

Review article

<https://doi.org/10.15828/2075-8545-2024-16-2-109-124>

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Modern strategies for the creation of polymer coatings. Part II¹⁾

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ABSTRACT

Introduction. Coatings on hard materials are widely used in many industries. Coating technologies help prevent or reduce corrosion, contamination and biofouling, chemical and structural degradation, and wear and tear of external surfaces due to exposure to the elements and natural environments. The range of materials used for functional coatings is wide enough: from organic polymers to hybrid composites and inorganic nanoparticles, depending on the desired properties and functionality of the final product. Despite the excellent anti-corrosion characteristics of non-polymer coatings, their usage causes environmental damage. Organic coatings are among the most widely used. Such compositions are applied in liquid form; organic solvents are one of the major components. Environmental concerns have encouraged the development of alternative technologies. The main areas for development are availability of raw materials and the cost of environmentally friendly coatings. **Results and discussion.** The review substantiates the relevance of research on the development of multifunctional polymer-based coatings. The market for polymer coatings is presented. Methods of surface protection, types of coatings formed, their main components, features of the formation of coatings, the influence of various factors on the formation of polymer coatings, including methods of preparation and pre-treatment of the protected surface are presented. Methods for preventing corrosion are discussed in detail, as well as the primary lines in the development of anti-corrosion coatings based on various protective mechanisms. The characteristics of the main components of protective coatings are given. The issue of destruction of polymer coatings depending on the operating environment is considered in detail. The types of media, their influence and mechanisms of action on protected objects are considered. Factors and mechanisms of destruction of polymer coatings, methods for preventing degradation of coatings are listed. The latest technologies for the formation of protective polymer coatings are highlighted. **Conclusion.** Currently, coatings provide a wide range of quality indicators. An important characteristic of modern coatings is minimal negative impact on the environment, which requires an integrated approach to the design and production of coatings.

KEYWORDS: adhesion, protection, corrosion, coating, polymer, solvent, thermosetting resin.

FOR CITATION:

Vikhareva I.N., Antipin V.E., Enikeeva D.V., Kruchinina P.A. Modern strategies for the creation of polymer coatings. Part II. *Nanotechnologies in Construction*. 2024; 16(2): 109–124. <https://doi.org/10.15828/2075-8545-2024-16-2-109-124>. – EDN: OIQCUA.

2.6. Ingredients of anti-corrosion coatings

To ensure long-term anti-corrosion protection and maintain an aesthetic appearance, it is important to select the right combination of coating components and process stages. The coating formulation includes five main groups of ingredients: binders, solvents, fillers, pigments and additives. Minerals such as magnesium silicate or calcium carbonate are often used as fillers. Their main function is to reduce the cost of the formulation. Typically, fillers do not improve anti-corrosion protection, but

some improve the specific characteristics of the coating: they help increase thermal stability, reduce flammability and smoke formation [100–101]. The author of the work investigated the range of fillers of inorganic and organic nature [102–103]. The choice of fillers used was made with the aim of incorporating production and consumption waste into the formulations of polymer materials to reduce their negative impact on the environment and sustainable development. Renewable raw materials have been tested as organic fillers, which promote the biodegradation of the resulting compositions [104–107]. Excipients

¹⁾ Continuation. Part I has been published in the journal "Nanotechnology in Construction". 2024; 16 (1).

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or functional additives are used in small quantities to solve certain technical problems or improve certain characteristics during production and operation. Examples include thickeners, anti-settling agents, pigment wetting improvers, ultraviolet or heat absorption stabilizers, cure accelerators, co-solvents and plasticizers [108]. Taking into account the development of work to reduce the negative environmental impact of polymer materials, one of the important aspects is the use of environmentally friendly components in the coating formulation. Among plasticizers, esters of aliphatic dicarboxylic acids are classified as non-toxic [109–112]. The author of the article obtained a wide range of similar esters and investigated them for possible use as plasticizers for various polymers [113]. In addition, such additives help to increase the thermal stability of the developed compositions [114].

Solvents

Originally, solvents made up the majority of the coating formulation and were used to dissolve and disperse the components. Solvent plays an important role in the coating and determines how well the coating will perform, as insufficient solvents can cause partial wetting of the substrate, resulting in exposed areas. Formulations often use a combination of solvents to control the rate of evaporation and dissolution of the viscous polymer binder, as well as to improve the solubility of the binder and provide good compatibility with other components while maintaining good film formation. In addition, solvents reduce the viscosity of liquid compositions, which makes it possible to apply the compositions by spraying or immersion.

A wide range of organic compounds are used as solvents, which causes problems from an environmental point of view, effects on the human body, poses a risk of fire or explosion, and requires careful storage.

The European Solvent Emissions Directive has encouraged the development of products with reduced levels of organic solvents, resulting in increased solids content in the formulation, as well as the development of powder formulations and environmentally friendly water-based formulations.

The choice of compound as a solvent for protective coatings depends on environmental requirements, application method, curing process, pigment content and the nature of the substrate. Alternatives include water-based and solvent-free coating formulations.

The solubility of polymers traditional for anti-corrosion coatings, such as epoxy, urethane, alkyd and acrylic, is generally much higher in organic solvents than in water. Binder dissolution in water poses a problem for coating formulators. The largest group of waterborne coatings are water-dispersion coatings. The first type of waterborne dispersion coatings developed were one-component

coatings based on styrene-butadiene and vinyl acrylic polymers. Then chemically curing, waterborne two-component epoxy coatings were developed, the range of which expanded with the advent of new binders [115].

The additives included in water-based coatings are fundamentally different from those used in organic solvent-based coatings. The influence of pigment morphology, surface treatment with inorganic pigments, the influence of anti-corrosion additives, fillers, and the nature of the binder material on the properties of the resulting compositions has been studied in detail in the literature [116–117].

Alkyd, acrylic latex, epoxy, and polyurethane are used in the formulation of water-borne coatings. Alkyd and acrylic latex coatings are widely used for finishing work. Epoxy is dominant for anti-corrosion purposes. Water-based compositions are developed mainly for architectural solutions in the operation of buildings for various purposes; highly effective solvent-based coatings are still widely used for industrial purposes [118].

