

Review

Thin Protective Coatings on Metals Formed by Organic Corrosion Inhibitors in Neutral Media

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Abstract: Protection of metals in neutral media with pH 5.0–9.0 (in humid atmospheres and various aqueous solutions) can be achieved by formation of thin coatings (up to several tens of nm) on their surfaces due to adsorption and more complex chemical interactions of organic corrosion inhibitors (OCIs) with the metal to be protected. The review contains three sections. The first section deals with coatings formed in aqueous solutions, while the second one, with those formed in organic and water-organic solvents. Here we consider metal protection by coatings mainly formed by the best-known classes of OCI (carboxylates, organophosphates and phosphonates) and estimation of its efficiency. The third section discusses the peculiarities of protection of metals in the vapor-gas phase, i.e., by volatile OCIs, and a relatively new type of metal protection against atmospheric corrosion by the so-called chamber inhibitors. OCIs with relatively low volatility under normal conditions can be used as chamber OCIs. To obtain a protective coating on the surfaces of metal items, they are placed in a chamber inside which an increased concentration of vapors of a chamber OCI is maintained by increasing the temperature. This review mainly focuses on the protection of iron, steels, copper and zinc.

Keywords: organic corrosion inhibitors; volatile corrosion inhibitors; chamber corrosion inhibitors; protective coatings; carboxylates; organophosphates; phosphonates; self-assembly; superhydrophobization



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1. Introduction

According to ISO 8044-1989, corrosion inhibitors (CIs) (Appendix A: Table A1) are chemical compounds or their formulations “which, when present in a system at a sufficient concentration, reduce the corrosion rate of a metal without significantly changing the concentration of the corrosive agent”. Their use in the practice of corrosion protection has been known for about 200 years. In recent decades it expanded into many areas of industry, ranging from oil and gas production and metallurgy to mechanical engineering, energy and microelectronics. Not only do our ideas about the mechanism of action of CIs continue to develop, but also the methods of their application, which largely depend on the composition of the corrosive medium and to a large extent on its pH. It is no coincidence that one of the most common classifications of CIs is to divide them by media into acid, neutral, and alkaline. Particular attention is paid to CIs for neutral media because they cover not only solutions with a wide pH range of 5.0–9.0, but also humid atmospheres whose corrosivity is responsible for at least half of all corrosion damage to metal products, structures and semi-finished items [1,2]. This is one of the reasons why we limit ourselves to neutral media in this review.

In these media, a CI always changes the state of the surface of the metal to be protected due to adsorption on its surface or by formation of hardly soluble compounds with its cations. These compounds can create coatings that act as a barrier to the corrosive components of the medium. However, we should not confuse such thin coatings with conversion coatings (CCs) whose thickness can reach tens and even hundreds of micrometers [3–6].

CCs are formed on the surface of a metal being protected by a chemical reaction of its cations with CIs such as chromates, molybdates, phosphates and tannin, phosphoric or phytic acids. However, CCs are usually obtained in acid or alkaline aqueous solutions that often contain oxidants and at elevated temperatures. They can be obtained chemically, electrochemically, and thermally. Chemically-produced CCs are usually up to 5 μm thick, but even then they have defects and often require additional passivation.

In neutral media, organic corrosion inhibitors (OCIs) are often used as efficient passivators. The development of new physicochemical methods for studying metal surfaces, including in situ methods, made it possible to obtain information on the specifics of formation of thin adsorption layers of OCIs ranging from fractions of a monolayer to a multilayer coating. For example, in the mid-1970s it was proved that iron can be transferred from the active dissolution region to the passive state in a neutral aqueous solution just due to adsorption of an OCI, i.e., in the absence of an oxide film on its surface, by a combination of electrochemical and ellipsometric methods [7].

Adsorption passivation of metals can occur when OCIs are chemisorbed on their surfaces, but it is often not limited to a single monolayer chemisorption coating. Subsequent physically adsorbed OCI layers provide an additional barrier to corrosive solution components and stabilize the passivation of the surface.

Another method of passivation of metals is the formation of coatings consisting of complex compounds of metal cations with anionic type OCIs on their surfaces. Typical representatives of such passivators include various azoles and phosphonates that often form complex polymeric films of their complexes with metal cations.

Since the end of the twentieth century, much attention has been paid to a relatively new method of passivation of metals—superhydrophobization of their surface, which is achieved by giving it a polymodal roughness and subsequent treatment with a hydrophobizing agent (HPA). It is most often performed from organic [8–11] or water-organic solutions [12,13], and sometimes from a vapor phase [14–16]. Not only the achievement of an appropriate water contact angle ($\Theta_c \geq 150^\circ$) but also the stability of the superhydrophobic (SHP) coating, which ensures the efficiency of metal protection from corrosion, depend on the choice of the method used to obtain polymodal roughness and HPA.

Such a wide variety of methods available for the preparation of thin protective coatings formed with the use of OCIs cannot fit in the framework of a single review. In this regard, we will limit ourselves to reviewing the articles (mainly published over the past 10 years) dealing with the preparation and study of the protective properties of the above-mentioned coatings in three cases.

It the first case, the aqueous solutions of the main classes of OCIs are analyzed. In the second case, the protective coatings obtained in organic and aqueous-organic solvents are considered, and in the third case, the coating obtained in a gas-vapor phase. We tried, though briefly, to review the most interesting or important articles in each of the sections, without claiming to cover the scientific works in this field comprehensively, and with the main focus on iron (mild steel), copper, and zinc.

