ROLE OF OXIDIZERS IN THE PROCESS OF PASSIVATION OF IRON IN NEUTRAL PHOSPHATE SOLUTIONS

M. D. Kononova, G. M. Florianovich, and Ya. M. Kolotyrkin

UDC 620.197.3

The use of phosphates as inhibitors of the corrosion of iron in neutral media is effective only in the presence of different types of oxidizers [1-5]; for the creation of a protective effect, it is necessary to determine the critical concentrations of the phosphate [2, 5] and of the oxidizer [5]. Introduction of phosphate into solutions in concentrations below the critical leads not to inhibition, but to acceleration of the dissolution of the iron. With an increased concentration of the oxidizer, the critical concentration of the phosphate decreases.

The assumptions have been expressed [2, 6, 7] that the role of oxidizers in the process of the inhibition of corrosion using phosphates reduces to their reaction with iron and to the formation of passivating oxides, and that the presence of phosphates in the solution leads to an improvement of the protective properties of these oxides.

We showed earlier [8] that, in phosphate solutions not containing oxidizers, the transition of iron, during anodic polarization, into the usual passive state is preceded by its initial passivation, which is specific for such solutions. If this initial passivation is taken into account, then the action of the oxidizers in the inhibition of the corrosion of iron presents itself in a somewhat different light.

In the absence of oxidizers the stationary potential of iron is rather negative, and rate of dissolution is correspondingly small. Introduction of phosphate into such a solution does not lead to a substantial change, since the inhibiting action of the phosphate on the reaction of the dissolution of iron develops only at higher positive potentials. With the introduction into a solution, not containing phosphate, of an oxidizer in an amount not sufficient for passivation, the stationary potential of iron shifts in the positive direction, and the rate of corrosion rises. The value of the potential shift under the action of the oxidizer can be enough so that, after introduction of phosphate into such a solution, there begins the electrochemical formation on the metallic surface of a protective layer of iron phosphate (initial passivation) and the corrosion rate drops correspondingly.

With time, the degree of coating of the iron with the protective layer should increase, if it is assumed that here the cathode reaction takes place at its previous rate over the whole surface of the electrode, * and that the anode reaction takes place only in the pores of the forming deposit, then, as we showed earlier [9], with an increase in the degree of coating of the electrode, its stationary potential will shift in a positive direction. † As a result, the potential of ordinary passivation is attained, and the iron starts to become passivated.

Taking what has been said above into account, it is evident that the concentration of the oxidizer necessary for passivation of iron in the presence of phosphate, should be less than the critical value required for ordinary passivation of this metal in solutions not containing phosphate.

* In support of such an assumption is the agreement of cathode polarization curves, measured in a 0.165 M phosphate solution, saturated with oxygen, in samples without a film and covered with a phosphate layer.

† In the case when the reduction of the oxidizer takes place under determined diffusion conditions, such a shift of the potential can, in principle, be explained also by the assumption that in the sections covered by the deposit there takes place, not only an anode reaction, but also a cathode reaction, as was done by V. M. Novakoskii et al. [10], to explain the facilitation of the passivation of iron in sulfuric acid, with partial coating of its surface. For this, however, according to [10], it is necessary to assume that the size of the inert sections on the surface of the electrode are small in comparison with the thickness of the diffusion layer.

L. Ya. Karpov Physicochemical Scientific Research Institute. Translated from Zashchita Metallov, Vol. 4, No. 3, pp. 315-318, May-June, 1968. Original article submitted June 13, 1967.

