

The Ferroxy Indicator in Corrosion Research, With Special Reference to the Controversy Regarding the Cause of Pitting.

BY ULICK R. EVANS, M.A.

(Specially contributed to THE METAL INDUSTRY.)

1.—Introductory.

During the last two years, a controversy concerning the cause of "pitting" in iron and steel has been conducted, partly in the columns of this journal, between Mackay, the well-known American authority on corrosion, and Liebreich, the eminent German investigator, on the same subject. This dispute, on a subject of the greatest importance to the practical man, turns ultimately on the question of the reliability of the so-called "Ferroxy Indicator." Liebreich has used this indicator in an experiment which—he maintains—disproves McKay's views; McKay replies—in effect—that the indicator has been inappropriately employed.

Now, the present writer has used the ferroxy indicator for several years—both in the laboratory and for lecture demonstrations, and has found that—unless certain conditions are observed—it yields results which are quite misleading. The conditions necessary to obtain accurate information have, however, never been published, and, since the indicator is now being employed to test a question of vital concern to metal-users, it would seem advantageous to place the matter on record.

2.—Early History of the Ferroxy Indicator.

The credit of the "invention" of ferroxy must be allocated partly to Cushman¹, and partly to Walker, Cederholm, and Bent². In the old method of using the indicator, pieces of iron are immersed in a warm solution containing a salt (say sodium chloride), along with some phenol-phthalein and potassium ferricyanide and enough agar-agar to allow the whole to set to a jelly when the liquid cools. The pieces of iron, thus embedded in a transparent jelly, soon develop pink and blue patches in different parts, the blue tint indicating the anodic areas where iron salts are produced, and the red colour showing the cathodic areas, where alkali is developed.

The indicator has been employed to ascertain which parts of an iron article become anodic and which cathodic. Thus it has been found that pieces of wire bent sharply or cut off at a point usually develop blue (anodic) areas to the points of bending or cutting (attributable to the local stresses produced, or to the removal of a protective film). Again, Cobb³ has used the indicator to show that certain phases often present in iron and steel, such as graphite and cementite, as well as iron sulphide or oxide, can function as cathodes to the iron itself.

Such an application is perfectly legitimate if we are quite sure that none of the three ingredients of the indicator (phenol-phthalein), potassium ferricyanide and agar-agar) themselves affect the natural distribution of cathodic and anodic areas. Unfortunately, this is not the case. It is known⁴, for instance, that the production of anodic and cathodic areas is largely dependent on the distribution of oxygen; cathodic areas tend to appear where the

oxygen-concentration is high, and anodic areas where it is low. If now we bury our pieces of iron in a rigid jelly, the distribution of oxygen over the metallic surface will be entirely different from that which would prevail if the metal were immersed in water or a salt solution, where convection-currents would have free play. Therefore the distribution of pink and blue in a specimen embedded in jelly are of little practical interest, except in so far as they serve to demonstrate the electro-chemical mechanism of corrosion.

3.—Ferroxy Indicator without Jelly.

To avoid the objection just indicated, the present writer⁵ decided to omit agar-agar or other gel-forming constituent from the mixture. The reagents employed by him are:

- (1) A 1 per cent. solution of phenol-phthalein in alcohol.
 - (2) A 1 per cent. solution of potassium ferricyanide.
- which should preferably be freshly made, although it can be kept for a week or more in the dark.

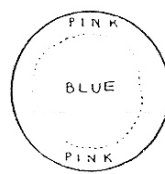


Fig. 1.

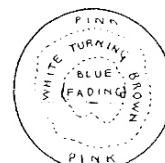


Fig. 2.

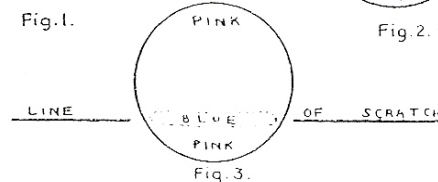


Fig. 3.

