FIGURE 1.—*Relative corrosion-resistance of anodic coatings formed in the 3-percent chromic acid baths, and corroded in the 20-percent* NaCl *spray.*

(1) Film formed with the Bengough cycle.
(2) Film formed 40 volts at 40° C for 1 hour.

Navy Department specification [10] covering acceptance tests for anodized duralumin, that is, a loss of not more than 10 percent in elongation after a 30-day salt-spray test. However, at the end of a 60-day corrosion period, the specimens coated by using the recommended voltage cycle lost less than half as much of their elongation in tensile tests as did the companion specimens, which were coated under constant-voltage conditions. The data on the corrosion-resistance of the coatings represent the percentage decrease in elongation in tensile tests, following exposure, either to a salt spray with a 20-percent sodium chloride solution, at 35° C, or to intermittent immersion in a

[3] The salt-spray tests were run at a constant temperature of 35° C. The 20-percent NaCl solution was made up with Cp NaCl and distilled water. The solution was filtered before use. The concentration of the solution was checked daily by gravity determinations.

solution containing 9 parts of normal NaCl and 1 part of 3-percent H_2O_2 at room temperature.

It was found that the quality of the coating and the conditions under which the process could be carried out satisfactorily varied with the chromic acid concentration of the bath. Specimens anodized in 5-percent (0.5 M) chromic acid at a constant voltage for 1 hour were found to compare favorably in corrosion resistance to the best coatings produced in the 3-percent chromic acid bath. The increase in concentration of chromic acid so changed the bath characteristics that the voltage cycle was not needed. An increase of the chromic acid concentration up to 10 percent (1 M) produced further improvement in

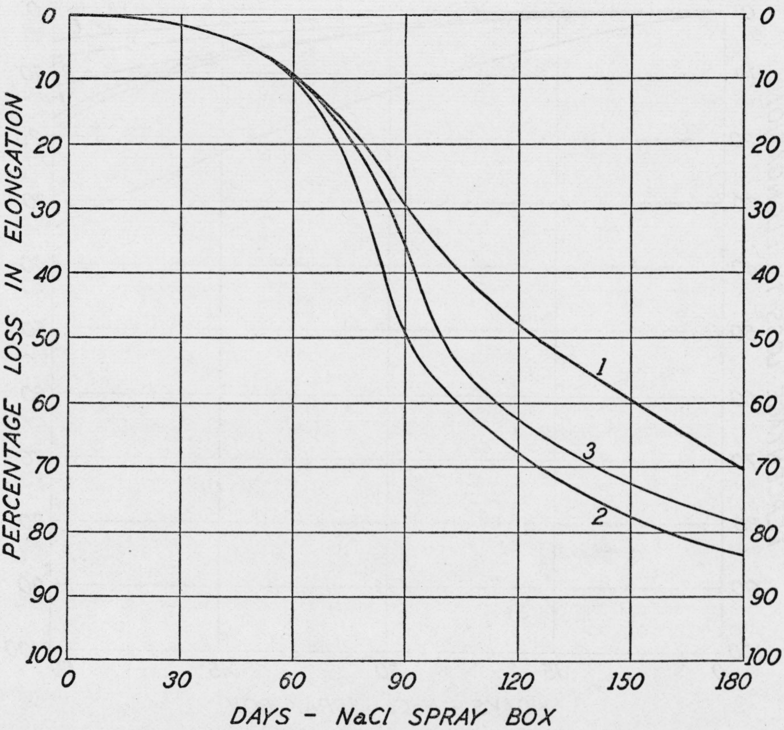

FIGURE 2.—*Comparative corrosion resistance of anodic films formed in varying concentrations of chromic acid and corrodea i ı the 20-percent* NaCl *spray.*

(1) 10-percent chromic acid bath; 40 volts at 35° C for 1 hour.
(2) 5-percent chromic acid bath; 40 volts at 35° C for 1 hour.
(3) 3-percent chromic acid bath with Bengough cycle.

both the quality of the coating and in the operating conditions. The improvement in the quality of the coating is illustrated by the three curves in figure 2.

