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### ANTI-CORROSION COATINGS WITH HIGH BARRIER CHEMICAL RESISTANCE PROPERTIES

The ways of solving actual problems of development corrosion resistant chemical resistant polymer coatings for containers, tanks, pipes and equipment in the chemical petrochemical industry are considered. It is shown that the widest range of resistance to aggressive media (acid, alkali, organic chlorine compounds, kerosene, diesel fuel, nitrobenzene, etc.) manifest a coating based on epoxy vinyl ester and epoxy novolac ester and oligomeric matrices with uniformly distributed therein particles of chemically resistant glass in the form of flakes or fibers of linear dimensions of 1 : 10 ratio. Thin plates of micaceous hematite ( $\alpha\text{-Fe}_2\text{O}_3$  hematite structure) are used as fillers. Such particles of chemically resistant fillers create a coating structure with high barrier properties, preventing the penetration of aggressive agents to the surface of the metal to be protected.

**Key words:** epoxy resin, amine curing agent, filler.

**Introduction.** Modern complex and expensive production equipment is operated under severe temperature and chemically aggressive conditions. Destruction of constructions, pipes, tanks and other chemical and petrochemical equipment caused by corrosion has always accounted for special attention paid to improving corrosion protection. Effective corrosion protection ensures long service life of the equipment without repair, reduces the metal production cost, and saves energy [1, 2]. That's why coatings from composite polymeric paint-and-varnish materials, the main components of which are film-forming substances of oligomeric type, hardener, filler and pigment [3] have found wide application in the chemical and petrochemical industry, aircraft and automobile production.

**Main part.** The protective characteristics of coatings are determined not only by physicochemical properties of the individual components of paint-and-varnish materials (PVM), but also interphase phenomena in the heterogeneous system of coatings and their structure.

During past five decades film-forming materials, namely, epoxy, unsaturated polyester and polyurethane resins are used for the industrial production of anti-corrosion PVM. Coatings based on them have high resistance to water, oxidants, heat and light.

The most important property of the protective film is its permeability due to the diffusion and sorption processes taking place in the polymer material. The active agent from the environment diffuses to the coating surface and is sorbed on it. Then diffusion of the active reagent in the coating layer and chemical interaction of the environment agent and coating components, followed by diffusion of the products of their interaction in the coating occur. The destruction of the coating actually takes place at the stage of interaction of the

active agent from the environment with coating components [3].

The permeability of polymers is a complex function determined by the structure of film-forming material and chemical nature of the terminal groups of macromolecules. The presence of active groups in the polymer matrix can change the polarity, influence the permeability of the matrix and the nature of interfacial interactions [4].

World experience of developing anti-corrosion coatings makes it possible to determine the type of polymeric materials which are more suitable to be used as matrix for polymer anti-corrosion coatings. It is obvious that the polymer film in the coating should be based on oligomer of low viscosity, and the hardener is to cause the formation of spatial structure at small shrinkage of the resulting polymer. In addition, the polymer matrix of the anti-corrosion coating should be characterized by high resistance under aggressive conditions. Chemical resistance of polymers depends on their active centers which may be unsaturated bonds, functional groups, halogen atoms, that under the influence of medium components can chemically interact with it. The active centers are functional groups that are required to create strong reticulate structure of the polymer film. The coating structure should be formed so that the active centers become inaccessible after curing of the coating.

The first corrosion-resistant oligomers for chemical equipment were polyester resins. They were synthesized on the basis of chlorendic anhydride and fumaric acid, and were stable only under acidic conditions. For coatings which were to be exploited under alkaline conditions compounds based on fumaric acid and bisphenol A were prepared, their resistance under acidic conditions being small. Epoxy resins synthesized from bisphenol A and epichlorohydrin turned out to be more chemically resistant ones (Fig. 1, a).

Preparing resins of improved resistance became possible on the basis of compounds synthesized from epichlorohydrin and bisphenol A, i.e. on the basis of epoxy resins.

These resins are distinguished by their elasticity and higher resistance to mechanical and thermal attack. Epoxy resins cure with the formation of macromolecules with spatial structures. Aliphatic amines or acid anhydrides are used as hardeners, which permits to prepare polymeric materials with different properties. Specially developed hardeners (polyfunctional amines, polybasic carboxylic acids, mercaptans and inorganic hardeners) permit to develop polymer matrixes with many various properties [5]. Mixtures of aromatic and aliphatic amines modified with organic acids can be used as hardeners, permitting to affect the nature of chemical bonds of over and intermolecular formations, which makes it possible to obtain polymers of necessary orientation. The polar nature of bonds in the epoxy cycle determines the ability of epoxy resins to open up the cycle under the action of nucleophilic and electrophilic hardeners. The curing process of nucleophilic type is polycondensation while electrophilic curing is polymerization on the cationic mechanism. When curing with amines, bonds between the epoxy- and amino-groups as well as ester ones are formed [6].

