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CORROSION PROTECTION OF METALS: PROSPECTS OF PRODUCTION AND APPLICATION OF URALKYD MATERIALS (REVIEW)

Uralkyd oligomers are considered to be promising film-forming. They are widely used in the production of high-quality paints and varnishes for various purposes (primeres, paints, priming-paints). The success of these materials is due to the high properties of coatings formed. These coatings have high adhesion, strength properties and corrosion resistance. The advanages of these materials is feedstock availability, low cost compared to other polyurethanes, their usability. Uralkyd materials is one-component and low-toxicity system. So they are promising in the protection of various metal from corrosion. Uralkyd oligomers sufficiently versatile in use. They can be applied a lot of methods and combined with many types of paints (nitrocellulose, chlorinated rubber and oily alkyd oligomers). They can be used at the factory painting and refit painting of metal products.

Key words: uralkyd oligomers, diisocyanate, corrosion protection, alkyd oligomers, repair coatings.

Introduction. Corrosion protection is the most important scientific and technical, economic and environmental problem, particularly for the industrialized countries with large metal reserves. Therefore, the requirements for operational and technical reliability, corrosion resistance and protection methods improvement of structural materials are steadily increasing.

Currently, the corrosion problem is becoming more urgent due to a rapid ageing of metal reserves, depreciation and obsolescence, lack of reconstruction and equipment renewability. Constant, intensive development of metal-intensive industries such as heat power industry, atomic engineering, chemical and petrochemical industries, contribute to the growth of corrosion losses. Exaggeration of operating conditions of metal products, i.e. the use of elevated temperatures, pressure and aggressive growth also promote corrosion losses. According to literature references data [1], each year about a quarter of the metal produced in the world is destroyed as a result of the interaction of metal structures with a corrosive environment. Reconditioning of equipment, different constructions and structures made of metal, the use of expensive methods of protection against corrosion, as well as control over the corrosion rate require significant material costs. According to calculations made in the USA all these costs amount to 80 billion dollars annually [1, 2]. Direct losses from corrosion are on the average about 4–5% of the national income of industrialized countries. In the Russian Federation, for example, the annual loss of metals due to corrosion is up to 12% of the total weight of the metal reserves, which corresponds to the loss of up to 30% of annual metal production [1, 2].

However, in many cases, due to the indirect costs caused by production lines downtime, reduction of equipment productivity and product quality, the damage can be several times the cost of repairs and reconstruction of metal structures and equipment.

Particularly difficult is the situation in the transmission, flow- and process pipelines of oil and gas transportation, recovery and processing. Half of Russia's oil pipelines were built 30–40 years ago; therefore, tens of thousands of failures are quite natural, 90% of these being due to corrosion. According to environmentalists, from 8 to 10% of the oil recovered is lost in the process chain "from the oil well to the consumer". In construction, support structures with expired service life account for more than 60%, which constantly threatens us with technogenic accidents and large economic losses. The depreciation amount of fixed capital stock is increasing [1–3].

Main part. To combat corrosion on steel structures there are more than 20 different ways of protection: alloying at a metal manufacturing stage, inhibition, electrochemical protection, metallization, etc., many of them being designed for temporary protection. To date, the most common method of corrosion protection is the application of paint (paint coatings share is about 85% of all the ways to combat corrosion) which prevents the penetration of moisture and corrosive gases to the surface of a metal. Ideally paint to prevent corrosion and mechanical damage should have a high penetrating power into the painted object voids (washouts, clearances, roughness, surface microfractures), high adhesion, good elasticity, low moisture and water absorption. It should also form high-strength insulating films on the metal surface [3, 4].

The attractibility of anti-corrosion protection is the variation in the choice of paint coating systems (PC), as well as its operational, technological and economic characteristics, which allows to choose their optimum combination. Optimal use of Pc is possible only with a deep understanding and taking into account all physical, chemical and mechanical phenomena occurring in the paint system in the process of its obtaining and exploitation. Typically, paints and varnishes (PV) form a multi-layer PC consisting of primer, intermediate and coating layers, referred to as a Pc system, each layer of which performs a specific function. After drying the primer forms a homogeneous film with good adhesion to the painted surface, providing adhesion of the PC upper layers with the painted surface. Intermediate (second) primer is designed to provide high-quality surface for the final color, high adhesion both to enamel and anticorrosive primer, improvement of the physical and mechanical and protective properties of the complex PC system. Enamels, paints and varnishes give the Pc system decorative and protective properties.

