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# Academician V. A. Kargin, M. I. Karyakina, and Z. Ya. Berestneva

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**Abstract**

**Full Text**

**Physical Chemistry**

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## **INVESTIGATION OF THE MECHANISM OF THE PROTECTIVE ACTION OF PAINT-AND-VARNISH COATINGS**

In considering the anticorrosive action of paint-and-varnish coatings, it is usually assumed that corrosion of the metal is governed by the rate of penetration of aggressive substances through the film; accordingly, coatings are selected by choosing a film with lower permeability. There is no doubt that preventing or slowing the penetration of aggressive substances through the film plays a significant role. However, from the literature data, as well as from practice, it is known that films often allow considerable amounts of water, acids, oxygen, etc., to pass through and nevertheless possess sufficiently high protective properties<sup>(1-3)</sup>.

It could be supposed that, alongside the ability of a film to prevent the permeability of aggressive substances, there are also other phenomena that determine the corrosion properties of the metal after a paint-and-varnish film has been applied to it. Their influence should manifest itself in the case when it is possible to deliver, over the same interval of time, the same amount of an aggressive substance to the surface of the metal, i.e., to exclude the influence of diffusion through the film.

The problem reduces to supplying the aggressive substance to the surface of the corroding metal in the presence of a film in such a way as if the film were ideally transparent to diffusion and did not slow the process of penetration of this substance to the metal; that is, to create conditions under which the penetration of the aggressive substance will be the same—regardless of whether the metal is covered with a film or not, and regardless of the composition and thickness of the varnish coating.

The most convenient method making it possible to exclude the influence of diffusion through the film is the electrochemical method of investigation.

Experimentally, the problem reduces to maintaining a constant current in a system with variable resistance, since the amount of iron corroded or the amount of oxide formed will be proportional to the amount of electricity passed, or to the product of the current and time, and is determined simply by Faraday's law.

Since paint-and-varnish films have high electrical resistance, the tests were carried out at a high potential difference. For this purpose, an instrument was constructed with a maximum voltage of 3000 V and automatic regulation to maintain a constant current equal to 10 mA.

The electrolyte was a 0.01 *N* solution of soda; the electrodes: the cathode was a platinum plate, and the anode was an iron rod coated with the paint-and-varnish material under test.

The specimens were tested for 2 hours and inspected every 15–30 min. The current density in all experiments remained constant, equal to 1.8 mA/cm<sup>2</sup> (4).

Thus, the amount of aggressive substance penetrating to the metal surface over the same interval of time should be the same; if corrosion of the metal were determined only by the permeability of the film, then the electrode coated with varnish and the uncoated electrode would corrode identically. However, the very first experiments showed that both the time of onset and the character of corrosion differ on specimens not coated and coated with a protective varnish, despite the fact that the same amount of substance is supplied. On a specimen not covered with a varnish film, corrosion arises quickly and spreads over the entire surface. On a specimen coated with varnish, only separate foci of corrosion arise, and the time required for their formation is incomparably longer than in the first case. Thus, for one and the same amount of substances formed during the electrochemical corrosion of iron, the formation of oxides on a free surface and on a surface protected by a paint-and-varnish film is different.

Consequently, in addition to the diffusion properties of films, other factors also influence the corrosion of a metal protected by a paint-and-varnish coating.

Corrosion is the transition of a metal into any chemical compounds that arise at the interface metal–film, and the separation of which signifies the appearance of a new phase.

For this new phase, arising at the metal–film interface, to form, activation work must be performed, corresponding to the energy of detachment of the film from the metal surface. This phenomenon is entirely analogous to any process of formation of a new phase inside a solid body (for example, the appearance of gas bubbles inside metals, etc.), and it is well known that such processes proceed with large heats of activation. If the process of separation of these substances in the form of a new phase proceeds with large heats of activation, considerable supersaturations may arise; the oxides formed may dissolve in the substance of the film, forming solutions with enormous degrees of supersaturation. Indeed, in testing coatings possessing high diffusion permeability and swelling well in water (gelatin and polyvinyl alcohol), it was found that iron oxide forms not on the metal surface but on the outer surface of the films, up to the formation of an abundant precipitate of ferric hydroxide in the solution without any destruction of the protective films. This shows that at the metal surface–film boundary there are no conditions for the formation of a new phase owing to the high adhesive capacity of these films, and the oxides formed dissolve in the substance

of the film and, diffusing through it, are released where formation of a new phase occurs without any difficulty, i.e., at the interface between the protective film and the solution.

Paint-and-varnish coatings were also tested by the method of cathodic polarization, i.e., the tested iron rod coated with varnish served as the cathode, and a platinum plate as the anode. When an electric field was applied, hydrogen was liberated at the cathode; with strong adhesion of the film to the metal, it diffused into the solution. In places of weakest adhesion, however, hydrogen could accumulate, creating pressure on the film, under the action of which detachment of the film from the metal surface is possible.

Indeed, when tested by this method, the film delaminated from the metal in the places of weakest adhesion to the metal surface, forming bubbles; the film itself, however, remained continuous. Then the specimen was subjected to anodic polarization, and corrosion arose first of all at the places where the film had detached. These experiments clearly show how important the role of the adhesive properties of paint-and-varnish coatings is.

Since internal stresses arise in paint-and-varnish coatings (5, 6), which, depending on the conditions under which relaxation processes proceed, may persist for a long time and contribute to premature destruction of the coatings, we carried out studies

effects of these stresses on the adhesive properties of the films, and it was established that an increase in stresses leads to a decrease in the adhesive properties of the films.

Consequently, the method we have developed makes it possible, by excluding the phenomenon of film permeability, to evaluate the protective properties of a coating either by the time to the onset of corrosion in the case of anodic polarization, or by the appearance of bubbles in the case of cathodic polarization; and it clearly shows how great the significance of the adhesive properties of films is in the protective action of coatings.

Thus, in contrast to the existing view that film permeability is the principal factor determining the protective properties of paint-and-varnish coatings, the present work has shown that the adhesive properties of coatings play no smaller, and sometimes a greater, role, since adhesive properties are important not only as a factor determining the adhesion of the film to the substrate, but also as a factor preventing the formation of a new phase at the metal-film interface.

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*Note: Figure translations are in progress. See original paper for figures.*

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