A small quantity of each solution should be added, just before the experiment, to the water or solution whose action on iron it is desired to study. The quantities chosen should be the smallest which will allow the pink and blue colours to be observed without difficulty; this should be found by previous rough experiments, as it will depend on the conditions of experiment, and on the nature of the illumination. The smaller the quantity used, the more confident can we be that neither reagent will—of itself—disturb the natural distribution of anodic and cathodic areas; this is discussed further below.

An example, suppose we wish to use the indicator in the study of the effect of a drop of normal sodium chloride solution placed on a steel surface. For this purpose, 0.5 c.c. of 1 per cent. phenol-phthalein and 3 c.c. of 1 per cent. potassium ferricyanide added to 100 c.c. of the sodium chloride solution are found to give quite conspicuous blue and pink areas (indeed, it is possible to observe the colours with as little as 1 c.c. of ferricyanide solution). The steel should be ground clean with emery before the experiment. When placed on the surface, a drop of the salt solution containing these additions develops within 2 to 4 minutes a blue centre surrounded by a pink marginal ring (Fig. 1); this indicates that the marginal portion, to which oxygen has best access, is

⁵ U. R. Evans, J. Oil Colour. Chem. Assoc. 6, (1923), 155.

¹ See, for instance, A. S. Cushman, and H. A. Gardner, Corrosion and Preservation of Iron and Steel (McGraw-Hill).

² W. H. Walker, A. M. Cederholm and L. N. Bent, J. Amer. Chem. Soc., 29 (1907), 1256.

³ J. W. Cobb, J. Iron Steel Inst., 83 (1911), 170.

⁴ J. Aston, Trans. Amer. Electrochem. Soc. 29 (1916), 449.
U. R. Evans, J. Inst. Met., 30 (1923), 239; Ind. Eng. Chem., 17 (1925) 363.

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(cópia parcial em 02/DEZ/2002) em 2003.*

cathodic, whilst the centre is anodic, and iron is there passing into solution. A little later there develops between the blue and pink areas, a nearly colourless ring (Fig. 2) indicating that the ferrous chloride (the anodic product) and sodium hydroxide (the cathodic product) are interacting to give ferrous hydroxide, so that soluble iron salts actually disappear from the intermediate zone. Sometimes the ferrous hydroxide can actually be observed as a white ring of precipitate, which, after a few minutes begins to turn brown through oxidation to ferric hydroxide; at the same time the blue colour in the centre begins to fade, and finally (about half an hour from the start) disappears, apparently through the adsorption of the iron salts on the hydroxide precipitate.

These, and many similar experiments, show that in the case of iron and steel, the distribution of anodic and cathodic areas is determined almost entirely by the oxygen-distribution in the liquid, and only to a small extent on the composition or physical character of the different portions of the metal. It is true that occasionally, although the whole of the outer ring shows a pink colour, there are certain spots on it where a particularly intense pink indicates a local high production of alkali; these may possibly represent places where some second constituent is embedded in the metal, which serves to promote the cathodic reaction—although this has not definitely been proved. Again, if the metal is exposed to dry air for 45 minutes before the experiment, and a scratch is made across the site just before the drop is placed in position, the length of the scratch will at first be blue practically to the edge of the drop, indicating that freshly abraded metal is anodic to metal previously exposed to oxygen (see Fig. 3); but this effect is temporary, and soon the pink area will begin to creep along the scratch at each end, whilst the blue area will become more central, until finally the distribution of pink and blue will approximate to the normal distribution shown in Figs. 1 and 2.

The ferroxy indicator can be used to show the position of anodic and cathodic areas in other cases, for instance, on specimens partly or wholly immersed in a liquid. It will be obvious that—to secure reliable results—the ferroxy should be added before the experiment starts; any attempt to apply ferroxy after corrosion has commenced must almost necessarily cause a stirring up of the products and a displacement of the areas; this will be specially the case if a mixture rich in alcohol is used, for then the differences between the surface tensions of alcohol and water may cause quite a serious commotion. If it is desired to ascertain the distribution of alkali and iron salts in a specimen which has already commenced to corrode, it is best, not to add ferroxy, but to withdraw very small samples by means of a fine tube from different parts and to test them externally; even by this method, however, it is not easy to avoid disturbance.