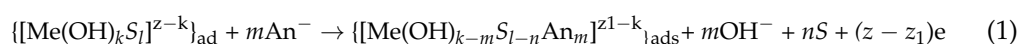
2. Water Solutions

2.1. Carboxylic Acids and Their Salts

Replacing toxic inorganic CIs (chromates, nitrites, etc.) with less environmentally hazardous OCIs, primarily salts of carboxylic acids, has encountered several difficulties. First, their lower homologues are usually hydrophilic, so they often have weak adsorption capacity and cannot form efficient protective coatings. Second, in order to reveal the effect of the chemical structure of OCIs on the efficiency of their protective properties in relation to metals and alloys, extensive experimental studies had to be performed. Since the identified patterns can differ significantly among metals and corrosive environments, it was important to create a working model of metal passivation and local depassivation inhibition using CIs. Third, since many years of experience in the application of corrosion protection of metals have pointed to the advantages of mixed CIs, one cannot limit oneself

to the use of individual compounds as OCIs. OCI-based formulations can not only enhance protection but also improve its environmental and economic aspects and expand the range of the metals and alloys to be protected.

At our Institute, such studies were initiated in the 1970s. The results obtained were summarized and analyzed in detail in a monograph [7]. Much attention in it is paid to the initial stage of metal depassivation, since in neutral media the surface of the majority of metals and alloys is covered by an air-formed oxide film and corrosion occurs locally in its defects. The concept of nucleophilic substitution of ligands (NSL) in the surface complex was suggested for the initial stage of corrosion in an aqueous solution or a humid atmosphere. According to it, an anion (An^-) adsorbed on a metal in such media can be regarded as a nucleophile attacking the surface complex. This is represented by the following reaction scheme:



To simplify the scheme, a single-charged anion and a one-step process are shown, which is not always the case. As one can see, An^- displaces oxygen-containing particles, such as OH^- , and solvent molecules S from the surface. The subsequent behavior of the metal depends on the reactivity of An^- and the properties of the resulting complex. If it is sufficiently stable and poorly soluble, the oxidized state of the metal surface is stabilized, i.e., this anion facilitates passivation and is a passivating CI itself.

If the complex that is formed is well soluble, adsorption of the attacking anion initiates metal depassivation. A characteristic of this process is often provided by the pitting potential (E_{pit}) on the anodic polarization curves. It reflects not only the complex formation thermodynamics, i.e., its equilibrium potential $E_{\text{eq}} = E_{\text{Me/Me}^{n+}}^0 - RT/nF \times \ln(K_s \times a_{\text{An}^-}/a_{[\text{MeAn}]})$, where K_s is the complex stability constant; a_{An^-} and $a_{[\text{MeAn}]}$ are activities of An^- and its complex, respectively. The kinetic constraints of the reaction taken into account by the following equation also play an important role:

$$E_{\text{pit}} = E_{\text{Me/Me}^{n+}}^0 - RT/nF \times \ln(K_s \times a_{\text{An}^-}/a_{[\text{MeAn}]}) + \eta_{\text{pit}} + \Delta \quad (2)$$

where η_{pit} is the overvoltage of the reaction that causes local metal depassivation, which depends on the nature of the metal and activator, while Δ reflects the potential drop in the passive film defect on which the reaction occurs.

It has been proved that the nature of the activator manifests itself in different affinity to water, and the hydrophobicity constants of atoms or groups of atoms composing the anion can be used as its characteristic. For example, in the initiation of local depassivation of Ni by aliphatic carboxylates of general formula RCOO^- in borate buffer with pH 7.4 at $C_{\text{An}^-} = 0.05 \text{ mol/L}$, the value of E_{pit} is described by the following equation:

$$E_{\text{pit}} = a - bf - c(2.6 + 0.6\sigma^* - 2.4 E_s) \quad (3)$$

where a , b , and c are constants for a reaction series; σ^* is the substituent constant of R which takes into account its inductive effect on the reaction center; f and E_s are constants that take into account the hydrophobic and steric effects of R , respectively. The equation shows that the σ^* constants reflecting the effect of R on the electron density of the reaction center (RC) of the nucleophile do not fully determine the reactivity of anions. In view of this, other characteristics of the nucleophile should be taken into account, among which its hydrophobicity is particularly important.

Application of the NSL concept showed that a good correlation can be obtained if E_{pit} is represented by a function comprising only the Hansch hydrophobicity π -constant and $\log MR$:

$$E_{\text{pit}} = a_1 - b_1 \pi + c_1 \log MR \quad (4)$$

where MR is the molar refraction of nucleophiles that characterizes their polarizability. This equation that is applicable to single-charged anions does not require knowledge of

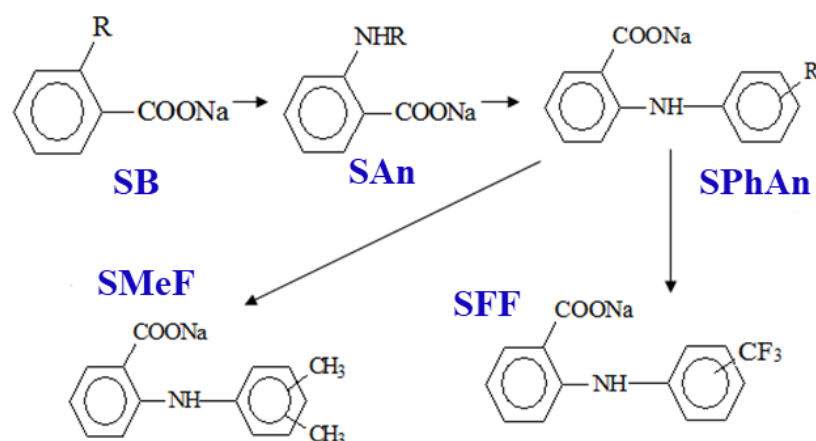
K_s , while the values of π and $\log MR$ of the corresponding atoms and groups are widely tabulated [17]. In contrast to Equation (3), it also applies to other types of anions: Hal^- , CNS^- , CN^- , NO_3^- , and sulfonates. The π -constants for monobasic carboxylic acid anions were chosen for the HC(O)O , $\text{CH}_3\text{C(O)O}$, $\text{C}_2\text{H}_5\text{C(O)O}$, etc. groups of atoms since their bond to the metal surface occurs through an oxygen atom. Similarly, the π -constants for the above inorganic anions were based on the formulas CNS^- and CN^- , respectively, considering that in these cases S and N, respectively, were the bonding atoms.