In the USSR anti-corrosion coatings were usually produced on the basis of epoxy resins developed in the 1950s, their production being started in Yaroslavl. Compounds to be used as hardeners were developed on the basis of polyethylene-polyamines, solution of hexamethylene diamine in ethanol, amino-phenolic and amino-acrylic hardeners being also employed. But since the early 1990s investigations concerning the development of polymer bases for chemically resistant coatings have not been carried out. Nevertheless, epoxy polymers can be modified

by reactive (epoxy and hydroxyl) groups present in their composition, materials with high physical-mechanical characteristics being produced.

Nowadays Russia produces anti-corrosion coating compounds based on imported raw materials, the largest manufacturers of epoxy polymers for the former being Dow Chemical, Shell, Nan Ya firms.

Better chemical resistance is shown by the group of oligomers developed in the 1980s. These are oligomers based on vinyl-ester- and epoxy-vinyl-ester resins (Fig. 1, *b*).

Epoxy-vinyl-ester resins (Fig. 1, *b*) are characterized by high chemical resistance and resistance to mechanical and thermal loads. Introduction of novolac groups into epoxy-vinyl-ester polymers have permitted to improve their chemical resistance to chlorine and strong acids.

Curing of epoxy-vinyl-ester resins is performed with amine or peroxide hardeners, a large group of coatings possessing various combinations of physical-chemical properties being obtained. Curing is characterized by peroxide mechanism of spatial bond formation [6].

Due to the presence of hydroxyl and epoxy groups resin can be modified to obtain reticulate structure polymers having higher resistance. Shrinkage of epoxy-vinyl-ester polymers during curing is moderate, and higher strength of modified resin prevents the microcracks formation. The resin base also improves the adhesion to the surface at the expense of the hydroxyl groups.

Today compounds based on epoxy-vinyl-ester resins are produced for preparing protective coatings of increased chemical resistance. A rational choice of polymer matrix for anti-corrosion coatings implies the selection of the base resin and hardener composition, the selection being based on experimental determination of chemical resistance to the action of various aggressive media.

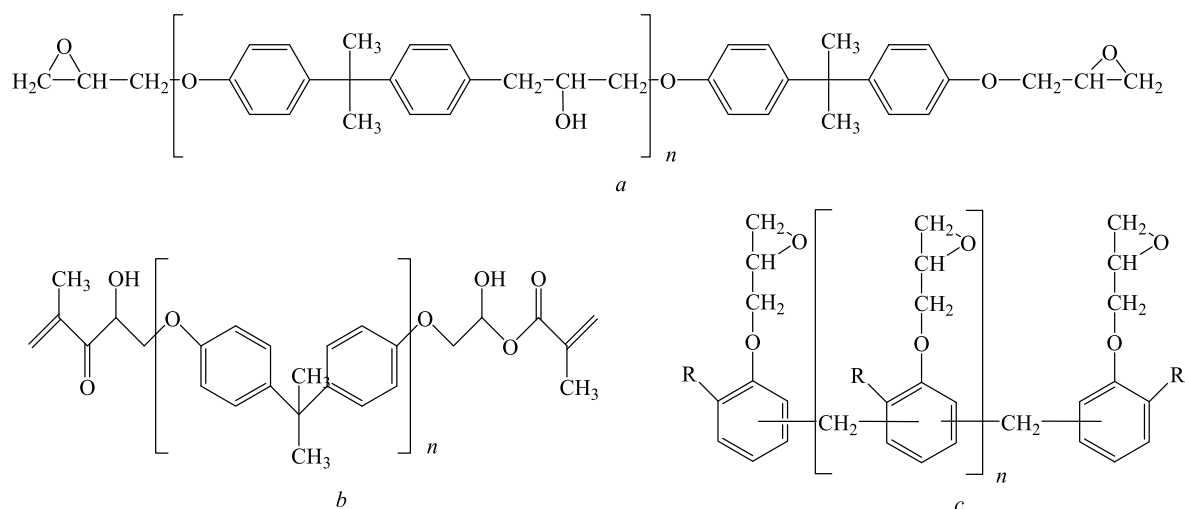


Fig. 1. Chemical structure of epoxy resins:  
*a* – epoxy resin; *b* – epoxy-vinyl-ester resin; *c* – epoxy-novolac-vinyl-ester resin

High corrosion resistance of epoxy-vinyl-ester resins is caused by the presence of  $-OH$  groups providing good adhesion and high strength at the expense of the epoxy base. The presence of  $-CH_3$  groups provides corrosion resistance, and the presence of double bonds is the evidence of temporary unsaturation before curing. Repeating  $-C=C-$  double bonds in epoxidated vinyl-ester resin are the reactive regions that enter the loosely radical reaction. The weakest region for chemical hydrolysis in vinyl-ester resins is the ester group. In the end of the molecular chain there are bonds that provide the possibility of the chain lengthening under mechanical and thermal action. Thus, the development of physicochemical fundamentals of polymer materials chemistry has permitted to produce polymer compounds characterized by higher resistance to different media, allowing to prevent corrosion and to create more durable materials. Lately great attention in the preparation of protective coatings has been paid to the vinyl-ester polymers with the structure of polyester polymers, in which the presence of reactive groups at the ends of macromolecules makes it possible to synthesize polymers possessing different properties. Coatings based on Derakane epoxy-vinyl-ester polymers are also produced by Ashland firm.