In addition, when choosing the paint coating system we must take into account how much the surface is subjected to thermal, mechanical and chemical stress and UV radiation. Combining different paints and varnishes allows to obtain a coating having a full range of positive characteristics [5].

Choice of anticorrosion primers in the PC system should be given special attention, since it determines the nature of the interaction between the coating and the metal surface. The range of primers for steel and cast iron is quite diverse. Galvanized steel and aluminum can be primed with acrylic, alkyd, urethane and epoxy primers. The range of primers for anticorrosion steel, copper, magnesium and titanium alloys is very limited [6, 7].

Compatibility of each layer and the total thickness of the coating determine the life of a PC system. In case of poor adhesion between the layers in the coating operation (under the action of internal stresses) there may occur such damage as cracking, blistering, peeling, which leads to the appearance of corrosion in the final layer and significantly reduces the service life of PC [8].

The PV spectrum applied for corrosion protection is very wide. They differ both in application areas (construction, petrochemical industry, transportation, marine transportation, etc.) and by the type of film-forming agent (polyurethanes, epoxies, alkyds, etc.). PV brand assortment currently has more than 2,500 titles, which, on the one hand, widens the desired properties of coatings but on the other hand, makes their choice and effective use difficult. Coatings resistance is primarily determined by the properties of film forming agents. For temperate climate the range of coatings is very broad, their weather resistance (depending on the type of film-forming substance) may be from 2 to 15 years. Alkyd PVs provide a lifetime of 2–4 years, urea- and melamine-alkyd – up to 8 years. Developed over the past decade, new modified materials allowed to increase the service life of coatings: alkyd-urethane – up to 8 years, acryl-urethane, epoxy-ether – up to 10–15 years, powdered polyether – over 15 years [6, 9, 10, 11].

Alkyd materials hitherto are widely used for corrosion protection of metals, but one of their main drawbacks is the long drying time. In this regard, one of the areas of metal corrosion protection is the use of modified alkyd PVs. The range of such materials is quite wide, but in natural conditions the time required for the formation of coatings on their basis can be several days. Therefore, the researchers of the Republic of Belarus, are working hard to create a modified alkyd PV (alkyd-styrene) characterized by accelerated drying and high anti-corrosion and mechanical and physical properties. Research is being conducted in the direction of creating anticorrosive fast-drying alkyd-styrene primers of natural cure [12]. Necessary protective and anticorrosive properties are achieved by the action of driers (in optimal concentrations) of different nature on coating structure based on styrene-alkyd film former. Simultaneously, we reveal coatings protective properties dependence on quantitative and qualitative composition of a pigment [13–15].

One of the most widely used materials for corrosion protection of steel structures are PVs based on polyurethane, which provide the most effective and long-term protection (up to 15–20 years). Polyurethane-based coatings have many advantages: high weather-, water- and oil resistance, gas-tightness, excellent dielectric properties. They are resistant to acidic media and organic compounds. They are characterized by a good set of physical and mechanical properties: hardness, elasticity, resistance to abrasion. They can withstand thermal gradient from 50 to 130°C. What concerns different aggressive factors (gases, acids, alkalis, aromatic hydrocarbons) polyurethane PCs surpass most famous paint PCs. The disadvantages of the polyurethane material include increased toxicity, relative high cost and yellowing of the PC when operating under atmospheric conditions [16, 17]. Despite numerous advantages of polyurethane PV, they account for only 5% of all world PV production. The reason for such a small volume of production is high cost of raw material, as well as high requirements for the production standards. For example, one of the requirements for the production of polyurethane PV is the production of stainless steel processing lines to prevent the entry of iron oxides in the paint, which can lead to reduced storage time and viability. A condition necessary for the development of formulations of polyurethane compositions is the use of components containing practically no moisture [17–19].

An alternative to polyurethane materials, when used in some areas, can be uralkyd (alkyd-urethane) materials and coatings based on them. Uralkyd materials are one of the major types of polyurethane binders for paints and varnishes. Wide prevalence of alkyd-urethane materials is due to their low cost and availability of diisocyanates, as well as to the convenience of working with them, compared with two-component polyurethane systems: lower toxicity, ease of pigmentation, the ability to be applied by all dyeing methods [20].

Uralkyd oligomers are well aligned with physically drying film formers (nitrocellulose, chlorinated rubber, and fatty alkyd resins) and dissolve in aliphatic and aromatic hydrocarbons, terpenes, alcohols, ketones, ethers and esters [20, 21].