The elimination of the empirical voltage cycle for the anodizing treatment by the use of higher concentrations of chromic acid permitted the process to be run continuously. This eliminated one of the major limitations previously encountered in anodizing in chromic acid solutions.

In general, the permissible ranges of temperature and voltage for anodizing were greatly broadened by use of the 10-percent chromic acid solution. With the 5-percent chromic acid solution no variation in voltage was permissible, whereas, with the 10-percent solution, satisfactory results were obtained by using any constant potential within the range from 30 to 40 volts. The effect of time, that is, the length of the anodizing period, on the quality of the coatings [4] produced at 30 and at 40 volts, respectively, was studied in the 10-percent chromic acid solution at 35° C. After anodizing, the coated sheet duralumin specimens were subjected to the salt-spray test for 60 days. It is evident from the results in figure 3 that treatment for periods of 30 minutes or longer at either 30 or 40 volts in a 10-percent chromic acid bath at 35° C produced excellent protective coatings. It is also

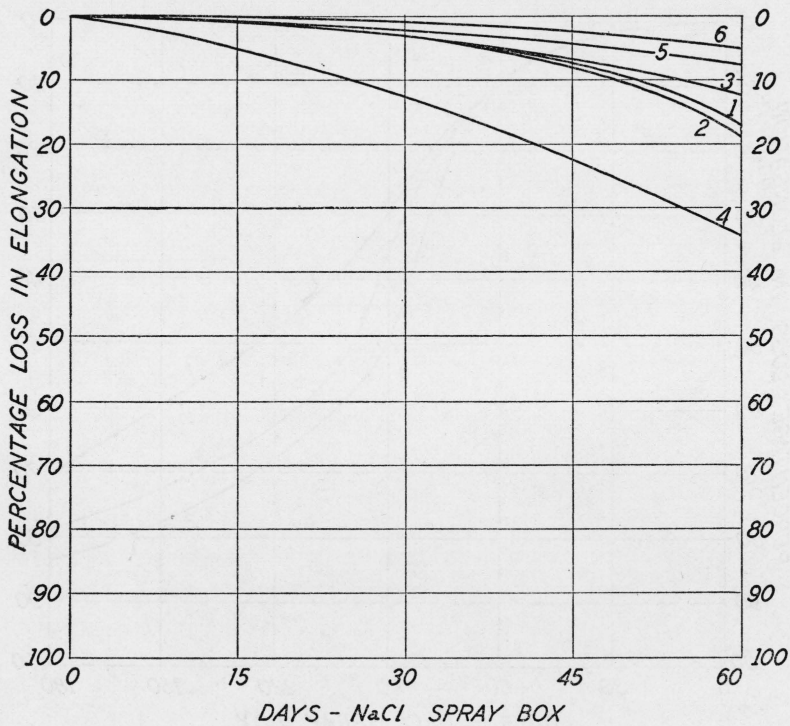

FIGURE 3.—*Effect of anodizing period on quality of film formed in 10-percent chromic acid and corroded in the 20-percent* NaCl *spray.*

Films formed at 40 volts and 35° C for:
(1) 15 minutes.
(2) 30 minutes.
(3) 60 minutes.

Films formed at 30 volts and 35° C for:
(4) 15 minutes.
(5) 45 minutes.
(6) 60 minutes.

apparent that, for the longer anodizing periods, 30 volts gave a better coating than did 40 volts. For producing coatings having maximum corrosion resistance, a 60-minute anodizing period should be used, although treatment for 30 minutes in the 10-percent chromic acid bath produced coatings which satisfactorily met the requirements of the Navy specification [10].

The comparative merits of anodic coatings produced in a 10-percent chromic acid solution, and of similar coatings produced in a 3-percent solution, are portrayed in figure 4. The upper series of curves sum-

[4] Anodized at Naval Aircraft Factory, Philadelphia, in a large commercial installation.