The main disadvantages of waterborne coatings are related to the use of water as a solvent. For example, although some hardeners such as amine are alkaline in nature and resist flash rust, an effective inhibitor such as sodium nitrate must be included in waterborne coatings to prevent flash rust on welds [116]. Other disadvantages of waterborne coatings are: their inability to withstand freeze/thaw cycles; the influence of relative humidity on the rate of water evaporation; expensive raw materials; drying and formation of a hard coating of latex particles. Water evaporation from waterborne coatings occurs relatively quickly, so edge marks may occur when paint is applied to previously painted areas. Another disadvantage of waterborne coatings is the insufficient time to make corrections to a freshly applied wet coating without brush marks (short “open time”) [118]. Water-based coatings must contain biocides to prevent the formation of bacteria and fungi. Some types of water-based coatings have problems with foam formation [119]. The technical challenges of developing environmentally friendly coating systems are described in detail in a review [120].

Powder coatings are especially often developed for the automotive and mechanical engineering industries. They are produced from both thermoplastic and thermosetting polymers. Commercially available thermoplastic formulations include fluorinated polymers, vinyl and acrylic polymers, polyethylene, polypropylene and polyamides. Among the recently developed coating technologies is sol-gel technology for the formation of hybrid materials. Acrylics, polyesters, polyester epoxy resins, acrylic epoxy resins and polyurethanes are used as thermosetting polymers for coatings [121].

Advantages of powder technology: high efficiency of compositions during application, coating service life, ease of cleaning and processing, environmental friendliness.

Among the limiting points are: large investments in spraying equipment, furnaces, high energy costs associated with firing temperatures, as well as the complexity of the application technology for large and complex elements, a small palette of color possibilities, and the inadmissibility of modifying the film thickness and coating formulation during the application process. A limiting factor is also the presence of large-scale defects in the treated surface, for example, craters. In this case, the application process is stopped, it becomes necessary to remove the contaminated powder, clean the system, and introduce a new portion of powder.

Binders

When choosing the type of binder, it is necessary to take into account the provision of a set of important criteria to be achieved: adhesion of the coating to the metal, mechanical strength and low permeability. The final characteristics of the protective coating are formed precisely at the curing stage and are clearly determined by the chemical structure of the binder. Thus, the anti-corrosion characteristics and appearance of the resulting coating are based on the chemical formula of the resin.

Film formation (i.e., the transition from liquid resin to solid film) can be accomplished by three methods: evaporation of a volatile solvent, chemical reaction, or their combined use. Physically drying and chemically curing films can also be classified by the type of chemical reaction performed or the type of solvent used (Figure 7). Only ambient-curing binders are included in the design because this is the only type of binder that is relevant for heavy-duty coatings intended for large-scale structures. Additionally, hybrid binders (eg., epoxies and acrylic-modified esters) are not included in the design.

Binders for cold chemically cured protective coatings are classified by the type of chemical reaction during the formation of the hard film (Figure 6). Oxidative curing occurs in the presence of a catalyst by absorbing oxygen from the air. Likewise, moisture-curing films, such as those based on zinc silicate, absorb water from the air and cure. Coatings based on two-component systems rely on the reaction between a binder and a hardener (often in the presence of catalysts) and are supplied by the coating manufacturer in separate containers.

Physically drying coatings, depending on the nature of the solvent, can be divided into two subgroups. Typically, physically drying coatings contain large amounts of organic solvents. Water-dispersed coatings, which contain large undissolved molecules dispersed in water, are not used as anti-corrosion coatings due to insufficient performance characteristics. The mechanism of film formation in the case of water-dispersion coatings includes the following stages: evaporation of water, coalescence, changing the shape of particles of the polymer structure, cross-linking of polymer molecules with increased cohesive strength. Binders in waterborne coatings are not subject to transformation. Accordingly, physically drying organic-based solid protective coatings are typically characterized as being partially reversible, i.e. the bottom layer dissolves slightly when the top layer is applied, which improves adhesion between applied layers.

Epoxy binders in the paint and varnish industry have gained great demand due to their high operational and technological characteristics: adhesion to metal, heat resistance, resistance to solvents and chemicals [122], which is ensured by the formation of persistent carbon-carbon and ether bonds during curing [123]. However, during the use of epoxy films, yellowing of the surface occurs when exposed to ultraviolet radiation, which limits their