Uralkyd PVs have high decorative and protective properties, and are universal in application. They are intended for coloring of metallic and nonmetallic surfaces, which are subjected to high decorative appearance and protective properties demands in an open industrial atmosphere and drying time. Areas of application are diverse: painting of municipal transport facilities, road and construction equipment, railway cars and other industrial and municipal facilities, shipbuilding, oil refining industry, as well as repair painting. PCs have high physical and mechanical properties. Another area of application of uralkyd materials is protective and decorative painting of wooden surfaces [21, 22].

Currently uralkyd materials are referred to as energy efficient as they form PC in natural surroundings or at low temperature within a short time [20]. Uralkyd based primers, enamels and priming enamels are used to protect metal surfaces in various industries. When painting special equipment units it was noticed that application of alkyd-urethane enamel reduces fogging, which allows the paintwork manufacturer to save PV consumption and improve sanitary working conditions.

Uralkyd materials are versatile enough; they can be used for product painting in production (factory painting) as well as in operation and maintenance (repair painting). Factory painting requires a special workshop or painting area, which has the necessary equipment: paint booths and drying equipment. Process steps and the quality of the coatings obtained and PVs can be controlled in the laboratory.

Repair painting has its own characteristics. Repair painting of equipment and vehicles is carried out directly at enterprises. It is necessary to paint quickly a large number of pieces of equipment and get enough high-quality coating, which should dry quickly. In addition, the choice of equipment for painting is very limited. The range of enamels used in repair painting is small. These are primarily alkyd enamels, forming coatings with sufficiently decorative properties, but their drying time is rather slow. Therefore it is necessary to introduce and distribute widely quick-drying alkyd PVs. Choosing PVs for repair painting of equipment and vehicles is not rich, especially if you take into consideration economic factors. The quality of factory painting for construction equipment and vehicles differs significantly from that of repair painting [23, 24].

PVs for shipbuilding are a special group among the materials for repair painting. The process of painting a vessel is considered in two aspects: as a primary painting and painting during its operation. Due to objective reasons it is difficult to ensure favorable painting conditions during vessel repair painting. Therefore, in such circumstances a priority should be given to easy-to-use and tolerant to the preparation of the surface materials. Full repair of the protective coating, providing for its total or partial removal, is performed by professional painters of ports or shipyards while the ship is in the dock. In this case, the choice of the coloring scheme is only determined by conditions of the painting works. At the same time, freeboard, superstructures, masts and open decks can often be repainted, and such cosmetic painting is often performed even while the ship is at sea. Alkyd-urethane systems based on fast drying and easy-to-use one-component materials are used for such repair works. These systems consist of two primer layers (each layer thickness 70 μm) and a layer of enamel (50 μm thick) on the basis of uralkyd film formers. It is also possible to use a system consisting of a single uralkyd primer layer (50 μm thick) and three alkyd pentaphthalic enamel layers (each layer thickness 30 μm) [25].

Uralkyd oligomers are products of chemical modification of alkyd oligomers by diisocyanates, the latter partially replacing diacid. To obtain uralkyds low molecular weight oil modified oligoesters with a high content of hydroxyl groups are used. The presence of urethane bond results in a significant change in coating properties compared to a similar fat alkyd oligomers: higher drying speed, hardness, chemical resistance, protective properties.

Alkyd urethane oligomers are prepared in a manner analogous to the monoglyceride process of alkyd resins synthesis. The process is carried out in two stages. In the first stage alcohol exchange of plant oils (transesterification) is carried out so as to avoid the use of such alcohol exchange catalysts which can simultaneously activate the formation of urethanes. The catalysts in this case are calcium oxide and sodium hydroxide, which can be neutralized prior to isocyanate administration. As a result partial esters of polyatomic alcohols are formed (Fig. 1).

In the second stage the partial esters of polyatomic alcohols react with phthalic anhydride to form partial esters (Fig. 2, *a, b*), which further undergo polycondensation reaction (Fig. 3).

The resulting hydroxyl alkyd oligomer is treated with diisocyanate. Typically, the process is carried out with an excess of hydroxyl groups, whereby the final reaction product hardly contains free isocyanate groups. Thus, the uralkyd molecule includes both ester and urethane groups (Fig. 4). Uralkyd curing occurs by oxidative polymerization of fatty acid residues of plant oils, as in the case of conventional alkyd oligomers.

