

## Determination of the Corrosion Behavior of Painted Iron and the Inhibitive Action of Paints \*

By R. M. BURNS and H. E. HARING

THE value of paints for the protection of metal surfaces depends upon their effectiveness as physical barriers against the corrosive elements of the surrounding environment and upon the electrochemical activity of the primer pigments in rendering the surfaces passive. Physical testing methods have been developed which furnish valuable information concerning the quality and rate of aging of paint films.<sup>1</sup> There is, however, an obvious need for direct methods of determining the condition and behavior of the metal surface beneath the paint film, the rate of penetration of corrosive agents through the film, and the mechanism of the inhibitive action afforded by the film. The present paper describes an electrochemical method of obtaining this information.

It is well established that the process of corrosion in the presence of moisture is electrolytic in character—that it occurs by means of the operation of small galvanic cells at the surface of the metal. It should be possible, therefore, to determine the corrosion behavior of a metal by measuring the electrical characteristics of these individual corrosion cells; but the multiplicity and minute size of the anodic and cathodic areas makes such measurements impracticable. However, it is readily possible to determine the resultant of all of the polarized potentials of the anodic and cathodic areas on the metal surface, and to follow the change in this potential (of the electrode as a whole) with time.<sup>2</sup> Experience in this and other laboratories has demonstrated that time-potential curves obtained in this manner indicate the corrosion behavior of a metal and the state of its surface.<sup>3</sup> In general, it has been found that if the potential of a metal becomes more electropositive (more noble) with time, the formation of a protective film and a retardation or cessation of corrosion is taking place, while conversely, if the potential becomes more negative, solution of a protective film and acceleration of corrosion is indicated.

\* Digest of a paper presented before the Spring Meeting of the Electrochemical Society at Cincinnati, Ohio, April 23–25, 1936, and published subsequently in volume 69 of its *Transactions*.

<sup>1</sup> Schuh, *Ind. Eng. Chem.*, 23, 1346 (1931).

<sup>2</sup> Burns, *Bell System Tech. Jour.*, 15, 20 (1936).

<sup>3</sup> May, *Jour. Inst. Met.*, 40, 141 (1928); Bannister and Evans, *Jour. Chem. Soc.* (June 1930).

The corrosion of iron can be predicted by proper interpretation of such time-potential curves. The fact that the iron is painted should not alter this conclusion, and therefore the method has been applied to a study of painted iron and primer pigments.

The customary procedure for determining time-potential curves was followed with the exception that the potentiometer ordinarily employed was replaced by a vacuum tube electrometer when measurements were made of the potential of painted iron or of iron in other media of high electrical resistance. This instrument, slightly modified to take advantage of certain improvements which have been made in compensated single tube circuits, is described elsewhere.<sup>4</sup>

Common usage has defined iron which is corroding as "active" and iron which is not corroding as "passive." In order to obtain a background of information which might serve as a guide in the study of painted iron and paint pigments, a series of time-potential curves depicting iron and steel in the active and passive states was determined. The results are shown in Fig. 1.

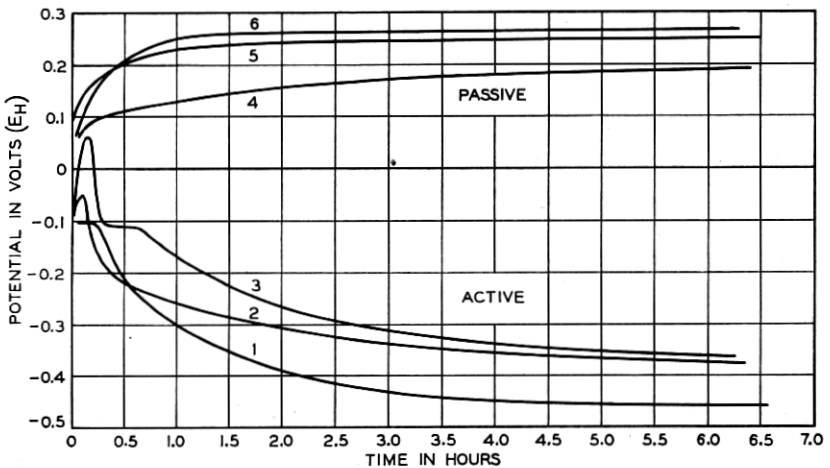


Fig. 1—Time-potential curves for active and passive iron.