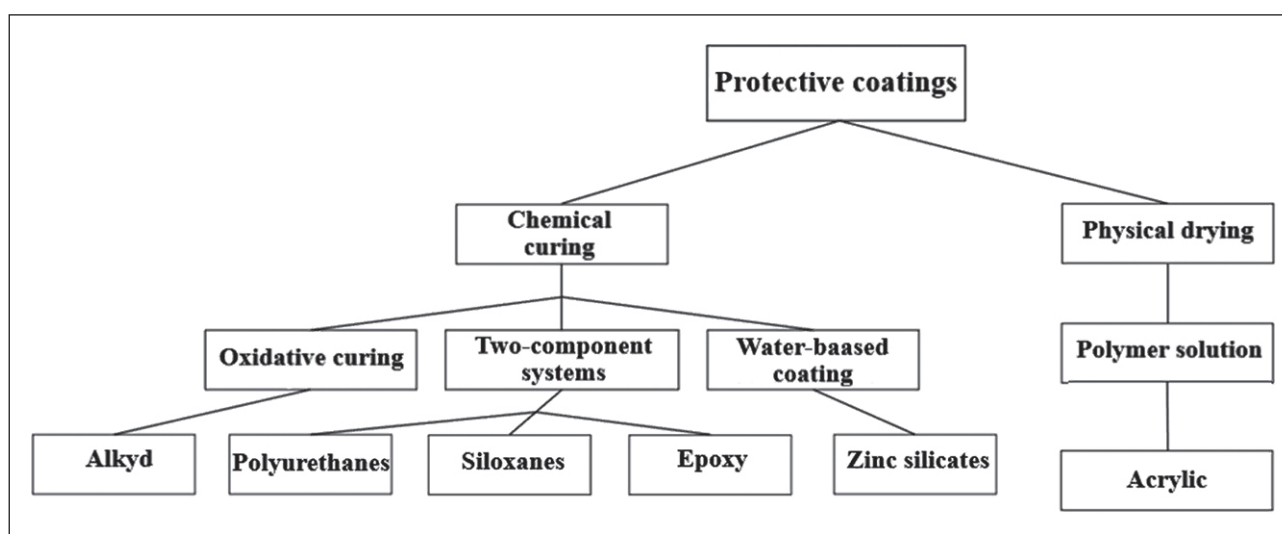


Fig. 6. Classification of protective coatings

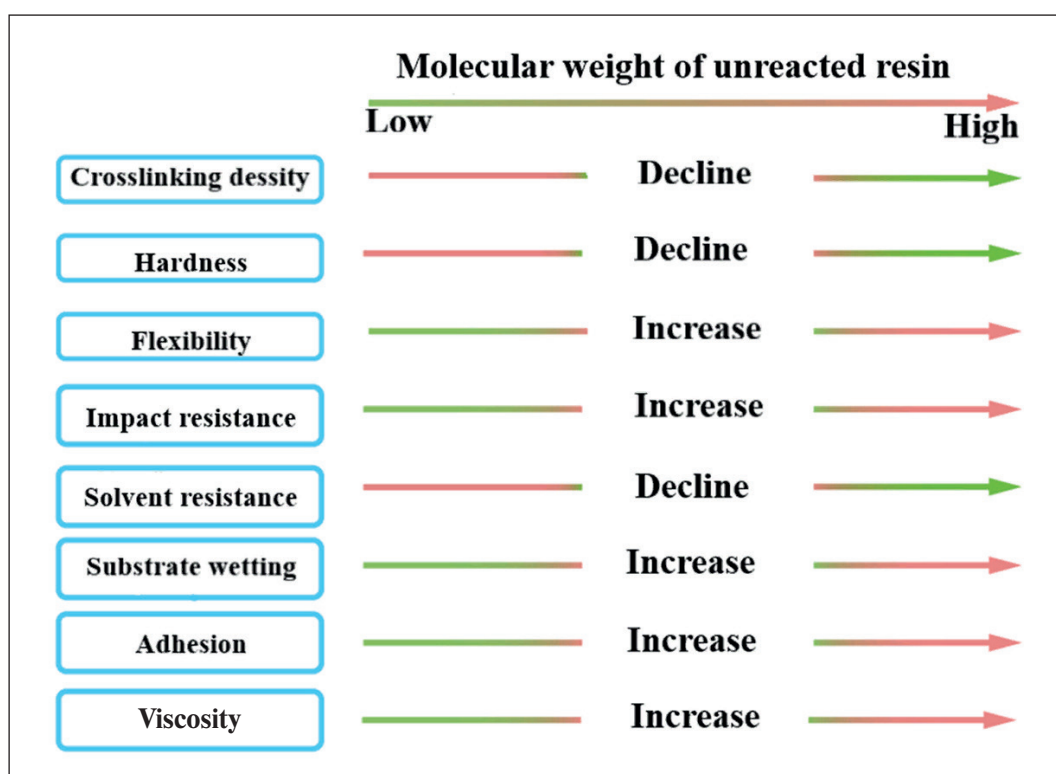


Fig. 7. Relationship between coating properties and structure of epoxy resin

use. Epoxy formulations have been developed that can maintain an aesthetic appearance and are resistant to ultraviolet radiation, but the protective anti-corrosion effect is weak. Therefore, epoxy films are often used as a primer or intermediate layer with a subsequent topcoat, such as a polyurethane-based one, providing color resistance and gloss retention [124].

Solvent-based epoxy coatings have traditionally been used in harsh environments for several decades. The application technology has proven itself, and the list of commercial products is quite extensive [124–126].

For the preparation of solvent-based epoxy resins, the most widely used diphenylolpropane derivatives are bisphenol A (a reaction product of phenols and acetone), bisphenol F (a reaction product of phenols and formaldehyde) and other modified epoxy resins such as epoxy ester and epoxy functional silanes [126]. For very aggressive environments, epoxy novolac coatings are preferred due to their high chemical resistance, which is ensured by the presence of a large number of epoxy groups per molecule compared to products based on bisphenol A and bisphenol F.

The use of epoxy resins of different molecular weights in different ratios makes it possible to develop a wide range of epoxy coatings with different characteristics (Figure 7).

Low molecular weight epoxy resins contain more functional groups per unit weight of resin compared to high molecular weight epoxy resins. This means that coat-

ings based on low molecular weight epoxy resins have a higher crosslinking density than coatings based on high molecular weight epoxy resins. The reduced crosslinking density of coatings based on high molecular weight epoxy resins leads to the formation of products with high elasticity, low hardness, and increased impact resistance [127]. A decrease in crosslinking density worsens the performance characteristics of the resulting coating in terms of resistance to chemicals [128–129]. The high degree of cross-linking of polymer coatings reduces free volume and segmental mobility [130]. Coatings based on high molecular weight resins have higher adhesion to the substrate.

The curing of epoxy resins is based on the opening of the epoxy ring by the active hydrogen atom in the amine hardener (Figure 8).

Traditionally, cycloaliphatic amines have been widely used as hardeners for epoxy materials because the resulting coatings provide a high degree of corrosion resistance. However, such products are gradually disappearing from the commercial market. As an alternative, polyamine and amide hardeners have emerged and are often used as a mixture to control film formation and produce superior coatings. The reaction between polyamide and epoxy resin is less violent and more controlled compared to cycloaliphatic amine [124]. The resulting coating is more flexible, but less corrosion resistant, has moderate resistance to acids and solvents, but is less susceptible to highlighting [128]. The toxicity of amine hardeners has