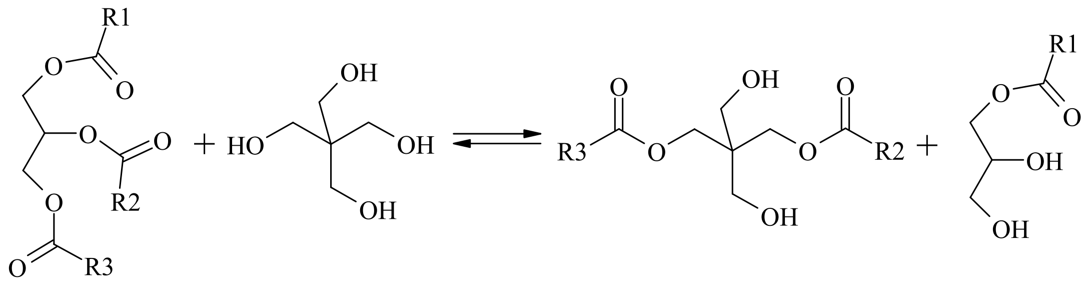
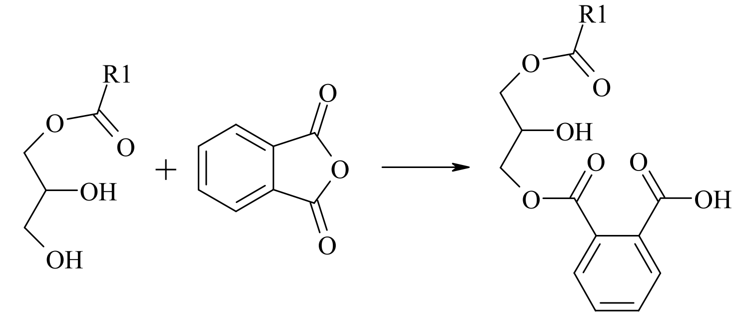
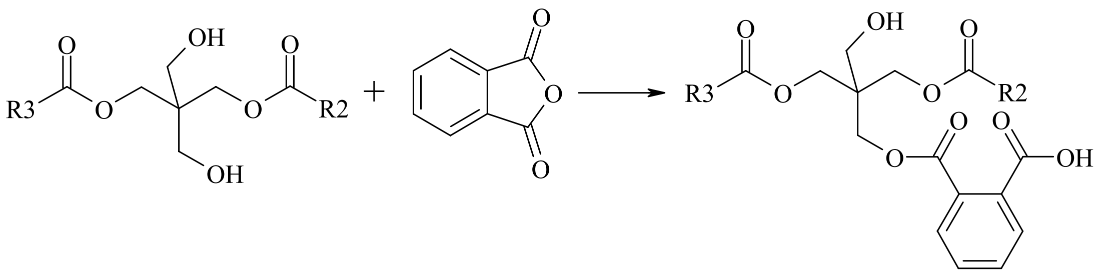