The validity of Equation (4) has been proved in many metal-oxide-solution systems, including depassivation of not only Fe, Ni, Co, Cu, Al, and Sn, but also of some alloys [7,18]. It gives important information about the mechanism of the process because at first, an increase in the anion hydrophobicity (π -constant) decreases E_{pit} , which facilitates depassivation due to a decrease in the energy barrier of the process. However, on reaching some critical value π_{cr} , a further growth in the ligand hydrophobicity reduces the complex solubility so considerably that Equation (4) ceases to be valid at $\pi > \pi_{\text{cr}}$. This is a consequence of a change in the controlling stage of the process itself, which becomes the transition of the complex into solution. A higher hydrophobicity of compounds, such as $\text{CH}_3-(\text{CH}_2)_n-\text{COONa}$ monocarboxylates, gives them passivating properties in relation to low-carbon steels. This has been proved by many authors in nearly neutral aqueous solutions [7,19–22]. Not surprisingly, carboxylates with a short hydrocarbon chain ($n_c < 4$ or sometimes longer) have low efficiency as OCIs and can be corrosive. According to [23,24], $n_c > 4$ is necessary for corrosion protection of low-carbon steel and salts of saturated dicarboxylic acids $\text{HOOC}(\text{CH}_2)_{n_c}\text{COOH}$, although the efficiency of even sodium sebacinate ($n_c = 7$) strongly depends on the concentration of corrosive chlorides in a solution. A common property of mono- and dicarboxylates is the ability of homologues with large n_c to form insoluble compounds with Fe(III) and improve the stability of the passive film.

It would be logical to expect that the value of π_{cr} should depend on the nature of the complexing agent, so the significant difference in the series of corrosive ions for different metals is understandable. For example, for Cu and Ni it is wider than for Zn, let alone for Sn. It was assumed that this is due to the difference in hydration energy of the cations of these metals which increases in the series: $\text{Sn}^{2+} < \text{Zn}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+}$.

It is essential that anions with $\pi > \pi_{\text{cr}}$ are usually inhibitors of local corrosion, and this is typical of alkyl- and arylcarboxylates as well as various amino acids. In addition, it is such OCIs that passivate metals in neutral media due to strong adsorption even in the absence of a primary oxide film on them. For OCIs of the carboxylate class, this is proven both by the results of laboratory experiments summarized not only in the monograph [7], but also in more recent review articles [19–21], as well as by the successful use of carboxylate passivators in industrial practice. For example, they are used in synthetic cooling lubricants where the treatment of the metal surface during cutting or grinding in the presence of these compounds is subject to rapid renewal and temperature fluctuations. Under such rather harsh conditions, a CI must have high adsorption and passivation capabilities.

The effect of the chemical structure of OCIs, including various classes of carboxylates [7], on their protective properties toward various metals in aqueous media was studied in detail in the last quarter of the 20th century. An important role in these studies was played by the use of the linear free energy principle first formulated by Hammett [25]. This principle made it possible to quantitatively describe and predict the efficiency of OCIs in the dissolution and passivation of metals and in the prevention of their local depassivation [7,19,26–28]. A good example of a change in the chemical structure of carboxylate OCIs, which increases the efficiency of their protective efficiency against corrosion in aqueous solutions of various metals, is the transition from sodium benzoate (SB) to sodium anthranilate (SAn) and then to sodium phenylanthranilate (SPhAn) [7]. Among the substituted SPhAn, sodium mefenamate (SMef) and flufenamate (SFF) deserve attention (Scheme 1).



Scheme 1. Structural formulas of SB, SAn, SPhAn and its substituted derivatives (SMeF and SFF).

Interestingly, SMeF contains two electron-donor CH_3 groups as substituents, while SFF contains a strong electron-acceptor CF_3 group. However, in both cases, the protective properties of OCIs increase significantly and on various metals. It is significant that in these studies, atoms and relatively small groups of atoms, both hydrophilic (OH , CH_2OH , NH_2 , NO_2 , etc.) and hydrophobic (CH_3 , C_2H_5 , F , Br , Cl , I , etc.) were used as R . However, linear or V-shaped correlation dependences of the measured protective characteristics, e.g., ($\Delta E = E_{\text{pit}}^{\text{in}} - E_{\text{pit}}^{\text{background}}$), on the electronic σ -constants of R did not reflect the effect of their hydrophilic-hydrophobic properties. At the same time, the use of a very hydrophobic and bulky alkyl as R may drastically reduce the solubility of OCIs, making it difficult to select a “progenitor” for a new reaction series. In aqueous solutions of carboxylate-type OCIs, it is important to evaluate not only the hydrophobicity of the acid itself, which is characterized by the logarithm of the distribution coefficient in the system of two immiscible liquids (octanol-water), $\log P$ [17], but also that of its anion. This also requires the knowledge of the pK_a of the acid and the pH of the solution in question. This allows one to calculate the value of $\log D = \log P - \log[1 + 10^{\text{pH} - \text{pK}_a}]$, which is usually lower than $\log P$ in neutral solutions. In view of this, sodium salts are better soluble in aqueous solutions than organic acids themselves, and their relatively long alkyl that favors the self-organization of the OCI makes it possible to apply a thin anticorrosion coating on the metal from an aqueous solution. In recent years, the excellent passivating effect of some carboxylates and their formulations in aqueous solutions toward ferrous and non-ferrous metals and alloys has been proved.