4.—Effect of Using Excess of the Indicator.

Emphasis has been laid on the fact that the two reagents (phenol-phthalein and potassium ferricyanide) must not be added in excessive amounts. In the case of the alcoholic phenol-phthalein solution, a larger addition may disturb the situation by making the liquid turbid, by causing a change in the surface tension and, no doubt also, by altering the oxygen-solubility.⁶ The addition of excess of potassium ferricyanide is, perhaps, even more detrimental. In the first place, the ferricyanide is itself an oxidising agent, and can sometimes, as pointed out by Wilson,⁷ play the same role as dissolved oxygen; the disturbing effect of this occurrence is obvious. The present

⁶ If, for any purpose, it was desired to have much phenol-phthalein present, it would be advisable to add it as a solution stronger than 1 per cent., so as to reduce the addition of alcohol.

⁷ R. E. Wilson, Ind. Eng. Chem., 15 (1923), 13.

writer, when working with ferroxy *in jelly*, has observed phenomena which confirm Wilson's statement, but in the absence of jelly-forming substances, the oxidising action of ferricyanide does not seem to be a dangerous source of disturbance; no doubt, this is because the diffusion of oxygen itself can occur so much more readily. In the presence of jelly, the abnormalities due to the oxidising action of ferricyanide can often be detected owing to the fact that, when ferricyanide, instead of oxygen, plays the part of "cathodic depolariser," no free alkali is produced, thus the cathodic areas are shown, not by the appearance of a pink colour, but merely by the disappearance of the yellow colour due to the ferricyanide.

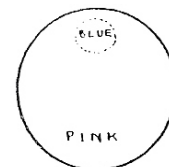


Fig. 4.

Screening Effect of Precipitate.

In the absence of jelly-forming constituent, the disturbance caused by an undue amount of ferricyanide connected with the fact that the blue precipitate formed at the anodic area, will itself tend to exclude oxygen from these areas. Thus the distribution of blue and pink in the specimen comes to represent the distribution of oxygen at the moment when the action started, and may not represent the distribution which would exist later, if no indicators were present. In the permissible proportions of ferricyanide indicated above in Section 3, the anodic areas are indicated by a blue "colouration," rather than by an actual precipitate; but if we increase the amount of ferricyanide solution added to 10 c.c. or 20 c.c. per 100 c.c. of N sodium chloride solution, a genuine precipitate appears over the anodic places, quite capable of screening the area behind from diffusing oxygen.



Fig. 5.

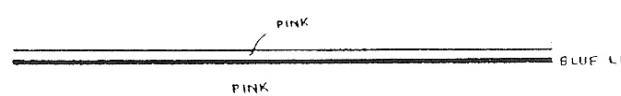


Fig. 6.

If, for instance, we take some of the solution containing the large amount of ferricyanide just indicated, and place a drop on a steel surface by means of a glass tube drawn to a fine point, touching the metal with the glass, a blue spot will appear at the point of contact, since the glass screens the metal locally from oxygen; this blue spot will continue to develop, after the glass has been moved on contact, owing to the screening action of the blue precipitates. It should be noticed that this can be made to occur even if the point of contact is quite close to the margin of the drop, thus producing the very asymmetric arrangement shown in Fig. 4; but in such a case, there will be a tendency for the blue to spread gradually towards the centre of the drop, the extension proceeding preferentially along the deeper grooves left by the emery treatment of the places which will first become exhausted of oxygen.

(To be continued.)

The Ferroxyl Indicator in Corrosion Research.

BY ULICK R. EVANS, M.A.

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Another interesting effect is produced if a glass tube drawn to a fine point is filled with a salt solution containing a large amount of ferricyanide and is drawn over the surface of steel so as to produce a streak of liquid. A fine blue line will be observed running lengthwise within the streak of liquid, representing the place where the glass actually touched the metal; if the tube and method of application are both symmetrical, the blue line will be central (Fig. 5), but it is easy to carry out the operation in such a way that the blue line comes close to the margin. (Fig. 6.)