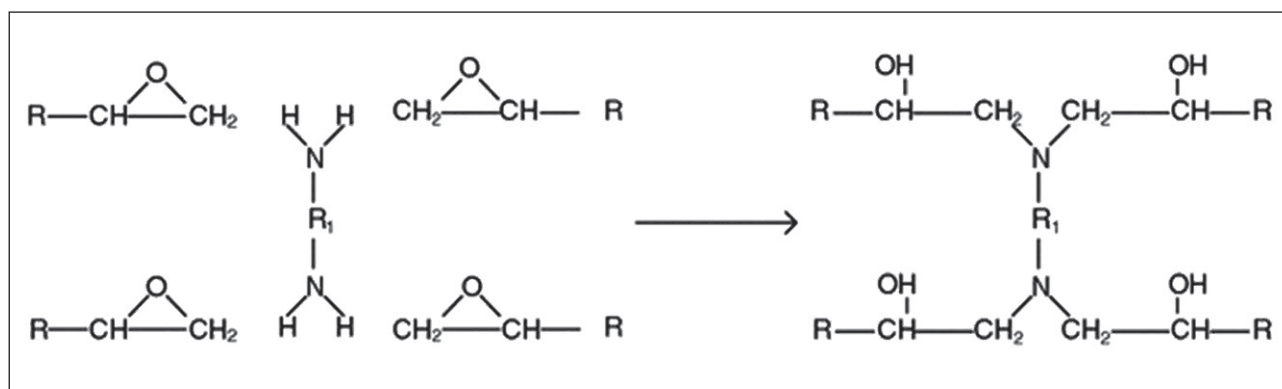


Fig. 8. Mechanism of curing of epoxy resin under the action of diamine

encouraged manufacturers to supply coatings in a form in which the original amine-epoxy adduct exists. These formulations require additional epoxy resin to complete the reaction. However, adducts are used to improve coating performance because polyamines limit reactivity and enhance UV stability and color change while maintaining the important properties of the resulting epoxy-based coatings when cured with an aliphatic amine [128].

Water-based epoxy coatings are produced using two fundamentally different technologies. Initial formulations contained liquid epoxy resins, such as bisphenol A diglycidyl ether, and a water-soluble amine hardener. To cure the resin, aqueous solutions of modified polyamidoamines or polyamides with the addition of a volatile organic acid such as acetic acid are used [131].

The second water-based epoxy coating technology uses a solid epoxy resin that is pre-dispersed in water and solvents. Water is added when the hardener and resin are mixed. In this case, the hardener passes from the aqueous solution into a dispersed epoxy particle and curing occurs. Pre-dispersion of epoxy resin can lead to the formation of heterogeneous films with epoxy and amine or amide domains, which is a key disadvantage of the described technology.

Water-based epoxy coatings are characterized by reduced anti-corrosion resistance compared to coatings based on organic solvents. However, cationic electro-deposited epoxy primers used on automobiles provide excellent corrosion protection due to excellent adhesion in wet conditions [132–133]. Innovations in waterborne, high-zinc primers (e.g., multifunctional resins and hardeners) provide superior corrosion protection for metal surfaces in highly corrosive environments, including marine environments [134]. Although the possibility of using zinc pigments in waterborne coatings poses a significant challenge due to the instability of zinc metal in water. In dilute acidic solutions, zinc releases hydrogen, which reacts explosively with oxygen. Therefore, waterborne zinc pigmented epoxy coatings are typically supplied as three-part systems.

Although modern waterborne coatings have eliminated most of the previous disadvantages, the major differences between waterborne and solvent-based coatings remain [134]. Thus, we can highlight the main advantages of waterborne coatings based on epoxy binders:

- 1) low content of organic solvents;
- 2) excellent adhesion between layers;
- 3) excellent adhesion to problematic surfaces (for example, wet concrete);

- 4) equipment manufacturability;
- 5) plasticization of the coating composition with water.

The main disadvantages of waterborne epoxy coatings:

- 1) short service life compared to organic solvent-based coatings;
- 2) limited gloss stability;
- 3) danger of flash rust on unprotected steel substrates;
- 4) low chemical resistance;
- 5) low rate of water evaporation at high humidity.

Acrylic polymers and copolymers are quite in demand in the protective coatings market due to their good adhesive and film-forming properties, photostability, non-wetting, chemical inertness, resistance to hydrolysis, and resistance to environmental influences and ultraviolet radiation during prolonged exposure [135]. However, acrylic automotive clear coats are susceptible to weathering. Modification of acrylic compositions by introducing epoxy resins, silanes and carbamates made it possible to solve this problem. Latex acrylic compositions exhibit high resistance to hydrolysis and UV radiation compared to formulations based on organic solvents. But such coatings are not chosen for constant and long-term immersion in water or soil [136].

Solvent-based acrylic coating technology has a strong position in the anti-corrosion segment. The main advantages of the technology compared to water-based systems are improved adhesion, quick drying and high strength.

The starting materials for the production of acrylic resins are acrylic and methacrylic acids or their esters. In this case, hard coatings are formed due to the evaporation of the solvent. Curing using isocyanates or amino

resins as crosslinking agents is possible. Curing does not depend on the solvent; the use of a catalyst significantly speeds up the process, for example, organometallic compounds or tertiary amines in an amount of 0.1–1.0 wt. %.

Modification of methacrylic resin with epoxy compounds made it possible to obtain coatings with high chemical and corrosion resistance while maintaining hardness and impact resistance [137].

Waterborne acrylic coatings on an industrial scale have helped reduce VOC emissions. Such compositions do not have a high anti-corrosion effect, like electrodeposited epoxy primers, but single-layer coatings are quite suitable for external use and are sufficient to provide the necessary characteristics.

Blends of copolymers and acrylic latexes allow high protection and durability to be achieved even at low thicknesses. The acrylic base is also used to develop radiation-curable coatings, which further contributes to expanding the range of environmentally friendly compositions [138].

Polysiloxanes, polymers containing the Si–O group, are synthesized from monomeric building blocks (Figure 9).

Polysiloxane coatings have excellent gloss with color retention, but the physical and mechanical properties of the resulting products are insufficient. Increased durability compared to carbon-based formulations is associated with a stronger silicon-oxygen bond – 443 kJ/mol. The strength of the carbon-carbon bond of organic binders is 360 kJ/mol [139]. To catalyze the curing of polysiloxane coatings, organic metals or compounds that react with the side groups of polysiloxane are used. Siloxane can react chemically with epoxy, acrylic or other organic compounds to form hybrid siloxane coatings. Epoxy modified siloxane provides improved gloss and color retention. The anticorrosion properties of bisphenol A diglycidyl

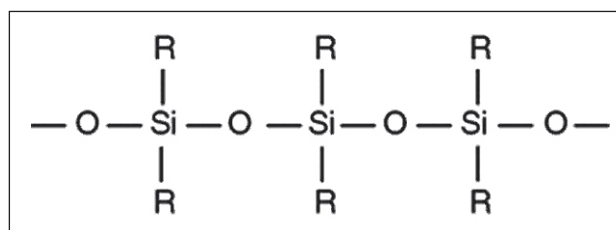


Fig. 9. Polysiloxane frame

ether were improved by modification with OH-terminated polydimethylsiloxane [138].