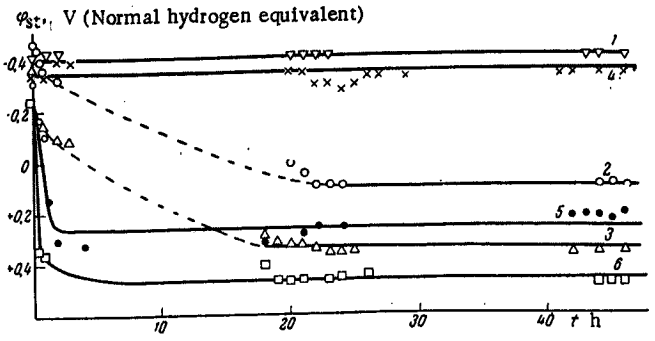

Fig. 1. Change with time of the electrode potential in solutions of 0.191 M borate (4, 5) and in 0.191 M borate +0.033 M phosphate (1-3, 6), containing different amounts of H_2O_2: 1) 2×10^{-4} M; 2) 4×10^{-4} M; 3, 4) 3×10^{-3} M; 5, 6) 4×10^{-3} M.

The present work was undertaken to verify the correctness of the assumptions advanced. Hydrogen peroxide was used as the oxidizer, with borate solutions as a background.

The investigations were carried out in an ordinary electrolytic cell in an atmosphere of purified nitrogen. The buffer solutions were prepared in double-distilled water from double recrystallized $Na_2HPO_4 \cdot 2H_2O$ and KH_2PO_4, and the borate solutions from H_3BO_3 and $Na_4B_2O_7$. The hydrogen peroxide was "specially pure." The iron electrodes, made of "Hilger," were pickled before the experiment in boiling sulfuric acid and washed with double-distilled water. Then the electrode was placed in the main cell containing the solution to be investigated, with addition of an oxidizer, the cathode was polarized for 20 min and, after the current had been switched off, was held up to the establishment of a constant electrode potential. The solution was poured off, and new portion of solution was filled into the upper part of the cell; this solution was previously saturated with nitrogen and contained a determined addition of hydrogen peroxide. The experiments included measurements of the stationary potential of the iron and determinaton of the rate of its corrosion from colorimetric analysis of the solution.* The duration of the experiments was 45-48 h. The measured values of the rate of corrosion are the average values for the time of the test. The potentials are expressed with reference to a normal hydrogen electrode.

It is evident from Fig. 1 that, at low concentrations of H_2O_2, the stationary potentials, φ_{st}, do not change with time, while at higher concentrations, they shift in a positive direction. The minimum concentration (C_{cr}) at which such a shift of the potential is observed, is lower in the presence of phosphate than without it. As Fig. 2 shows, in pure borate solutions it is $\sim 5 \times 10^{-3}$ M, and in solutions with phosphate $\sim 3 \times 10^{-4}$ M. With an increase in the H_2O_2 concentration, the corrosion rate of iron at first rises, and then falls markedly (curves 1 and 2, Fig. 2); the drop in the corrosion rate is observed at those critical concentrations of peroxide at which there is also a sharp change in φ_{st} (C^b_{cr} in borate solutions, and C^{ph}_{cr} in phosphate solutions).

As follows from the results presented in Fig. 3, in the region of potentials corresponding to the start of the active dissolution branch, as well as in the passive region, the rate of dissolution of iron, with an unchanged ionic composition of the solution, depends only on the potential, and does not depend on whether this potential is achieved by anode polarization in a solution without oxidizer (curves), or by the introduction of an addition of H_2O_2 (points) into the same solution. Consequently, in the above regions of the polarization curve, the action of the oxidizer, as in the dissolution of nickel in sulfuric acid [11] can be reduced to its participation in the cathode act. However, if the relationship established at the start of the active region between the concentration of H_2O_2 and the current in the dissolution of iron which this entails is extrapolated to C_{cr}, it is found that the limiting rate of dissolution (and consequently, also the limiting current for the reduction of H_2O_2) at C_{cr} is substantially less than the critical current for passivation in the absence of an oxidizer.

