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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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The Influence of Adsorption of Volatile Inhibitors on the Electrochemical Behavior of Iron

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In recent years a new, highly effective method has been developed for protecting products and instruments from atmospheric corrosion. The essence of the method is that chemical compounds possessing a definite vapor pressure—the so-called volatile inhibitors—are introduced into the enclosed space where the instrument is placed; by saturating the air space, these inhibitors completely prevent corrosion. The mechanism of their action has scarcely been studied, although many assumptions and conjectures have been expressed concerning it (^{1}).

Fig. 1. Dependence of the stationary potential of an iron electrode on the character of adsorption of benzylamine.
1 —electrode exposed to benzylamine vapor before application of a film of 0.01 N Na_2SO_4;
2 —electrode exposed to benzylamine vapor after application of a film of 0.01 N Na_2SO_4;
3 —a film of a 25% solution of benzylamine in 0.01 N Na_2SO_4 was applied to the electrode (layer thickness 160 μ).

Proceeding from the electrochemical theory of metal corrosion, it was most probable to assume that the inhibiting action of volatile inhibitors is connected with the ability of compounds adsorbed on the metal surface to alter the kinetics of the electrode reactions that determine the corrosion process (^{2}).

The adsorption process was studied by us using electrochemical methods (measurement of stationary potentials), which at the same time made it possible to obtain data on the direction of change in the electrochemical kinetics.

The usual methods of investigating inhibitors under conditions in which they are introduced into the electrolyte beforehand are very far from the real conditions of use of a volatile inhibitor, which is usually adsorbed from the gas phase, and therefore, as will be shown below, they do not make it possible to establish the specific features of the action of such compounds.

In the present work we used a method for investigating electrochemical kinetics in thin layers of electrolytes, developed by one of the authors (^{3}). The procedure was improved in such a way that films of electrolytes could be applied to the electrode surface after adsorption of the inhibitor from the gas phase, without breaking the hermetic seal of the space.

Benzylamine (C_7H_9N) and morpholine (C_4H_9NO) were studied as volatile inhibitors. Preliminary experiments established that these compounds protect iron well from corrosion.

Figure 1 presents the dependence of the iron potential on the time of preliminary exposure of the electrode in an atmosphere saturated with benzylamine (curve 1). It is evident from the figure that adsorption of the inhibitor shifts

stationary potential in the positive direction. With increasing time of holding the electrode in an atmosphere saturated with inhibitor vapor, the observed effect increases, reaching after a certain time a constant value, which for benzylamine is approximately 40–50 h. Evidently, during this period the surface becomes completely saturated with the inhibitor. The potential shift in this case reaches more than 200 mV.

It is interesting to note that adsorption of the same inhibitor from the gas phase, occurring, however, under conditions in which there is a thin layer of electrolyte on the metal surface, leads to much smaller effects (see curve 2). In the latter case the iron potential shifts by only 50–60 mV.

Adsorption of a volatile inhibitor from a concentrated solution of the inhibitor (25%) in 0.01 N sodium sulfate is likewise unable to shift the stationary potential of iron by the amount that we record upon adsorption of the inhibitor from the gas phase (see curve 3). The latter is evidently due to preferential adsorption of SO_4^{--} ions.

Thus, it should be concluded that adsorption of the inhibitor from the gas phase leads to more substantial shifts of the potential and, consequently, to a higher degree of passivation of the electrode.

The adsorption bond of the inhibitor with the metal surface and the stability of the passive state can to some extent be characterized by data on the change in the metal potential with time after a film of electrolyte has been applied to its surface.

Figure 2 shows curves of the change in the stationary potential of iron with time as a function of the duration of preliminary exposure of the metal in the atmosphere of the volatile inhibitor (benzylamine).

Fig. 2. Change in the stationary potential of an iron electrode with time as a function of the time of preliminary contact of the electrode with benzylamine vapors. Electrolyte: 0.01 N Na_2SO_4 (layer thickness 160 μ). 1 –without volatile

Fig. 2

Figure 2: Fig. 2

inhibitor. Time of preliminary contact of the electrode with benzylamine vapors before application of the electrolyte film: 2 –1 h; 3 –17 h; 4 –24 h; 5, 6 –42-72 h.