5.—The McKay-Liebreich Controversy.

We are now in a position to consider the dispute regarding the cause of pitting. McKay⁸ explains pitting as follows: The ferric hydroxide (rust) produced by corrosion tends to flocculate; it may congregate at a point by settling or be distributed by currents in the solution. Where a little heap lodges on the metallic surface at any point, it will screen the metal locally from oxygen, and the portion thus screened will become anodic to the unscreened part around. Corrosion, being thus concentrated on the point in question, soon digs down into the metal.

Liebreich⁹, however, considers that this explanation is improbable, and proceeds to test the matter experimentally; he takes an iron pipe showing pits covered with "warts" of rust, and tests the polarity of different parts with the ferroxyl indicator (the old form containing agar-agar, as well as phenol-phthalein and ferricyanide), breaking open the warts to allow access of the indicator. The distribution of pink and blue is not, he states, that which would be expected from McKay's theory; he finds, for instance, that the inner walls of the warts become distinctly pink. Consequently he rejects McKay's explanation. To this McKay¹⁰ replies that the introduction of the indicator probably produced a serious change in the conditions, and alludes to the fact that ferricyanide itself can act as an oxidising depolariser.

Liebreich gives so little description of the experimental method adopted that it is difficult to form an estimate regarding the importance to be attached to his observations. But the application of the indicator after the rust-wart had already formed was not the happiest method of procedure, and it seems impossible to reject McKay's theory on so slender a piece of evidence. Whether the concentration of ferricyanide employed was sufficient to cause further disturbance is a matter on which no opinion can be expressed, since Liebreich does not state the concentration employed. But the breaking open of the wall of the rust-wart, and the application of a gel-forming substance, can hardly be considered to leave the distribution of anodic and cathodic areas unchanged.

A better procedure would be to remove small samples of the liquid from the interior and exterior of the rust-wart and to test them in an external vessel. Now it happens that another experimenter has done this, and his results are in agreement with McKay's theory. If McKay's theory is correct, the interior of the wart should contain an iron salt (chloride or sulphate, according to the predominant ion in the water causing the corrosion) and should

re-act weakly acid, through hydrolysis¹¹; the water outside—assuming that it originally contained salts of sodium, potassium, calcium, or magnesium—should be alkaline. As early as 1909, Huntley¹² described a case of corrosion in a boiler, in which the surface of the metal was covered with big blisters; he examined the liquid inside the blisters, and found it to be a solution of iron sulphate, distinctly acid, although the liquid outside was appreciably alkaline. This accords with McKay's theory, and the fact that the observation was made long before the theory was put forward increases the value of the evidence; indeed, the explanation suggested by Huntley is quite different from that put forward either by McKay or Liebreich, and involves the supposition that the sulphur came from the iron. (In the light of recent work Huntley's views on corrosion are, in many respects, difficult to accept, but there is no reason to regard his observations as lacking in accuracy.)

More recently, Baylis¹³ has carried out an examination of vast numbers of tubercles found on the inner walls of rusting cast-iron pipes. He has measured the pH value of samples taken from the blisters, and finds them always to be acid, rich in sulphates or chlorides of iron. Here again the facts appear to accord with McKay's view, but not to agree with Liebreich's statement that the inner walls of the warts are alkaline.

6: The Mechanism of Pitting.

There seems no serious reason, therefore, to doubt the substantial truth of McKay's explanation of the fact that when once corrosion has set in at a given point, it continues there in preference to other points. But the question still remains, what determines the initiation of corrosion at one point rather than another?

