The mechanism of the protective action of coatings

The ability of coating to prevent or slow down the corrosion of the metal is determined by five major groups of its properties:

1. barrier;
2. adhesive;
3. dielectric;
4. passivating;
5. physical and mechanical.

Different sources give different assessments to the effect of these properties on the overall effect of the protective action. Some prefer the barrier properties, while others believe that the most important ones are adhesive strength, etc. In fact, the protective properties of the coating are determined by a complex of the above properties, which also provide other mutual influence. For different coatings various properties or their combinations may predominate.

The barrier properties of the coating firstly is the ability to restrict the supply of water, oxygen, chlorides and other corrosive agents to the metal and the removal through the film products of corrosion. Second, the barrier properties require resistance of the coating to the effects of the environment. Barrier coating properties (permeability, sorption) is closely related to the structure of the polymer film, its content, the degree of hydrophilicity and so forth. There are linear and crosslinked polymers. Obviously, polymer with common three-dimensional network is a more serious obstacle to the particles of the environment, rather than a linear polymer. The polymer with hydrophilic and polar groups will absorb water increasingly than the hydrophobic polymer. The permeability of the film will be less, if it be filled, for example, with glass particles of scaly shape.

The adhesive properties of the coating are explained by a complex interaction of functional polymer groups (physical, chemical, electrical) with the active centers of metal. Arisen connections interfere with the interaction of the metal particles of the environment, that is, the process of corrosion. So, the higher the adhesion is, the more connections of the metal to the polymer and the stronger are they, the less potential sections are appeared, which may cause the corrosion process.

The dielectric properties of the coating are characterized by electrical resistivity of the material in the environment and they are the sum of its two components - the ohmic and polarization resistance. The essence of the effect of electric corrosion resistance is to reduce the flow of electrons and ionic charge from the metal surface through the film in environment that is both in the inhibition of the anode and the cathode process. There is a direct relationship between the electrical resistance of the coating and its protective properties. In particular, good protection in sea-water ensured coatings having an electrical resistance of less than 108 ohms / cm^2.

Passivation properties characterize the ability of the coating to passivate the metal under the film in places of adhesion failure using pigments which are extractable from the coating or corrosion inhibitors. Passivation properties may occur on the metal in different ways: by varying the potential of the anode or cathode sections, the change pH of the environment under film by formation of oxide films and inhibiting complexes. Efficiency pigments and inhibitors in the coating determine the optimum concentration of the passivation solution under the film and the duration of the metal maintain in the passive state.

Physical and mechanical properties characterize the resistance of coatings against mechanical destruction of the film under the influence of external and internal stresses. The mechanism of paint material destruction and corrosion of painted metal includes a plurality of serial and parallel transformations of the physical, chemical, electrochemical and mechanical nature.

Conventionally, this process can be divided into four successive stages:

Stage 1 is the diffusion of corrosive agents (water, oxygen, chloride) through the film material to the metal. Because of the roughness and presence of non-adherent areas, are observed unfilled paint material cavities. At first the water penetrates in these portions (a water molecule is smaller), then oxygen and chlorides. Process of diffusion penetration involves the absorption of environment regents on the surface of protection coating, their dissolution in the coating film, transformation of chemical potential gradient under the influence of adsorption on the metal surface.

At this stage, for the entire life of coating begins and continues its interaction with the environment and conversion in the physical, chemical and physical-mechanical characteristics of the material. The result of such interactions are swelling of the film, intermolecular bonds weakening, solvents washout from the matrix polymer, pigments, low molecular weight polymer fractions, degradation of macromolecules, etc. This reduces the strength of the film, weakening of adhesive bonds.

Stage 2 is the dissolving of passivating pigments by water (if they present), the inhibition of corrosion processes, osmotic water penetration in the areas of nonadherent coating.

The water penetrates into the coating, partially dissolves anticorrosive pigments, forming a passivation solution to the metal coating. At a certain concentration of this solution the corrosion of the metal is completely inhibited. The content of water-soluble pigments in the coating usually is chosen taking into account the optimal combination of their positive (corrosion protection) and negative properties (osmosis, a decrease of barrier properties). Filling the cavities by osmotic water increases the pressure and leads to the formation of osmotic blistering under the film. As time passed, the pressure highly increases which leads in some places to a violation of weak adhesive bonds. Wedging action of the solution helps to make this process.

Stage 3 is the concentration reduction of the passivating solution under the film coating below the minimum level of protection, the beginning of the corrosion process. With increasing of volume of osmotic blistering the concentration of passivating begins to decrease and, accordingly, it increases the rate of corrosion under the coating film. The destruction of adhesive bonds is ongoing and it leads the growth of microcavities at the expense of osmotic penetration of water and because of generated corrosion products pressure (their volume, as you know, several times exceed the amount of destruction of metal).

Stage 4 is the cohesive or adhesive failure of the coating. At this stage, the material on the film is influenced by mechanical stress from the corrosion products pressure, osmotic pressure, deformations of painted design, and internal pressure in the film. Destruction of the coating can occur either as a film fracture at the place of the osmotic bubble or film peeling because of destruction of the adhesive bonds.

The described process of destruction of the coating system is largely related to the operating conditions of the painted designs which are used in the sea or fresh water, and in a humid atmosphere. In aggressive acid or alkaline environments at elevated temperatures, solar radiation, bacterial environment and other external factors the process coating materials destruction can flow through a different mechanism. For example, in a dry atmosphere with an elevated temperature primary destructive factors may not be the products of corrosion, it could be the internal shrink stress in the film; in this case, visible defects in the coating are not bubbles but cracks and delaminations.

The corrosion of coating material is determined not only by external influences, but also by nature of the painting materials. First of all it is type of film-forming warp and filler. For example, silicone coatings have high heat resistance, but have a low resistance by contact with water and humidified.

Often the critical state of the painting material isn’t determined by metal corrosion or destruction of the film, but of its decorative appearance. In this case, the coatings are evaluated by such indicators as the chalking, discoloration and burning, loss of gloss.

So, described above mechanism of coating destruction is the most typical for anti-corrosion materials. However, the process may have substantial differences on the basis of different operating conditions and different coating materials. This should be considered when choosing the optimal coating systems for specific conditions of operation.