The potential of an electrode that had not been previously exposed in the atmosphere of the volatile inhibitor becomes more noble with time (curve 1). Brief exposure of the electrode to the vapors of the volatile inhibitor practically does not change the initial potential of the electrode. With time, as a result of activation of the electrode surface by the electrolyte, and possibly also adsorption displacement of oxygen from the electrode surface by sulfate ions, the iron potential begins to become more noble (curves 2 and 3). (It is interesting to note that at first the electrode surface acquires more negative potentials than in the absence of the inhibitor. The latter phenomenon is possibly connected with the fact that preliminary adsorption of the organic cation formed during hydrolysis of the inhibitor facilitates adsorption of anions.)

Subsequently, as a result of adsorption of the inhibitor from the gas phase occurring through the film, the passivating properties of the inhibitor already begin to manifest themselves, and the electrode potential shifts increasingly into the positive range of potentials (curves 2, 3).

As the time of preliminary exposure of the electrode in the atmosphere of inhibitor vapors increases, the metal potential becomes increasingly

stable (curves 4, 5, 6); no activating effect of the electrolyte is observed. The potential is strongly shifted in the positive direction (curves 5 and 6), which indicates the stability of the passive state.

Adsorption of morpholine has an analogous effect on the electrochemical behavior of the iron electrode. The dependence of the potential on the time of exposure of the electrode in an atmosphere saturated with morpholine vapor (Fig. 3, curve 1) is similar to that considered above. The time required for limiting saturation of the surface with the inhibitor for morpholine, however, is approximately two times less than for benzylamine. Even with a short contact time of the electrode with the vapors of this compound, the potential shifts strongly (by 180-200 mV) in the positive direction. As in the case of benzylamine, adsorption of morpholine through the film produced a much smaller effect (curve 2). Moreover, in the initial period the potential of iron becomes less noble, which is due to activation of the surface by the electrolyte under conditions in which adsorption of the inhibitor is evidently still weak or has not occurred at all. After some time the electrode potential begins to become more noble, which is explained by adsorption of morpholine vapor by the electrolyte film and subsequent adsorption of the inhibitor from solution by the electrode. With time the potential establishes itself at a constant level; however, it does

Fig. 3 and Fig. 4

Figure 3: Fig. 3 and Fig. 4

not reach the values acquired by the electrode upon preliminary adsorption of the inhibitor from the gas phase. Adsorption of morpholine from a solution in which the inhibitor concentration was very high (25%) also gave a smaller effect (curve 3). The potential of such an electrode in a film of 0.01 N Na_2SO_4 is close to the potential of an electrode previously exposed to morpholine vapors for a very short time. In this case the potential does not change with increasing time of exposure of the electrode under the solution and does not acquire values characteristic of an electrode that has reached a state of complete saturation of the surface from the gas phase.

Fig. 3. Dependence of the stationary potential of an iron electrode on the character of morpholine adsorption.
1 –electrode exposed to morpholine vapor before application of a 0.01 N Na_2SO_4 film;
2 –electrode exposed to morpholine vapor after application of a 0.01 N Na_2SO_4 film;
3 –a film of a 25% solution of morpholine in 0.01 N Na_2SO_4 was applied to the electrode (layer thickness 160 μ).

Fig. 4. Change in the stationary potential of an iron electrode with time as a function of the time of preliminary contact of the electrode with morpholine vapor. Electrolyte 0.01 N Na_2SO_4, layer thickness 160 μ.
1 –without volatile inhibitor. Time of preliminary contact of the electrode with morpholine vapor before application of the electrolyte film:
2 –1 h; 3 –17 h; 4, 5 –42–72 h.

The strength of the bond between morpholine and the metallic surface, and its passivating properties, are characterized by curves showing the change in potential with time after application of a 0.01 N Na_2SO_4 film to an electrode that had previously been exposed in an atmosphere of morpholine vapor (Fig. 4). Incomplete saturation of the electrode surface with the inhibitor (exposure for 1 and 17 h) makes the potential still unstable (curves 2 and 3). However, after 48 h contact of the electrode with the volatile inhibitor, the potential shifts strongly in the positive direction and becomes stable (curves 4 and 5). The latter indicates that the passive state of the electrode in the presence of morpholine is very stable. Thus, we come to the conclusion that volatile inhibitors are adsorbed by the metal surface and strongly alter its electrochemical properties. The greatest displacement of the stationary potential is observed when the inhibitor has been adsorbed beforehand by the electrode from the gas phase. In this case, maximum saturation of the surface with the inhibitor and considerable stability of the passive state are achieved.

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