Zinc silicates are inorganic coatings that provide cathodic protection. The curing mechanism occurs when exposed to moisture from the atmosphere and is a reaction between polysilicic acid and zinc metal. The main amount of metallic zinc particles is surrounded by an insoluble layer of zinc silicate (Figure 10) [140–141]. The curing process is also believed to depend on the reaction between the zinc and the steel surface. In this case, to obtain a coating, the moisture content in the atmosphere is important – at least 50–60% [142]. Otherwise, the formation and precipitation of silica occurs and the required specified coating strength will not be obtained.

Ethyl silicate binders based on organic solvents usually exhibit greater protective effectiveness than water-based metal silicates, despite the formation of ethanol as a by-product during polymerization [143].

Alkyd resins are a type of polyester resin produced by the reaction between oils or fatty acids, polyols and a dibasic acid or anhydride such as phthalic anhydride, isophthalic acid or maleic anhydride [144]. Varying the amount of fatty acids and oils makes it possible to obtain alkyd resins with a wide range of properties [145].

Alkyd-based coatings are characterized by good adhesion, flexibility, durability and durability. Alkyd coatings

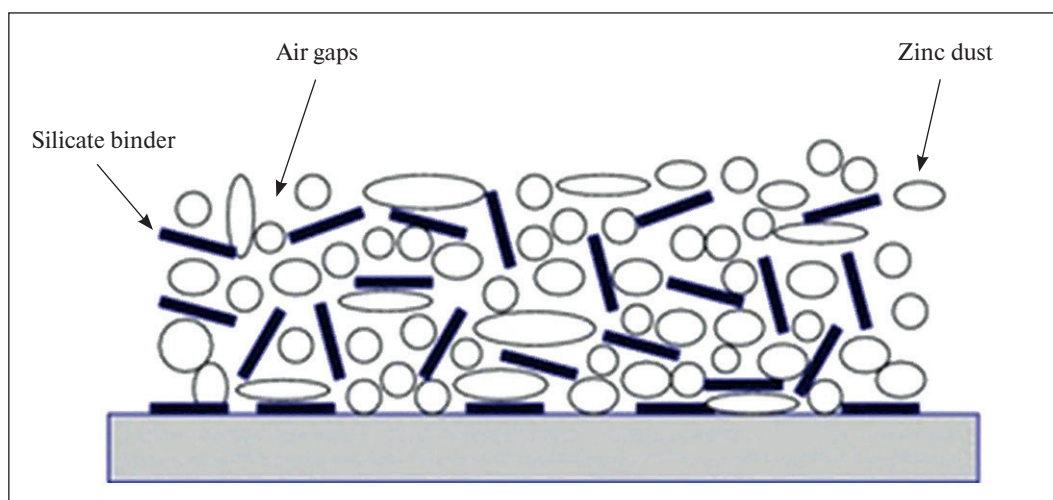


Fig. 10. Scheme of porous coating

are often used in aggressive environments as primers in conjunction with an inhibitory pigment, where the influence of water on the surface is not too great. However, their use in aggressive environments can lead to hydrolysis of the ester groups of the alkyd resin [144]. Saponification is a common problem when selecting alkyd primers for application to galvanized surfaces [145–146].

Solvent-based alkyd resins are the most widely used. Curing of oil chains in an alkyd coating proceeds through an oxidative mechanism, as a result of the action of oxygen in the air. In this case, the presence of catalysts (organic complexes of transition metal ions) is important [146].

Modification of alkyd resins to achieve improved characteristics can be carried out during the production process, using components of urethanes, polyamide, silicone or vinyl resins for this purpose. To develop anti-corrosion water-borne systems based on alkyd resins, modification with maleic acid is used, which makes it possible to increase compatibility with water. It has been found that coating properties are improved either by incorporating acid resins or multifunctional acrylates into the formulation, or by modifying the alkyd resin with methyl methacrylate.

An advantage of polyurethane coatings is their excellent weather resistance [43, 45]. Therefore, they are often used as finishing coatings. Polyurethane coatings provide improved performance, which is an essential performance criterion for industrial applications. Another advantage is the ability to “self-heal” (scratch resistance) due to the formation of hydrogen bonds. Polyurethane coatings are commercially available [148].

Among the important disadvantages of most polyurethane coatings are low resistance to mechanical deformation and thermal stability [148].

Polyurethane coatings can be one-component (moisture-curing) or two-component.

Solvent-based PU coatings are formed as a result of the reaction of an isocyanate with compounds containing an active hydrogen atom (for example, a hydroxyl or amine group) [149] (Figure 11).

The presence of cross-links in a solvent-based polyurethane cured coating provides increased tensile

strength, abrasion resistance, chemical resistance to acids, alkalis and solvents. The listed qualities are very significant in the case of industrial use of coatings. In general, curable PU films have high potential due to their ease of synthesis and processing, high glass transition temperature, ability to form high-quality films, and good solvent resistance.

Aliphatic PUs exhibit high resistance to UV radiation and maintain aesthetic characteristics. Therefore, they are often used for outdoor applications and where color stability is important. However, such polyurethanes are more expensive than those obtained using aromatic compounds.

A negative factor in the use of polyurethane coatings is the isocyanate method for producing intermediate compounds. In this regard, the authors of this work are conducting research on replacing toxic components to obtain this polymer [43, 45]. As raw materials for the production of alternative non-isocyanate polyurethanes, cyclocarbonates based on epoxidized soybean oil and epoxy resins ED-20 and ED-16 were obtained by carbonylation [43]. Calculations using machine learning were carried out to identify optimal synthesis parameters for obtaining key components [45].

Water-based polyurethanes are usually two-component systems in the form of separate aqueous dispersions of polyol and isocyanate. Such coatings exhibit low chemical and corrosion protection and are rarely used as anti-corrosion coatings [150]. Proper dispersion of constituents poses a challenge to coating formulators.

In the paint and varnish industry, several other types of binders are used to formulate anti-corrosion coatings.