2.1.1. Iron and Mild Steels

It is obvious that for the formation of thin protective coatings from aqueous solutions of OCIs, the most promising are those of them that have the chemisorption and self-organization ability. In this regard, adsorption assessment by in situ methods is important in the selection of an OCI. Of these, ellipsometric measurements deserve attention as they are easily combined with the electrochemical method which can give its surface a reduced or oxidized form by changing the electrode potential. In both cases, it must be ensured that at a given E , the measured ellipsometric phase shift angle Δ in the background solution does not change in time, then when an OCI is introduced into the solution, the change $\delta\Delta = \Delta_{\text{in}} - \Delta_0$ can be attributed to adsorption ($\delta\Delta < 0$) or desorption ($\delta\Delta > 0$) of solution components. The change in ellipsometric angle $\delta\Delta$ as a function of adsorbate concentration (C_{in}) can be used to determine the type of the adsorption isotherm. Its equation makes it possible to calculate the adsorption equilibrium constant:

$$B = 1/55.5 \exp \left[\left(-\Delta G_A^0 \right) / RT \right] \quad (5)$$

where R is the gas constant, T is the absolute temperature, and $(-\Delta G_A^0)$ is the standard free energy of adsorption. It is logical to use the Temkin isotherm to describe the chemisorption of OCIs on solid metal surfaces, since it considers the displacement of oxygen, hydroxyl and solvent molecules by the adsorbate from an energetically heterogeneous surface. Indeed, it is often described by a logarithmic expression [29–31]:

$$\Theta_i = 1/f \ln[B_{i,\max} C_i] \quad (6)$$

or the full Temkin isotherm [32]:

$$\Theta_i = \frac{1}{f_i} \ln \frac{1 + n^{-1} B_{i,\max} (C_i - C_{i0})}{1 + n^{-1} B_{i,\min} (C_i - C_{i0})} \quad (7)$$

where the concentration C_i is the independent variable, C_{i0} is the known value of the minimum concentration, n is 55.5, f_i is the surface energy heterogeneity factor characterizing the change in the enthalpy of adsorption with its coverage; $B_{i,\max}$ and $B_{i,\min}$ are constants corresponding to the highest and lowest values of adsorption energy.

In some cases, the adsorption of carboxylate OCIs in a neutral solution is adequately described by the Frumkin isotherm equation [29,31]:

$$BC = [\Theta / (1 - \Theta)] \exp(-2a\Theta), \quad (8)$$

where a is the attraction constant characterizing the interaction between the adsorbed particles (attraction forces $a > 0$ and repulsion forces $a < 0$).

Note that in a single reaction series, e.g., the sodium salts of substituted phenylanthranilates, the adsorption of some compounds can be adequately described by Equation (6), whereas that of others, by Equation (8) (Table 1). The adsorption on a reduced ($E = -0.65$ V) and pre-oxidized surface of zone-melted Fe ($C \leq 0.0013\%$) can also be different for them. The adsorption of SFF is adequately described by the Temkin isotherm with a higher value of $(-\Delta G_A^0)$ on an oxide-free Fe electrode surface than that of SPhAn and its other substituted derivative, SMeF. However, compared with SPhAn whose adsorption occurs slightly more easily on a pre-oxidized surface and is described by the Frumkin isotherm, adsorption of its derivatives on such a surface is clearly weaker. The value of $(-\Delta G_A^0)$ for SFF remains high enough to claim the presence of its chemisorption chemisorptive interaction with an oxidized surface as well. Since the charge at the electrode-solution interface at $E = -0.65$ V cannot be more positive than that at $E = 0.20$ V, the electrostatic forces do not play here an essential role here and the OCI chemisorption appears is stronger on the surface of “pure” Fe than on the oxidized surface iron. This assumption is confirmed by the fact that the introduction of an R into the second aromatic ring of SPhAn strengthens the adsorption of its substituted derivatives on a reduced Fe surface. The conclusion about the same character of SMeF adsorption is very probable for the oxide-free surface but requires other evidence in the case of adsorption of its anion on the oxide.

Not only the presence of an oxide on the electrode surface but also, even to a greater extent, its chemical composition has a noticeable effect on the adsorption of these OCIs. In fact, the adsorption of SFF on Armco iron, and even more so on St3 low-carbon steel, is described by the isotherm Equation (8) with significantly lower values of $(-\Delta G_A^0)$, which do not allow us to state that chemisorption of OCI takes place.

The decrease in the adsorption activity of SFF anions in the transition from zone-melted Fe to St3 steel was explained in [20] by the fact that the impurities it contains are less active than the adsorption centers on the surface of Fe itself.

Table 1. Adsorption characteristics of sodium carboxylate anions on an electrode from a borate buffer solution (pH 7.4) at $E = -0.65$ and 0.20 V (adapted from [21,31] with permission; Copyright 2011 Springer Nature).