Active (Corrosion)

1. Iron in tap-water.
2. Iron in 0.01N NaCl.
3. Uncleaned iron in tap-water.

Passive (No Corrosion)

4. Stainless steel in tap-water.
5. Iron in 0.01N  $K_2Cr_2O_7$ .
6. Uncleaned stainless steel in tap-water.

<sup>4</sup> Compton and Haring, *Trans. Electrochem. Soc.*, **62**, 345 (1932); D. B. Penick, *Rev. Sci. Inst.*, **6**, 115 (1935) and *Bell Laboratories Record*, **14**, 74 (1935).

It will be noted that the potentials of the test electrodes are initially quite similar, but diverge with time and form two distinct groups of curves, which ultimately become separated by about 0.7 volt. It was observed that invariably electrodes did not corrode if their potentials became more electropositive (more noble) over a long period of time, while, on the other hand, marked corrosion accompanied a negative trend of potential. A state of equilibrium was reached ultimately by the passive electrodes between 0.25 and 0.30 volt, and by the active electrodes between  $-0.40$  and  $-0.45$  volt.

Red oxide and red lead paints were selected for study because practical experience indicates that they are representative of the two types of protective paint, viz., (1) those which protect merely because they serve as physical barriers, and (2) those which exert a chemical inhibiting action as well.

The test electrodes were commercial iron, of high purity, in the form of  $1/8$  inch rods. The pigments were technical grades of red oxide ( $\text{Fe}_2\text{O}_3$ ) and red lead ( $\text{Pb}_3\text{O}_4$ ) of high quality. Raw linseed oil and a lead-cobalt dryer were used in the preparation of all of the paints, which were formulated and compounded in the customary manner. Approximately 20 per cent of a flexible type varnish and 10 per cent of blown linseed oil were incorporated with raw linseed oil to form the vehicle in one of the red oxide paints.

As a rule, the primary purpose of a protective paint is to shield iron from the corrosive action of water and water vapor. Total immersion is an extreme condition, but a condition to which all such paints are frequently subjected. For this reason, and also in order to speed up possible reactions and save time, all of the potential measurements on painted iron recorded in this paper were made on submerged specimens. Similar measurements on painted iron exposed to the atmosphere are equally possible and can be made without disturbing service conditions. It is planned to extend this study to include such measurements.

The time-potential curves obtained in the study of primers are presented in Fig. 2. There are included for reference typical curves (6 and 7) for iron in the active and passive states, and a curve (curve 5) for iron coated with a dried film of linseed oil. It will be noted that the linseed oil coated electrode behaved in much the same manner as bare, active iron, except that a much longer time was required for the potential changes to take place. Several days elapsed before the potential reached the equilibrium value attained by bare iron in a few hours, and at this point rust was clearly visible.

The potential of iron painted with red oxide primer (curve 1), immediately after immersion in water, was approximately 0.33 volt.

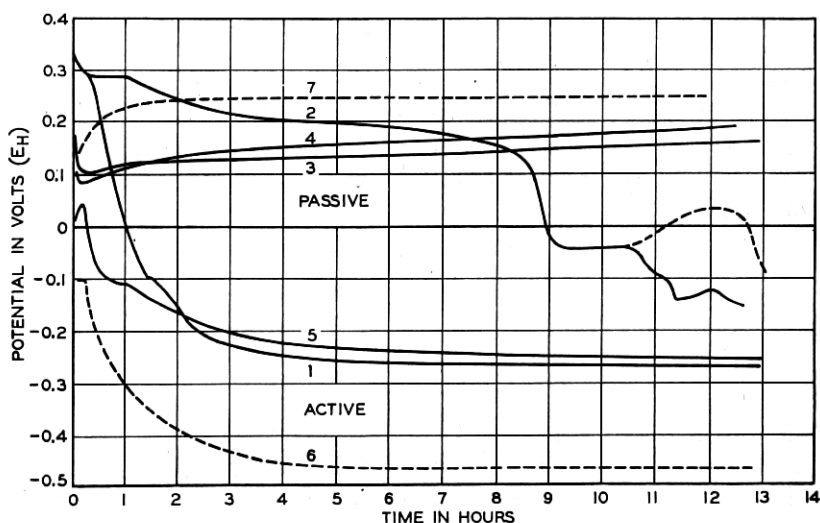


Fig. 2—Time-potential curves for painted iron in water.