Chlorinated rubber coatings are physically drying one-component coatings based on solutions of chlorinated rubber in organic solvents. This type has good water resistance and is widely used as industrial coating, on ships and offshore structures above and below the waterline. Accordingly, the resistance of such coatings to organic solvents is low [138, 139]. Protective films based on chlorinated rubber have low thermal stability and emit hydrogen chloride at high temperatures [151].

Vinyl coatings are one-component formulations based on solutions of various copolymers and polyvinyl chloride in organic solvents. They do not provide high thermal stability and decompose at high temperatures, releasing hydrogen chloride. However, vinyl-based films are widely used in various industrial environments, even in quite aggressive applications, including acids and alkalis, but exhibit low resistance to organic solvents. Vinyl coatings for use below the waterline are modified with tar [152].

Epoxy esters are one-component coatings in which the binder is synthesized by the reaction of an epoxy compound and an alkyd. The curing mechanism of epoxy esters is based on oxidation by atmospheric oxygen. Such films dry quickly. Compared to alkyds, they are harder and chemically resistant, but tend to chalk [133].

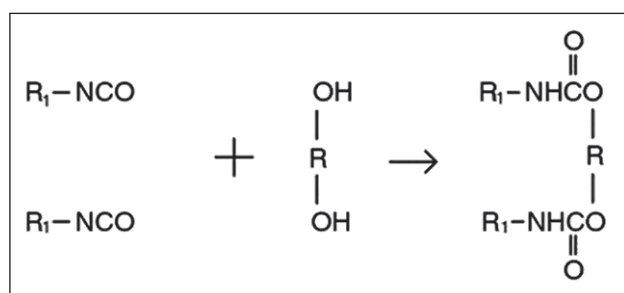


Fig. 11. Curing of isocyanate with diol

Polyester coatings are high-strength coatings reinforced with glass flakes that are applied in thick layers, often 500–1000 μm thick [133]. To chemically cure them and speed up the process, catalysts are used, for example, cobalt octoate and some amines. The coatings exhibit very high abrasion resistance and excellent resistance to aqueous environments. However, polyester coatings have a short service life [149].

Cement coatings are two-component coatings based on a mixture of cement with water or latex solution. The coatings are highly alkaline and exhibit passivation properties to the steel substrate [150]. This mechanism is used to maintain reinforcing iron in concrete [136].

Bituminous coatings are one-component formulations, based on physical drying, obtained from the residues of the fractional distillation of crude oil. This type of coating has limited resistance to UV radiation. Disadvantages and mechanical fragility can also be noted among the disadvantages. Coatings can only be produced in black or brown, which limits the potential areas of use. Excellent for elements immersed in water and widely used in areas with high humidity [136].

Tar-based coatings are a type of physically drying one-component compositions obtained from pyrolysis residues of carbon-containing raw materials (for example, coal). The anti-corrosion protection mechanism is based on the barrier effect; they do not contain anti-corrosion pigments. Coatings are highly water resistant and resistant to dilute solutions of alkalis and acids, but are susceptible to sunlight and are considered carcinogenic [136].

Coal tar epoxy coatings are two-component coatings in which the epoxy resin is modified with coal tar. The modification results in increased flexibility and water resistance and also reduces the cost of the coating. Such coatings do not contain anti-corrosion pigments and protect steel due to the barrier effect. Coal tar epoxy coatings are widely used for submerged structures. Disadvantages of coal tar epoxy coatings include sensitivity to sunlight and discoloration during application, and carcinogenicity. Many countries already have restrictions on such coverages [136].

Pigments

The ratio of pigment and binder is an indicator that determines the production of coatings with the required characteristics [153–155]. Pigment volumetric concentration (PVC) indicates the proportion of pigment and fillers in a dry coating [156]:

$$\text{PVC} = V_p / (V_p + V_b), \quad (1)$$

where V_p is the volume of fillers and pigments,

V_b is the volume of binders (polymers, resins, plasticizers).

Critical pigment volume concentration (CPVC) is a concept that was first used in 1949 [157]. CPVC is the amount of pigment at which the polymer matrix is sufficient to wet and fill the voids between individual particles of pigment and filler. To determine the CPVC, an express method is often used, which consists of determining the amount of linseed oil absorbed by the pigment. However, flaxseed oil is completely different from polymers and oligomers and, accordingly, the CPVC value obtained by this method is based on assumption and is not accurate. Other experimental methods, for example, determination of density and optical properties, give more plausible results [158–161], but such methods are labor-intensive, as they require studying changes in the properties of the coating in the range of volume pigment concentrations.

When compiling coating formulations, it is convenient to use another indicator – the ratio between PVC and CPVC, λ . Therefore, for $\lambda \leq 1$, a dry coating can be represented as a composite consisting of pigment particles randomly embedded in a continuous polymer matrix. When $\lambda \geq 1$, the polymer matrix is not enough to cover the entire surface of the pigment. Therefore, voids filled with air are formed, which dramatically affects the mechanical, thermal, transport and optical properties of the coating [156, 162–164].

To a certain extent, any particle included in a coating that is impermeable to aggressive substances provides barrier protection [165]. However, a certain type of pigments is designed exclusively to provide the barrier properties of a polymer film, which is to prevent the migration of aggressive substances to the surface of the substrate. Basically, plate-shaped pigments are located parallel to the surface of the substrate and create a tortuous path for the diffusing particles to the substrate (Figure 12). In addition, lamellar or lamellar pigments enhance the mechanical properties of the coating. While in coatings containing spherical pigments, aggressive substances easily penetrate through the coating layer.

The most widely used flake pigment for anti-corrosion barrier coatings can be considered mica iron oxide, a type of hematite (Fe_2O_3) [166–167]. The effect of the diameter of Fe_2O_3 particles on the adhesion and corrosion resistance of the coating was studied in [168]. The smallest particle size provides the best anti-corrosion protection. Depending on the type of binder in pigmented coatings with Fe_2O_3 , anti-corrosion characteristics are achieved with optimal λ values corresponding to the range of 0.67–0.82 [169].