OCI, Anion Hydrophobicity at pH 7.4 (logD), Electrode Material	Adsorption Characteristics	
	Reduced Surface, $E = -0.65$ V	Oxidized Surface, $E = 0.20$ V
SPhAn, 1.32, Equation (8), zone-melted Fe	$(-\Delta G_A^0) = 15.6 \pm 0.2$ kJ/mol $a = 1.6 \pm 0.2$	$(-\Delta G_A^0) = 16.8 \pm 0.3$ kJ/mol, $a = 2.1 \pm 0.3$
SFF, 2.57, Equation (6), zone-melted Fe	$(-\Delta G_A^0) = 56.4 \pm 0.1$ kJ/mol $f = 2.0 \pm 0.3$	$(-\Delta G_A^0) = 49.6 \pm 0.1$ kJ/mol $f = 2.17 \pm 0.45$
"-", "-", Equation (8), Fe Armco	$(-\Delta G_A^0) = 36.8 \pm 1.8$ kJ/mol $a = 0.3 \pm 0.1$	$(-\Delta G_A^0) = 20.4 \pm 1.0$ kJ/mol, $a = 1.4 \pm 0.1$
"-", "-", Equation (8), St3 steel	$(-\Delta G_A^0) = 23.1 \pm 0.1$ kJ/mol, $a = 1.5 \pm 0.1$	$(-\Delta G_A^0) = 21.1 \pm 1.1$ kJ/mol, $a = 1.0 \pm 0.1$
SMeF, 2.29, Equation (8), zone-melted Fe	$(-\Delta G_A^0) = 40.50 \pm 0.02$ kJ/mol, $a = 0.3 \pm 0.1$	$(-\Delta G_A^0) = 27.25 \pm 0.04$ kJ/mol, $a = 1.3 \pm 0.1$

However, the results of angle-resolved XPS studies of thin films formed by this OCI on steel showed that SFF chemisorption also occurs here. SFF is a convenient object for detection on the metal surface being studied since it contains a CF_3 -group serving as a label in XPS spectra [33]. It was shown that the thickness of the film firmly bound to the surface through the oxygen of the $-\text{C}(\text{O})\text{O}^-$ group is less than 2 nm, as the metal peak is clearly visible in the $\text{Fe}3p$ spectrum. The angular dependence of the peak intensities indicated that the SFF anion is oriented almost perpendicular to the surface. In this self-organizing layer, the OCI particles are held together by the π -interactions of the benzene rings, which enhances the adsorption on steel.

The value of joint ellipsometric and XPS measurements of the metal surface on which the OCI is adsorbed should be noted. In spite of the fact that XPS is an ex-situ method here, since the sample is removed from the cell, washed with a stream of water and cleaned in an ultrasonic bath, the thicknesses of chemisorbed thin films measured by these two methods on mild steel may not differ much, as noted earlier [20]. Among other in situ methods capable of providing valuable information on the adsorption of OCIs from aqueous solutions, we should mention electrochemical impedance spectroscopy (EIS) [20] and the electrochemical quartz crystal microbalance (EQCM) method based on the variation in the frequency of the quartz resonator when the mass of the substance adsorbed on its surface changes [34]. In [20], the similarity of the results obtained by the EIS or EQCM methods with ellipsometric measurements of SPhAn adsorption isotherms in borate buffer with pH 7.4 has already been discussed. This contributed considerably to the expansion of the range of objects for ellipsometric studies.

The efficiency of steel protection with monocarboxylate OCIs can be improved if they are used as salts with rare earth metals (REMs) [35]. According to [36], praseodymium 4-hydroxycinnamate $\text{Pr}(\text{4OHCin})_3$ is an efficient CI of steel in CO_2 -containing and naturally aerated NaCl solutions. The authors attributed the ability of $\text{Pr}(\text{4OHCin})_3$ to inhibit corrosion in naturally aerated solutions to the formation of a thin protective film on the steel surface. In the case of CO_2 corrosion, $\text{Pr}(\text{4OHCin})_3$ forms thicker protective deposits on active surface areas. Using salts of 3-(4'-methylbenzoyl)propionate (MBP) with various REMs as an example [37], it was shown that they were much more efficient in inhibiting the corrosion and anodic dissolution of steel in chloride solutions than its sodium salt, while $\text{Y}(\text{MBP})_3$ was capable of inhibiting not only the anodic but also cathodic reaction on steel. Recently, Hinton and Forsyth et al. [38] analyzed the results of numerous studies on carboxylate compounds with REM and came to the conclusion that the efficiency of steel corrosion inhibition in chloride solutions by them depended on the nature of the cation. In particular, in the case of $\text{REM}(\text{MBP})_3$, it increased in the series $\text{La} < \text{Ce} < \text{Nd} < \text{Y}$. It is assumed that this is due to the formation of REM complexes in solution. As a result, thin

protective films with a complex structure containing Fe and REM oxides/hydroxides as well as the organic ligand are formed on the surface.

Higher carboxylates can form self-assembled monolayers (SAMs) even from aqueous solutions to form very thin (several nm) coatings on Fe and steels [39]. Aramaki and Shimura [40] applied SAM from an aqueous solution of sodium salt of hydroxyhexadecanoic acid $\text{HO}(\text{CH}_2)_{15}\text{COOH}$ (HOC_{16}A) or carboxylic acids $\text{C}_{n-1}\text{H}_{2n-1}\text{COOH}$ (C_nA) with $n_c = 12\text{--}18$. For this purpose, they pre-passivated a Fe electrode in borate buffer with pH 8.49 and then treated it for (5–115) h in a solution containing 0.1 mmol/L of the above mentioned OCIs. During this time a carboxylate monolayer formed on the passive electrode due to replacement of the OH group in the surface complex $[\text{FeO}]\text{OH}$ to give another complex $[\text{FeO}]\text{O}_2\text{CR}$, where R is a long alkyl or hydroxydecanate. In essence, the authors follow the NSL concept (Equation (1)), somewhat simplifying its scheme (without considering the partial dehydration of the complex by the inhibitor). Since HOC_{16}A is poorly soluble in water, it was also used in a mixed solvent (water–methanol 2:1) to reduce the duration of electrode treatment.