This bears witness to the fact that, at potentials close to the potential of passivation, hydrogen peroxide can exert also a direct inhibiting action on the anode process of the dissolution of iron, as has already been remarked for sulfuric acid solutions [12]. It is evident that, inhibiting the dissolution of iron, and assuring (as described at the beginning of the article) a shift of the electrode potential to the positive side,

* Such a method permits a correct evaluation of the rate of dissolution of iron in borate solutions, but leads to low results in the case of phosphate solutions, since the dissolution of iron in these solutions is accompanied by the formation of a $Fe_3(PO_4)_2 \cdot 8H_2O$ [8] deposit on the surface of the electrode. In connection with the small value of the surface of the wire electrodes, weight determination of the amount of the covering layer in phosphates was not possible. By special experiments, carried out on samples of Armco iron, having the form of plates, it was shown that the fraction of the current going to the formation of the film, at the potentials of the active region, is 30%, and at the potentials of initial passivation, it is 70-80%.

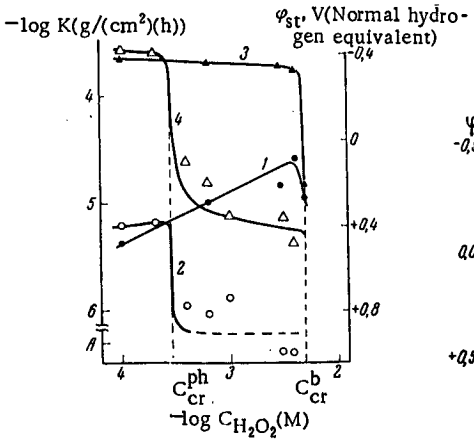

Fig. 2

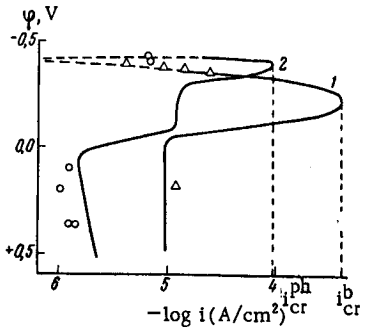

Fig. 3

Fig. 2. Dependence of the corrosion rate (curves 1, 2) and the stationary potential (curves 3, 4) on the H_2O_2 concentration in the solutions: 1 and 3) 0.191 M borate; 2 and 4) 0.191 M borate +0.033 M phosphate. Point A corresponds to the limiting sensitivity of the analytical method (4.5×10^{-7} g/(cm²)(h)).

Fig. 3. Stationary polarization curves, measured in iron in solutions of: 1) 0.191 M borate; 2) 0.191 M borate + 0.033 M phosphate. The points represent the values of the corrosion rates and the stationary potentials of iron in the corresponding solutions (1 and 2), in the presence of different amounts of hydrogen peroxide.

the initial phosphate films can promote the development also of this property of H_2O_2 (which may be inherent also in certain other oxidizers). It is evident also that, the less the concentration of H_2O_2 exceeds the critical, the higher the degree of initial phosphate passivation which is required for final passivation under the action of H_2O_2. There is a corresponding increase also in the time required for complete passivation. This fully confirms curves 2, 3, and 6 on Fig. 1.

On the other hand, for formation of the initial protective layer, as has also been pointed out earlier [2, 5], there is required a certain minimum concentration of phosphate. Lesser concentrations of phosphate do not facilitate passivation. Thus, at a H_2O_2 concentration of 10^{-2} M, a decrease in the phosphate concentration from 0.165 to 0.0165 M brings about an increase in the rate of dissolution of iron from 3×10^{-5} to 2×10^{-4} g/(cm²)(h). Such a decrease in the phosphate concentration in a solution with an oxidizer leads to the disappearance of the initial passivation section on the anode polarization curve.

Confirming the correctness of the concepts developed, the results obtained thus indicate that the inhibiting effect can exist only at determined critical concentrations of the phosphate and the oxidizer. The critical concentration of phosphate is that value at which, on the curve of the dependence of the rate of dissolution of iron on the potential, there appears a region of initial passivation. The critical concentration of oxidizer is that value which is sufficient to insure a shift of the stationary potential of iron up to values which are more positive than the initial passivation potential of iron in the given solution.

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