Unfortunately, most domestic developers of the resins have stopped their activity. The production of coatings is performed on imported equipment on license technologies, which often prevents consumers of anti-corrosive coatings from making correct choice.

Epoxy-vinyl-ester resins are cured by using the following combination: peroxides (dibenzoyl peroxide, cumene hydroperoxide, methylethylketone peroxide), cobalt naphthenate.

Methyl-ethyl-ketone peroxide (MEKP), a widely used hardener, is a colorless liquid, produced in the form of a 50% solution of two activities. Activity of industrial MEKP depends on the amount of oxygen released during the decomposition of peroxide groups, their number determining the activity of the MEKP (the more oxygen, the

higher the activity). MEKP of low activity (i.e. the substance with smaller amount of oxygen formed and, consequently, lower foaming) is advisable for curing vinyl-ester polymers at higher temperatures. The release of oxygen during curing should be controlled just to avoid the formation of micropores and inclusions in the cured polymer composition. If there is a necessity to carry out curing for a long time it is recommended to use MEKP hardener with inhibitors. For vinyl-ester compounds it is possible to use cumene hydroperoxide as an inhibitor.

Besides, developing effective coatings of improved stability with vinyl-ester resin as a base is possible by applying composite technologies. Composite formulations based on polymeric matrices and inorganic fillers permit to obtain coatings that combine plasticity and durability of the resin with the durability of the fillers. Polymer fillers may be mineral materials and glass, which have been known as such in paint-and-varnish coatings for a long time. But lately the development of technology of obtaining nanocomposites has shown the possibility of controlling the properties of composite materials not only using fillers of different composition but also by varying their dispersion and particle shape [7].

As fillers it is effective to use layered minerals such as clays, mica, vermiculite, vitreous mineral, basalt. Good results can be expected when using fillers prepared from artificially synthesized fibers or glass flakes by their dispergation from the melt. An obligatory condition for making anti-corrosive coatings is their chemical resistance, so by taking into account this characteristic of anti-corrosion polymer coatings it is feasible to use fibers or flakes of chemically resistant borosilicate glass.

Application of products from the finest glass particles, those of iron oxide in the form of flakes of very small thickness provides obtaining dense and strong coatings in which filler particles form overlapping layers, hindering the access of aggressive components (Fig. 2).

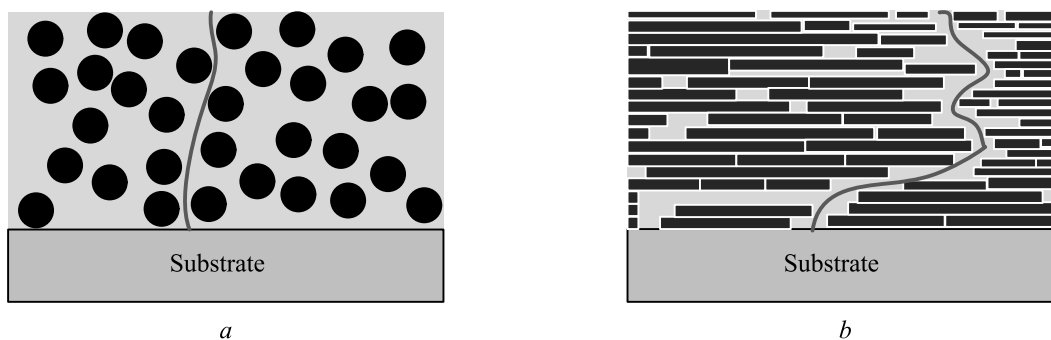


Fig. 2. Scheme of agents influence on coatings with fillers:  
*a* – granular filler; *b* – scaly filler

The properties of composites with mineral fillers are also affected by the chemical composition of the filler, and when using the filler of a particular composition the degree of dispergation and the uniform distribution in the polymer layer are the defining factors. This explains the fact that a rather great work is being carried out concerning the development of compounds and techniques for obtaining composite paint-and-varnish materials [8].

When choosing a combination of oligomer and filler it is important to take into account the nature of the particles, their shape, size, distribution in the

matrix as well as the nature of their interaction in the contact zone.

**Conclusion.** Thus, to prepare chemically resistant anti-corrosive coatings, epoxy-vinyl-ester resins with chemically resistant glass particle fillers in the form of flakes or fibers can be used, allowing the production of dense and durable coatings of the desired thickness. The development of technological parameters for preparing coatings is to be conducted using the results of the study of created coating formulations influence on the chemical resistance of the composite material.

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