The presence of a SAM on the oxide coating was confirmed by XPS and FTIR methods. The protective effect of the passive film was determined from the anodic polarization curves in borate buffer containing 0.1 mol/L NaCl by the increase in E_{pit} compared to its value for the electrode uncoated with the SAM. SAM blocks Cl^- diffusion to the oxide film defects, preventing its breakdown in a wide range of passive potentials.

It has long been known [41] that the corrosion protection efficiency of metals (mild steel, Cu, Al) by alkyl monocarboxylates (ALCs) and α,ω -dicarboxylates with a straight chain $\text{NaOOC}(\text{CH}_2)_n\text{COONa}$ in neutral aqueous solutions depend on its length. An ALC is characterized by an increase in the efficiency of steel protection followed by its sharp decrease, which was explained by the difference in their solubility in water, a competition of their adsorption with complexation on the surface of the metal, and formation of micelles in the solution. Apparently, a more complicated situation is observed in the adsorption of dicarboxylic acid anions. Recently, the authors [42] studied the effect of aging of the natural oxide film during exposure in the air (from 4 to 120 h) on a carbon steel sample upon its passivation in neutral aqueous solutions of sodium glutarate, $\text{NaOOC}(\text{CH}_2)_3\text{COONa}$. They used XPS to study the effect of exposure to air on the passivation of carbon steel electrodes in a neutral aerated glutarate solution. They found that the oxide film had a two-layer structure (the inner layer is enriched with Fe(II), while the outer layer is iron oxyhydroxide). Over time, the Fe(III)/Fe(II) intensity ratio increases and passivation is facilitated by the progressive hydroxylation of the oxide films formed in air. Increasing the number n in α,ω -dicarboxylates, as well as in ALC, first increases their protective capacity for steels but then decreases it.

In addition to ALC and the above-mentioned salts of SPhAn and its substituted derivatives, other monocarboxylates deserve attention, such as sodium oleate $\text{C}_{17}\text{H}_{33}\text{COONa}$ (SOL) or sodium N-oleylsarcosinate (SOS) $\text{NaOOC-CH}_2\text{N}(\text{CH}_3)\text{C}(\text{O})\text{C}_{17}\text{H}_{33}$, whose anions have an even greater hydrophobicity ($\log D = 5.48$ and 4.03 at pH 7.4, respectively) than in the case of SFF ($\log D = 2.57$). Their high protective properties in neutral media are well known both for ferrous and other metals (Cu, Zn, Al and their alloys) [7,21]. Both OCIs are colloidal surfactants widely used in practice in passivating and process formulations. For example, it has been shown that SOS is adsorbed more strongly from a neutral aqueous solution on Fe and mild steel in the absence of an oxide than on their oxidized surfaces. The $(-\Delta G_A^0)$ value was 38.9 kJ/mol even on oxidized steel, which allows us to assume that chemisorption of SOS occurs.

Interesting results were obtained in a study of adsorption of the disodium salt [2,4-di(1-methoxyethyl)-deuteroporphyrin IX], i.e., dimegine (DMG) from a borate buffer (pH 7.4) on low-carbon steel (Figure 1) [43]. This compound belongs to the class of porphyrins which, due to their ability to form complexes with various metals, have been long attracting the attention of researchers as potential OCIs [44–46]. However, in most cases, porphyrin derivatives were studied as OCIs for steels in acid solutions and H_2S^- or CO_2 -containing

media [47,48]. The presence of two ethylenecarboxylic substituents in DMG opens up the possibility of its chemisorption on Fe and steels from neutral media, and, consequently, their protection from corrosion. In fact, DMG even at $C_{in} = 10.0 \mu\text{mol/L}$ decreases the passivation current density (i_p) of St3 steel in borate buffer from 83.0 to $55.0 \mu\text{A/cm}^2$ and increases E_{pit} by 0.07 V, though C_{NaCl} in it is three orders higher than the OCI concentration. At $C_{in} = 80.0 \mu\text{mol/L}$, spontaneous passivation of steel occurs and the E_{pit} increases to 0.25 V.

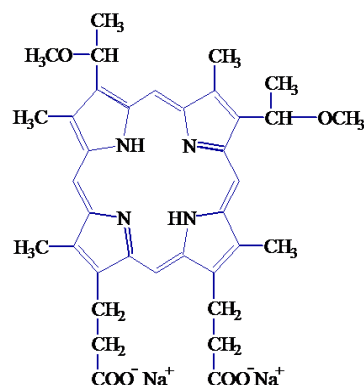


Figure 1. Structural formula of dimegin.

The study of DMG adsorption on pre-oxidized Fe at $E = 0.2$ V in borate buffer with pH 7.4 by the ellipsometric method confirmed the assumption about its chemisorption. It was adequately described by the Temkin isotherm (Equation (6)) with $(-\Delta G_A^0) = 43.3 \pm 2.6 \text{ kJ/mol}$ and $f = 1.0 \pm 0.12$. Moreover, replacement of the DMG solution by the pure buffer did not reveal desorption of OCI within 2 h of observations, which also indicates the strength of its adsorption.

Increasing the protective properties of carboxylic acid salts by their use in combinations with oxidizing agents is a well-known technique that is often discussed in monographs and reviews [7,19,21,28,49]. In contrast to inorganic oxidants such as chromates, molybdates, etc., that are capable of generating oxides (hydroxides) on its surface upon reduction on Fe (steel), which are part of the passivating film and increase its barrier properties, organic oxidants act by a different mechanism. They accelerate the cathodic reaction, alkalize the near-electrode layer, and facilitate the transfer of Fe (steel) to the passive state. An increase in temperature that accelerates oxidant reduction and OH^- accumulation can increase the effect of another OCI, for example, an adsorption inhibitor. The combined use of SPhAn with a salt of nitrophthalic acid to suppress the local corrosion of Fe may serve as an example [7]. However, here we are more interested in other ways to increase the protection of metals against corrosion.