No doubt, as McKay suggests, the fortuitous settling of a blob of rust, arriving from elsewhere, at a point, may often start the local attack there. But there are probably other factors which can initiate the first attack at a particular point. Where an iron surface is covered with an oxide-scale (produced by heating during the process of manufacture or subsequently) any break in the scale will expose bare iron, and an electrical cell, with the bare iron as anode and the scale as cathode, will be set up when the surface is wetted; since the cathodic area will vastly exceed the anodic area, the corrosion, being concentrated on the small bare patch, will burrow rapidly at that point. It will also undermine the scale, which may peel off, but the action, once localized, is likely to continue even if all the scale is removed, owing to the screening effect of the new rust, which keeps the metal below it anodic to the rest. This sort of action—to which attention has recently been called by Speller¹⁴—is probably quite important in the corrosion of metal which has not been de-scaled.

The initiation of pitting on de-scaled iron and steel is—in the author's opinion¹⁵—often connected with pre-existing capillary pores opening on to the surface; the existence of such pores—even in rolled metals—has long been suspected by engineers, and their importance in corrosion phenomena has been emphasized from time to time—notably by Newman in his book on "Metallic Structures."

¹¹ If the water were quite free from salts, the interior might react alkaline, as the only possible anodic product would be ferrous hydroxide, which is weakly alkaline; but it is rather unlikely that a typical rust-wart would form in such a water, the rust being usually of a most incoherent character. This may, however, conceivably be the explanation of Liebreich's observation that the inner walls of the warts sometimes show an alkaline reaction.

¹² G. N. Huntley, *J. Soc. Chem. Ind.*, 28 (1909), 339.

¹³ J. R. Baylis, *Ind. Eng. Chem.*, 18 (1926), 370.

¹⁴ F. N. Speller, *Ind. Eng. Chem.*, 17 (1925), 344.

¹⁵ U. R. Evans, *Chem. Ind.*, 43 (1924), 222; *J. Soc. Chem. Ind.*, 45 (1926), 37T.

⁸ R. J. McKay, *Ind. Eng. Chem.*, 17 (1925), 23.

⁹ E. Liebreich, *Korrosion und Metallschutz*, 1 (1925), 67.

¹⁰ R. J. McKay, *METAL INDUSTRY*, 28 (1926), 434.

published in 1896. Indeed, Liebreich himself, in collaboration with Maass, has expressed the view that, in brass condenser tubes, surface defects may serve to initiate corrosion^{15a} in this manner, Bengough and May^{15b} consider that it is the microscopic, invisible pores, rather than visible defects, which are most liable to set up localized attack.

The Newer Electrochemical Theory explains how a pore of appropriate dimensions may come to promote pitting. If a pore opening on to the surface of iron becomes filled with liquid, the interior, being inaccessible to oxygen, will be anodic to the outer surface; the total corrosion will depend largely on the amount of oxygen reaching the large surface outside the pore, and the attack, being entirely

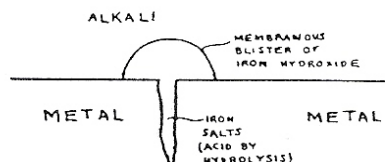


Fig. 7.

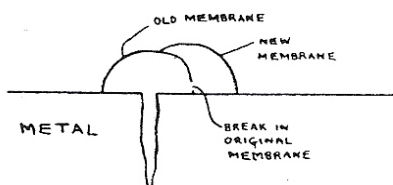


Fig. 8

concentrated on the small area inside the pore, will dig rapidly down into the metal. Over the mouth of the pore, the interaction between the soluble iron chloride or sulphate formed inside with the alkali formed at the cathodic area outside will produce a bulging membranous blister, brown on the outside (through oxidation to the ferric state), but dark green or even white on the inside (Fig. 7); it is these blisters which Liebreich calls "rust-warts" and Baylis describes as "tubercles." The membrane may, for a time at least, promote the action by shielding the iron below from oxygen, and thus keep the action localized on



Fig. 9.

the pit. But there are many ways known in which the action may extend laterally, and thus become less localized and, therefore, less dangerous. Not infrequently the skin may burst at a point^{15c} and liquid rich in iron salts may exude; but the boundary of the exuding liquid will soon become encased in a new membrane of iron hydroxide, due to interaction with the alkali without; thus we arrive once more at a complete blister, but it is a bigger blister than before (Fig. 8.) Cases of this kind have been observed by Baylis¹⁶ and also by the present writer.