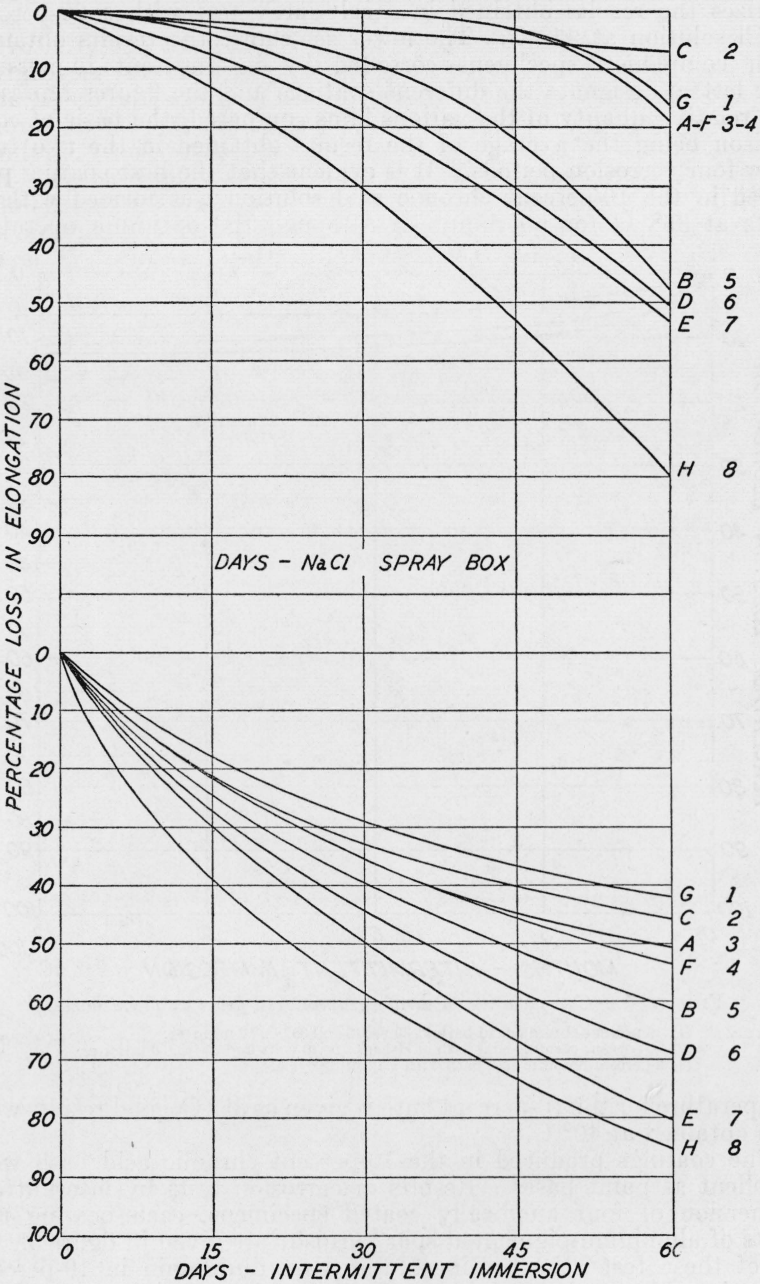

FIGURE 4.—*Comparative values of anodic films formed under varying conditions.*

(a) 3-percent chromic acid bath with Bengough cycle.
(b) 3-percent chromic acid bath at 40 volts and 40° C.
(c) 10-percent chromic acid bath at 35 volts and 40° C.
(d) 10-percent chromic acid bath at 30 volts and 30° C.
(e) 10-percent chromic acid bath at 38 volts and 30° C.
(f) 10-percent chromic acid bath at 40 volts and 35° C.
(g) 10-percent chromic acid bath at 30 volts and 35° C.
(h) 10-percent chromic acid bath at 35 volts and 35° C.