Red Oxide Primer

1. Linseed oil vehicle.
2. Linseed oil plus varnish.

Red Lead Primer

3. No visible pores.
4. Visible pores.

Reference Curves

5. Dry linseed oil film.
6. Iron in tap-water.
7. Iron in 0.01N  $K_2Cr_2O_7$ .

In other words, the metal was passive initially and, judging from the behavior of the curve, it tended to remain so for a period of about twenty minutes. By the end of this time, water appears to have permeated the paint film in sufficient quantity to induce the active corrosion indicated by the sharp drop in potential which followed. From this time on, the curve is similar to that for the linseed oil coated electrode. Ultimate equilibrium required a much longer time, however. After several days' immersion, the paint film was removed and the iron was found to be corroded. The very gradual slope of the curves for active painted electrodes, after their sharp breaks from the passive region, may be attributed to the action of the films as partial barriers to moisture.

The impermeability of primers and their adherence to iron are known to be increased by the addition of varnish. Accordingly, red oxide

primer containing a moderate amount of varnish was subjected to test. The results are represented by curve 2 in Fig. 2.

This curve is of especial significance, not only because its characteristics are so much more pronounced than those of curve 1, but also because it furnishes an explanation for the divergence of results which have been obtained with red oxide primers in practice. The marked increase in the length of time required for this curve to pass through its various phases as compared to curve 1, is evidence of the water-excluding effect of the added varnish. The period of definite passivity has been extended to at least three times its former length, and the momentary halt in curve 1 at approximately  $-0.09$  volt has been prolonged to an hour and a half at a slightly more positive potential. Curve 2 continues somewhat erratically in the active direction after the half-way halt in its course. Examination of the iron after several days' immersion revealed corrosion. The broken line represents, in days rather than hours, the quite different behavior of a duplicate specimen, which prior to this time had acted similarly except for the fact that it had required a somewhat longer time to pass through its various phases. Apparently a slightly less permeable paint film made it possible for the corrosive action to be stifled, temporarily at least.

Alternations of corrosive attack and film formation were observed generally when iron corroded in contact with red oxide pigments and primers. In a relatively dry atmosphere there is no doubt that iron painted with red oxide is maintained in a passive condition, but exposure to excess moisture must result eventually in active corrosion. Since, then, the protective value of red oxide primers is dependent primarily upon their ability to exclude moisture, they must be classed as physical inhibitors of corrosion.

The corrosion behavior of iron painted with red lead is clearly indicated in Fig. 2 by curves 3 and 4. The presence of a few small pores or imperfections in the paint film on one of the test electrodes did not materially affect the results. The initial potentials were somewhat lower than was the case for red oxide, and the initial trend of the curves was in the active direction, but a reversal soon took place and the iron became definitely and permanently passive. An equilibrium potential of approximately  $0.25$  volt was attained. Inspection of the iron after several weeks' immersion failed to reveal any sign of corrosion.

Red lead primer continues to inhibit corrosion even after moisture has fully penetrated the film. On the basis of its action, both as pigment and primer, red lead must be classed as a chemical inhibitor of corrosion. The reason for its passivating action is a disputed question. Paint chemists have inclined to the view that a highly protective lead

soap is formed, but this theory becomes untenable in view of evidence that red lead pigment alone passivates iron in much the same manner as red lead primer, and that even water solutions of the pigment have an effect. Other theories are that the iron is rendered passive by the alkalinity of the red lead, or because it is an oxidizing agent. In all probability, both of these factors are involved.

The ease with which it has been found possible to make potential measurements on painted iron with the aid of the vacuum tube electrometer, suggests the application of the time-potential method of study to the determination of the corrosion behavior of iron encased in concrete or buried underground or immersed in oil or other highly resistant media. Field study would be facilitated by substitution of a vacuum tube voltmeter for the electrometer.

The fact that there is a potential difference of at least 0.5 volt between the active and passive states of iron suggests a rapid potentiometric method for the determination of the permeability of all types of organic coatings. The time-potential curve for an iron electrode coated with the organic material and immersed in a salt solution, for example, would break sharply at the moment penetration was attained.