Flake aluminum pigments are also commercially available in sheet and non-sheet grades. Their surface for use in formulations is usually treated with stearic acid to reduce surface tension. Due to the difference in surface tension between the coating and the treated surface of aluminum pigments, the particles are oriented toward the top of the coating when the coating is applied. In the case of oleic acid stabilized non-sheet aluminum pigments, the

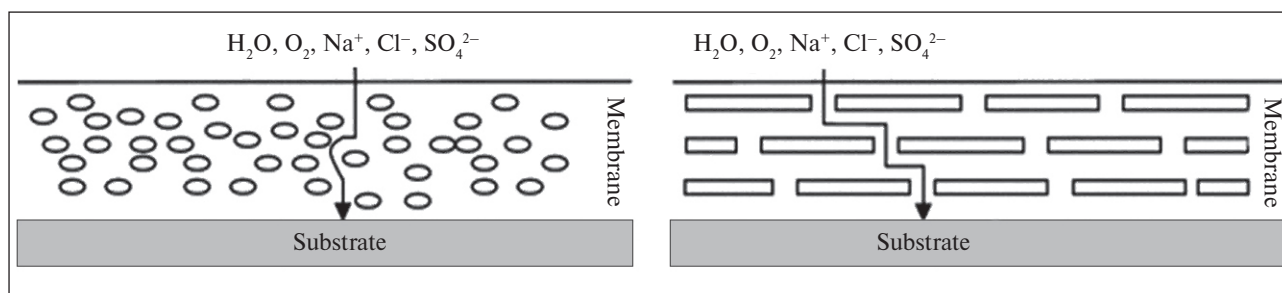


Fig. 12. Barrier effect of pigments

particles are uniformly distributed throughout the film [170]. For the preparation of barrier coatings, mainly sheet aluminum is used, which is used in the form of a paste to facilitate mixing of the composition. However, the use of aluminum sheet in anti-corrosion barrier coatings has little effect on the cathodic disbondment rate unless the coating is applied directly to the steel in the first layer [171–172]. Aluminum is slightly corroded and can act as a buffer by reacting with OH ions produced by the cathodic reaction and reducing cathodic stratification [173]. This theory is confirmed by microscopic and electrochemical studies of aluminum pigmented coatings [174–175].

Flake glass pigments are used less frequently in anti-corrosion barrier coatings. The large particle size (100–400 μm) limits their use only in thick coatings. Despite the flakes' impermeability to oxygen and moisture and their reflective properties, glass pigments do not improve cathode stratification resistance [176].

In addition to these pigments, barrier coatings use other inert or chemically resistant pigments, such as titanium dioxide, and fillers, such as silicates.

The anti-corrosion properties of tread coatings are largely determined by the amount of metal pigments. Any metals that are electrochemically more active than the substrate being protected can be used as sacrificial pigments in anti-corrosion coatings. However, currently, zinc particles are the most widely used among sacrificial pigments. The ability to protect the substrate from corrosion is significantly affected by the size and shape of the pigment. Small spherical particles provide higher anti-corrosion protection than large ones. For spherical zinc particles, the best anti-corrosion performance is achieved with an average diameter of 2 μm [177]. This is explained by the filling of free spaces between smaller zinc particles. In the case of larger particles, the pores are not completely filled with zinc corrosion products, which increases the permeability of the coating [177]. By widely distributing the equivalent size of spherical particles, the packing ability of the particles can be improved [178]. Accordingly, improved sealing reduces porosity and permeability while increasing the number of electrical contact points in high-zinc coatings and more galvanic current can be transferred from the metal surface.

The influence of the shape of pigment particles is due to the larger surface area to volume ratio of non-spherical particles compared to spherical ones [176]. To obtain a high degree of corrosion protection, fewer particles of lamellar zinc are required than of spherical zinc: the larger surface area of the lamellar provides better electrical conductivity [177] and lower permeability. The use of a combination of lamellar and spherical zinc particles [178] made it possible to significantly reduce the pigment content without reducing the protective effect.

The protective mechanism of zinc metal particles is the formation and precipitation of insoluble corrosion products. In epoxy coatings with a high zinc content, cyclic corrosion tests revealed the insoluble compound ZnFe_2O_4 in areas with defects [179]. The introduction of zinc-ferrite pigments into the compositions increases the protective effect [180]. The diagram in Figure 13 shows the dependence of the potential on the acidity of the medium, that is, on the amount of ZnFe_2O_4 in the Fe–Zn– H_2O –Cl system at 25°C.

High costs for zinc raw materials contribute to the development of compositions with a reduced amount of zinc in coatings. To reduce corrosion, it is possible to use partial replacement of zinc particles with conductive pigments [181]. Carbon black has been studied for this purpose, but conflicting results have been obtained [182–184]. For example, in the automotive industry, on fasteners and bicycle parts, the need to increase the service life of the coating has led to the partial replacement of zinc with zinc alloys [185–186]. The high corrosion resistance of alloyed zinc under atmospheric conditions has been well studied and described [187–188]. For corrosion protection, Zn–Ni, Zn–Co, Zn–Mn, and Zn–Mo alloys are widely used [189–196]. Their protective mechanisms are not fully understood. For nickel-alloyed zinc, the resulting nickel alloy layer is believed to act as a protective barrier and enhance corrosion protection [197]. It is assumed that in the Zn–Mn system the formation of zinc and manganese hydroxo salts occurs, which increase the durability of the coating.

Inhibitory pigments are classified into anodic and cathodic. Cathodic inhibitors, such as inorganic magne-