Fig. 1. Alcohol exchange of plant oils



a



b

Fig. 2. Partial ester interaction of polyatomic alcohols with phthalic anhydride

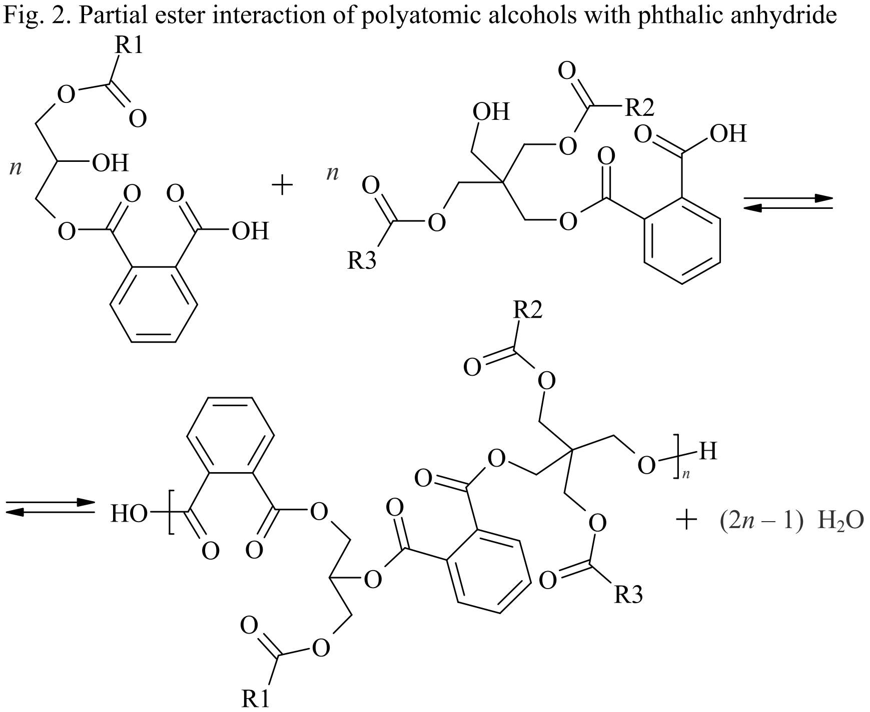


Fig. 3. Partial ester polycondensation

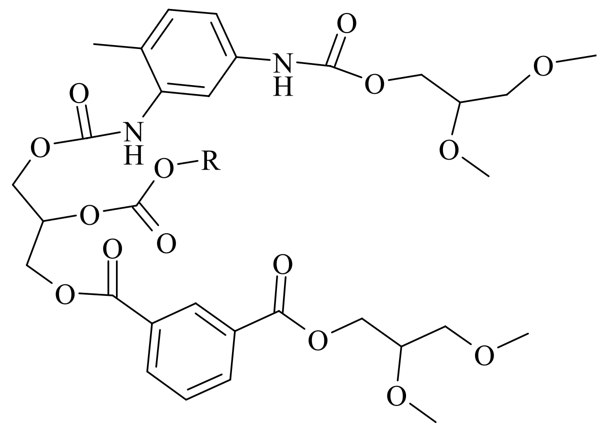


Fig. 4. Uralkyd oligomer molecule

Uralkyd oligomer properties depend on the type of oil, fatness, polyatomic alcohol structure, hydroxyl groups number, oligoester functionality as well as on the structure and amount of diisocyanate [26].

Drying and semi-drying oils are used as fatty acid part of uralkyd materials: linseed, soybean, sunflower oils, dehydrated castor oil, tall oil fatty acids and others. Selection of the oil type is determined by the application area of uralkyd oligomers and economic considerations [27].

Systems containing alkyd urethane oligomer based on linseed oil form more solid coatings with better resistance to abrasion and good chemical resistance compared to uralkyd materials based on other types of oils. So, they are recommended for floor painting. Uralkyd oligomers modified by soy oil or a mixture of soy and dehydrated castor oil and their fatty acids provide higher coatings resistance to light than linseed oil uralkyds. The speed of drying and a number of other properties depend largely on the resin oil length.

Uralkyd materials, containing 63–70% of fatty acids and 17–22% of diisocyanate, are recommended for systems applied by brush. Semifat uralkyd oligomers (about 55–63% of fatty acids) form very fast drying systems and can be used for coatings applied by various industrial methods [28].

Uralkyd oligomers based on rich in linolic acid plant oil are used as varnishes for interior and exterior coatings with a high mechanical strength and high gloss. Safflower oil oligomers are used as thick-layer primers, while soy oil oligomers with a 55% fat content – for quick-drying primers. Oligomers in enamels are applied for different purpose machines.

The type of alcohol used in the synthesis affects the uralkyd oligomer properties. Thus, the rate of drying and the chemical resistance of uralkyd oligomer films depend both on the nature of the alcohol used for transesterification, and on its amount. Lower alkali resistance of coatings at lower amounts of the taken for the transesterification alcohol is explained by higher triglycerides content in the final product. Uralkyd oligomer modification by polyglycols allows to obtain coatings with high hardness and drying rate. However, increasing the amount of polyglycol leads to deterioration of water resistance [29].

The main diisocyanates used for uralkyd oligomer preparation are 2,4 toluene diisocyanate, isomeric mixtures of 2,4 and 2,6-toluene diisocyanate (in the ratio of 80 : 20 and 65 : 35), hexamethylene diisocyanate, as well as 4,4'-diphenylmethane diisocyanate, isophorone diisocyanate, 4,4'-dicyclohexylmethane diisocyanate [28, 30–33]. Uralkyd coatings properties are more dependent on the number of urethane bonds than on the double bond cross-linking. When the content of the diisocyanate is less than 15%, the Pc has a low hardness, if more than 24% – high brittleness. Alkyd urethane materials based on isophorone diisocyanate are superior to alkyd ones in hardness, coating formation rate, chemical and light resistance. Uralkyd oligomers obtained from an aromatic diisocyanate, have insufficient light resistance (grow yellow when exposed to UV light) [29, 34].

Conclusion. At present, quite a number of large and medium-sized companies throughout the world are engaged in the production of uralkyd materials. Paints and varnishes based on uralkyd oligomers have a wide range of application: quick-drying industrial primers, enamels, wood varnishes, materials for metal products, enamels for large-sized products.

It can be recommended to extend the scope of alkyd-urethane coatings in the Republic of Belarus following the results of this review. A particularly promising area of application of these materials is the repair painting of metals, transport and various metal constructions.

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