^{15a} E. Maass and E. Liebreich, *Zeitsch. Metallkunde*, 15 (1923), 245.

^{15b} G. D. Bengough and R. May, *J. Met. Met.*, 32 (1924), 196.

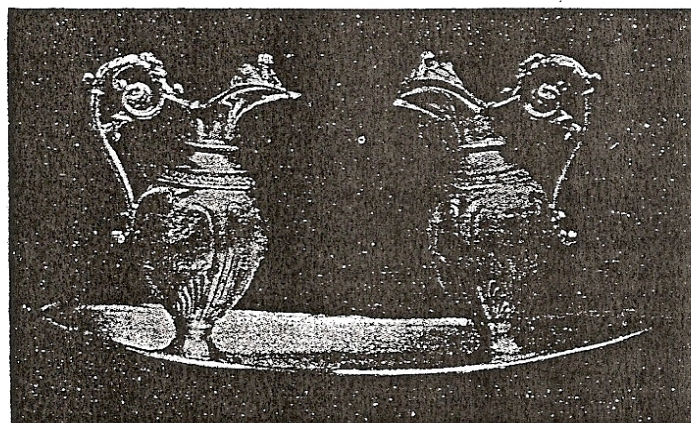
^{15c} The bursting may occur as a result of mechanical injury, but it seems likely that it may also be caused by variations of osmotic pressure; at periods when the salinity of water flowing through a pipe becomes unusually low, the osmotic pressure within a tubercle may exceed that outside, and there is a tendency for water to be drawn in through the membrane, which may become distended until it bursts.

¹⁶ J. R. Baylis, *Ind. Eng. Chem.*, 18 (1926), 379.

But there is another more important manner in which attack—originally localized at a point—may become more extensive, and therefore less intense. Whilst in some waters (notably saline waters containing a limited quantity of sodium carbonate), the walls of the blisters have a tough character, and are firmly rooted to the metal, thus tending to keep the action localized, in other waters the precipitated hydroxide is of a loose, feathery character, easily moved from the site of the pit by water-currents or even by gravity. If it accumulates upon the metallic surface anywhere, the area thus blanketed being screened from oxygen, will also become anodic to the unblanketed area and the attack, being no longer confined to the pit, will be far less intense. This development from localized "point corrosion" into long streaks or streamers will be familiar to many; in stagnant water, the streaks extend vertically downwards, the corrosion product moving under the force of gravity (Fig. 9); in gently flowing water, the streaks usually point in the direction of flow (Fig. 10); where the water current swirls against a surface, a remarkable series of spiral rust-streaks is sometimes seen. It should, however, be noticed that rapidly moving water usually prevents the corrosion-product from settling on the main part of the surface, and only the mouths of the pits remain covered with blisters or tufts of hydroxide; thus increased rapidity of motion of the water, although under some conditions reducing the total corrosion (as indicated by the researches of Heyn and Bauer¹⁷ and of Friend¹⁸) often tends to keep the action localized upon small points, and thus renders the attack more intense and more dangerous.

(THE END.)

The Metal Craftsman's Art.



Miniature Silver Ewers for Church Use.

These two little vessels and their tray were made some 100 years ago for ecclesiastical use. Both ewers are so set on the tray that each can be lifted on and off, a short pin adding materially to their stability if the tray be moved about. One ewer has amongst its decorative ornamentation a bunch of grapes, thus indicating it as the vessel for wine, the other little ewer being ornamented with bulrushes to indicate it as the water cruet.

The whole is a skilful and pretty piece of metalwork and is now in the possession of a clergyman in one of the Midland Counties, by whose courtesy our photograph has been provided. The ewers are of wrought silver and are barely six inches in height.

¹⁷ E. Heyn and O. Bauer, *Mitt.-Kgl. Materialprüfungsamt*, 28 (1910), 93, 130.

¹⁸ J. A. N. Friend, *Trans. Chem. Soc.* 119 (1921), 932.