One of them involves the joint application of two salts of carboxylic acids. For example, the passivation of St3 steel in a solution with a formulation of SPhAn with SOL, even at low C_{mix} , is more efficient than the best one of them, i.e., SOL [7]. Contrary to the opinion that it is better to make a mixture of weak CIs, replacement of SPhAn in the formulation with SOL with its derivative, which is a stronger passivator, i.e., SFF, gives much better results [50]. Another example of an efficient mixture of salts of higher carboxylic acids for passivation of mild steel is represented by a formulation of SMeF with sodium hydroxynaphthoate $\text{C}_{12}\text{H}_6(\text{OH})\text{COONa}$ (SHN) [21]. The carboxylates do not compete with each other in the adsorption process because their equimolar mixture protects steel better than the individual components. They have almost equal $(-\Delta G_A^0) \sim 27.0 \text{ kJ/mol}$, but their mixture is better adsorbed on the surface. The C_{in} value required to inhibit the corrosion of a rotating cylindrical mild steel specimen in a neutral solution is two times smaller for the mixture than for each carboxylate alone (Figure 2).

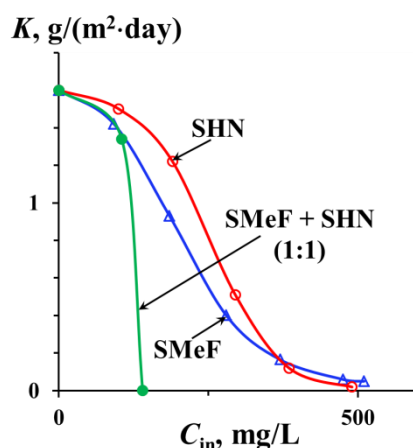


Figure 2. Dependence of the corrosion rate of a rotating cylindrical sample made of St3 mild steel on the content of SHN, SMeF and their equimolar mixture [21].

German researchers [23] found that the protective effect of α,ω -dicarboxylates could be increased by using them in mixtures with monocarboxylates. They attributed this result not only to the better adsorption of monocarboxylates, e.g., caprylate, on oxidized steel than that of sebacate, but also to the dense packing of the thin layer formed by these two OCIs.

Information is available about the possibility of increasing the protective effect of carboxylates through their use in a mixture with some amines. For example, it was shown [51] that in a liquid concentrated fertilizer, i.e., an aqueous solution of ammonium nitrate and urea, the corrosion of carbon steel could be nearly suppressed in the temperature range of $t = 25\text{--}50\text{ }^{\circ}\text{C}$ by diethanolamine and hexamethylenetetramine, but at $C_{in} > 0.5\text{ wt.}\%$. The concentration of amines can be reduced to 0.3 wt.% by adding 0.1–0.5 wt.% cinnamic acid to the solution.

In addition to the corrosion protection of carbon steel by relatively small additions of mixtures of two OCIs in corrosive concentrated aqueous solutions of inorganic salts considered above, we should mention a similar problem with phase change materials (PCMs) for cold storage [52]. They usually consist of hydrated salts, e.g., 43.2% $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, 12.3% $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ and additions of some chlorides (6.2% NH_4Cl , 3.1% KCl , and 1.9% $\text{Na}_2\text{B}_4\text{O}_7$, 3.1% $\text{NH}_4\text{H}_2\text{PO}_4$, and 27.8% H_2O) and are used in solar energy storage, air conditioning systems, and water product storage and transport. The authors showed that a mixture of methionine and histidine (at a concentration ratio of 5:3) in a PCM solution can markedly increase the corrosion protection of carbon steel to $Z = 94.3\%$ (instead of 80.4 and 65.9% for its components, respectively, at $C_{in} = 0.05\text{ mmol/L}$). They believe that this is a consequence of the formation of a thin chemisorbed film of these OCIs.

The development of methods for the formation of thin protective coatings on metals is not limited to the creation of efficient mixed OCIs. In this respect, the “layer-by-layer” (LbL) method, which was developed over the past decades for various physical and colloidal chemistry applications, should be noted [53–55]. Although due to innovations in assembly techniques and methods for characterization of nanoscale films, the interest in sequential assembly is certainly growing, the use of OCIs in it is currently very limited [56–59]. Meanwhile, it was shown 15 years ago by ellipsometric and electrochemical measurements that it is possible to increase the adsorption of sodium 11-phenylundecanoate (SPhU) by pre-modification of the metal surface by adsorption of another carboxylate (SMeF). This was first observed when SMeF adsorption started at lower C_{in} if SPhU was pre-adsorbed on the surface of an oxidized Fe electrode (Figure 3) [2,21]. It is assumed that the attraction interaction of the SMeF anions with the already adsorbed SPhU anions is stronger than that of the SMeF anions with the surface of oxidized Fe. This is indicated by the formally calculated values of $(-\Delta G_A^0)$ for SMeF on an oxidized Fe electrode without and with a monolayer coating of SPhU on it (27.3 and 38.4 kJ/mol, respectively). In addition, after adsorption of SMeF anions corresponding to a monolayer, the solution was replaced with

pure borate buffer and SPhU was introduced. It was found that the adsorption of the third nanolayer in the medium coverage region was well described by the Langmuir equation with $(-\Delta G_A^0) = 39.2$ kJ/mol. It is higher than the calculated value for the first SPhU layer adsorbed on the oxidized surface: $(-\Delta G_A^0) = 33.1$ kJ/mol.