The letters represent the relative quality of the coatings, based on the average of the results of the two corrosion tests for four intervals.

marizes the results obtained in a salt-spray test with a 20-percent NaCl solution at 35° C. The lower set shows the results obtained with companion specimens corroded by intermittent immersion. The letters designate the different coatings and the figures represent the relative quality of the various films compared, the basic of comparison being the average of the results obtained in the two tests after four corrosion periods. It is evident that the best coating produced in the 10-percent chromic acid solution was formed with 30 volts at 35° C for 60 minutes. Although the optimum operating

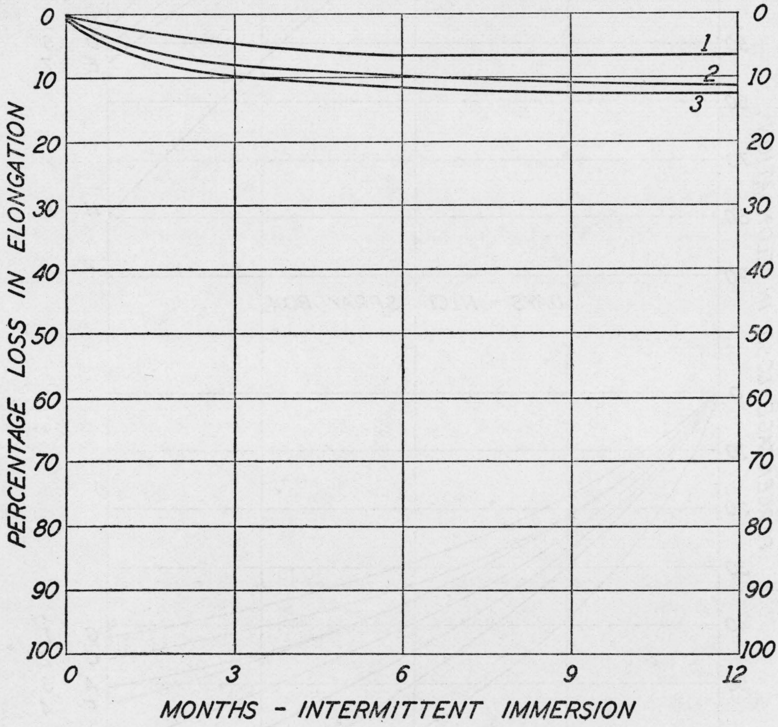

FIGURE 5.—*Comparative value of chromic acid films as paint bases.*

(1) 10-percent chromic acid bath at 30 volts, and 35° C, 60 minutes.
(2) 10-percent chromic acid bath at either 35 or 40 volts and 35° C, 60 minutes.
(3) 3-percent chromic acid bath with Bengough cycle.

temperature for the 10-percent bath is given as 35° C, good results were also obtained at 40° C.

The coatings produced in the 10-percent chromic acid bath were excellent as paint bases. Results of corrosion tests by intermittent immersion of four anodically coated specimens, each bearing two coats of aluminum-pigmented spar varnish, are given in figure 5. In all of these tests, the coatings formed on duralumin in 10-percent chromic acid were better as bases for pa nt than were those prepared in 3-percent chromic acid.

III. SUMMARY

1. The necessity for using the empirical voltage cycle recommended for anodizing baths containing 3 percent of chromic acid has been

verified. However, by increasing the chromic acid concentration from 3 percent to either 5 or 10 percent, this cycle is no longer necessary.

2. The use of a voltage cycle in processes of this kind necessarily limits the method to intermittent operation. Good coatings have been formed at constant voltages by using a more concentrated solution, that is, from 5 to 10 percent of chromic acid. This method may be operated as a continuous process.

3. The range of voltage and temperature over which the anodizing process can be satisfactorily used is widened by increasing the chromic acid concentration and the required time is decreased.

4. The coatings formed in a 10-percent chromic acid solution at a constant voltage are superior in many ways to those formed in the 3-percent solution with the recommended voltage cycle.

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WASHINGTON, December 22, 1936.