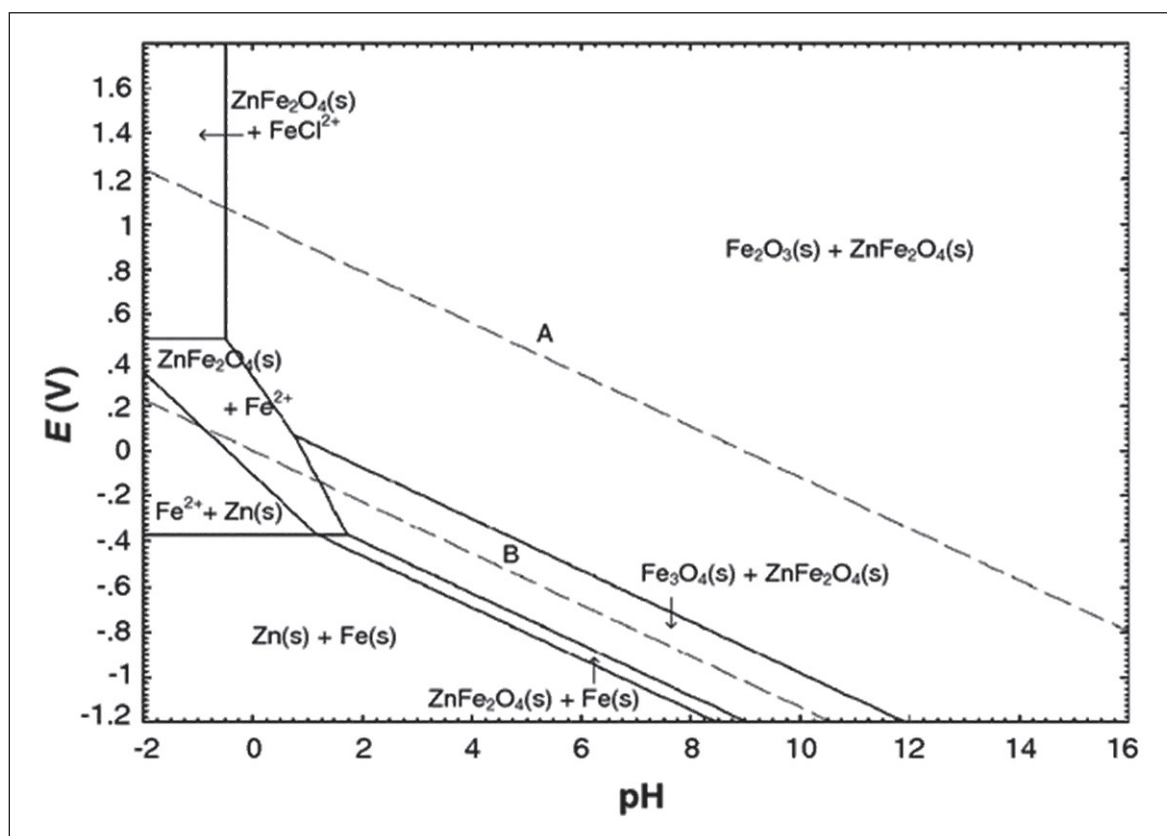
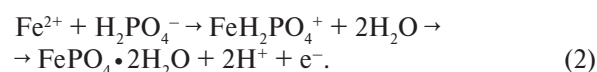


Fig. 13. Diagram of the composition and potential of the system

sium and manganese salts, inhibit corrosion by forming insoluble compounds with hydroxyl groups in the form of deposits. These pigments increase cathodic resistance to polarization. In acidic environments, inhibitors increase the concentration of H^+ ions at the cathode and enhance the polarization process. Anodic inhibitors, for example, inorganic salts - phosphates, borates and silicates, form a protective oxide film on the metal surface. Anodic inhibitors reduce the corrosion rate by increasing anodic polarization [198]. In case of insufficient amount of anodic pigment, an undesirable anode is formed towards the cathode region and an increase in the corrosion rate occurs [199]. An insufficient amount of cathodic inhibitory pigment reduces the corrosion rate as the active cathodic area decreases.

Currently, phosphate pigments are the most widely used type of inhibitory pigments in the paint and varnish industry [200]. In particular, zinc phosphate [200–203] has been studied in compositions based on various binders. Overall, zinc phosphate provides good performance for industrial applications. Zinc phosphate protection of a steel substrate is based on passivation of the metal surface [204–205], and the salt's protective mechanism involves polarization of the cathode regions due to the deposition of insoluble basic salts on the surface according to the reaction (2):



It has been proven that the best anti-corrosion coatings containing zinc phosphate are obtained at low PVC values of about 0.7 [206].

Modification of zinc phosphate with molybdenum or organic inhibitors improves the corrosion resistance of inhibitor coatings in highly contaminated industrial environments. Molybdate ions are absorbed on the surface of the steel, repassivate corrosion pits in the steel and provide an inhibitory effect. Polarization measurements have shown that the protective anodic film formed on steel suppresses oxygen reduction by blocking active cathode centers [207–209].

For many years, inorganic lead salts and chromates have been used as pigments in protective coatings [210], which are toxic and carcinogenic, and their use has declined [211]. In this regard, the search for “non-toxic” inhibitors that provide the same degree of protection is relevant.

Zinc and strontium chromates are capable of passivating metals and have long been used in coatings for various applications [212]. The inhibitory effect of these pigments has not been fully studied, but it is known that it depends on the leaching of chromate ions into solution [213]. The passivation of aluminum alloys with chromium salts has

been studied in detail [214–217]. Chromate ions (Cr^{6+}) in solution are reduced to Cr^{3+} and balance the anodic oxidation of the metal substrate, so Cr^{3+} ions are present in the surface layer [214].

Some studies have determined that the protective film is formed from a layer of hydrated chromium(III) oxide on top of a layer of mixed alumina [218]. There is also another opinion on this matter: the protective layer is formed directly by chromium (III) hydroxide [218–219]. The structure and composition of the resulting protective layer depends on several factors, such as pH and potential.

Studies on chromate passive layers on zinc are poorly represented in the literature, but a passive Cr^{3+} film without zinc has been reported [220].

Another group of inhibitory pigments are spinel-type pigments based on mixed metal oxides [221]. Spinel-type pigments are crystalline substances. The first generation of

spinel pigments was based on a combination of two ferrites with a lattice structure (ZnFe_2O_4 , CaFe_2O_4). The protective mechanism is associated with the formation of zinc and calcium soaps as a result of reaction with the binder, which simultaneously increases the mechanical strength of the coating and reduces its permeability to aggressive environments [222]. The anticorrosion resistance of coatings with spinel pigments is significantly improved by including pigments of the following types: $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ and $\text{Ca}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ [223]. In industrial conditions, the anticorrosion characteristics of coatings containing them were superior to coatings containing Zn–Al phosphomolybdate, which is more effective than zinc phosphates [224]. The promise of spinel-type pigments lies in the reduction of toxic effects compared to most pigments used in inhibitory coatings.

To be continued.

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The authors declare no conflict of interest.

The article was submitted 11.01.2024; approved after reviewing 02.02.2024; accepted for publication 06.02.2024.