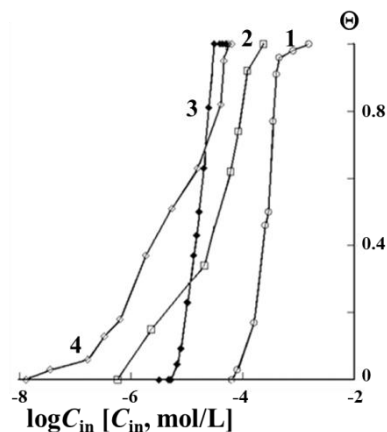


Figure 3. Adsorption isotherms of sodium salts of organic acids and their mixtures on an oxidized Fe surface at $E = 0.2$ V: SMeF without (1) and with preliminary SPhU adsorption (2), SPhU without (3) and with preliminary formation of a SPhU + SMeF two-layer coating (4) [21].

Thus, sequential adsorption of the studied carboxylates on zone-melted Fe increases their $(-\Delta G_A^0)$, which can increase the protective properties of this nanoscale film whose thickness does not exceed 5 nm. The advantage of the sequential adsorption method is that it is implemented in very dilute OCI solutions. Later it was shown that modification of a metal surface by carboxylate chemisorption can increase the adsorption of other OCIs as well.

Mixtures of carboxylates with triazoles, which are known to be efficient OCIs of Cu and Zn, are of interest for the protection of metal products and systems comprising not only ferrous but also non-ferrous metals [20–24,60–63]. The interaction of SFF with 5-chloro-1,2,3-benzotriazole (5-Cl-BTA), which is a well-studied and efficient substituted BTA, is indicative in this respect [64–67].

The adsorption of 5-Cl-BTA on an oxidized St3 steel surface at $E = 0.2$ V in borate buffer is adequately described by Equation (8) with $(-\Delta G_A^0) = 37.4 \pm 1.9$ kJ/mol, which exceeds the similar value for BTA by more than 10.0 kJ/mol. The mixture of 5-Cl-BTA with SFF at the ratio of components (2:3) adsorbed on such an electrode significantly better than not only SFF itself but also its similar mixture with BTA. The $(-\Delta G_A^0)$ value of this OCI reaches 58.5 ± 2.9 kJ/mol. Interestingly, BTA does not adsorb on a SFF monolayer, while 5-Cl-BTA adsorbs slightly more easily on such an electrode than on oxidized steel with $(-\Delta G_A^0) = 39.0 \pm 2.0$ kJ/mol. The authors assumed that the increase in the adsorption properties of 5-Cl-BTA in combination with carboxylates was caused by the formation of associates by the components of the mixture.

The dicarboxylate DMG discussed above can also be used to modify the Fe surface in order to improve the subsequent adsorption of triazoles [43]. In this case, it is not necessary to modify the electrode surface to such an extent that a DMG monolayer would be formed. It was found that at a relatively low degree of surface coverage, $\Theta_{\text{DMG}} = 0.27$, the subsequent adsorption of BTA was described by Equation (6), like on a pre-oxidized electrode, but its characteristics increased, namely, $(-\Delta G_A^0)$ increased from 19.2 to 38.7 kJ/mol, while f increased from 3.6 to 5.1. Increasing the Θ_{DMG} to 0.5, 0.70, and 1.0 first increases $(-\Delta G_A^0)$ to 45.1 but then decreases it to 44.6 and 39.9 ± 2.0 kJ/mol, respectively. The surface energy heterogeneity factor f gradually decreased to 4.7.

Back in the 1990s, Aramaki and Shimura began a series of studies in which the possibility of increasing the stability of the passive state of Fe obtained in borate buffer and additionally treated with a water-alcohol solution of carboxylate SAM (the thickness of the

passive film did not exceed 5.6 nm) and then modified with alkyl triethoxysilanes was investigated. The results of these studies summarized in [40,68] and continued in [69] confirmed the possibility of significantly increasing the stability of the Fe passive state in neutral 0.1 mol/L solutions of corrosive salts (NaCl, Na₂SO₄, NaNO₃) or in a humid atmosphere.

Later it was found [70] that the protective properties of sodium salts of various carboxylates in the passivation of St3 steel could be enhanced by using aqueous solutions of [3-(2-aminoethylamino)propyl]trimethoxysilane (H₂N(CH₂)₂NH(CH₂)₃Si(OCH₃)₃, AEAPTS) that have a good stability. AEAPTS adsorbs well on a reduced steel surface at $E = -0.65$ V and can facilitate steel passivation in borate buffer at pH 7.4. Its small addition to a carboxylate solution enhances the passivation efficiency of steel not only with a relatively weak OCI of this type (sodium benzoate), but also with one of the best passivators, i.e., SOS.

The passivation of St3 steel in an aqueous 16.0 mmol/L solution of a SOS and AEAPTS mixture (at their ratio 3:1) and $t = 60$ °C for 20 min prevents corrosion even under severe conditions of high air humidity and daily condensation. The duration of such protection of steel reaches 456 h, while a similar treatment with a SOS solution itself preserves steel for only 196 h. Interestingly, such passivation has also proven good for other metals, in particular, Al alloys [71].

2.1.2. Copper and Its Alloys

Copper and its alloys are the most important structural materials with good corrosion resistance, but due to the high requirements for preserving their surface they have long been in the focus of attention of OCI specialists. The best-known class of OCIs for Cu is represented by azoles capable of chemisorption on its surface and formation of thin films of complex compounds. The specifics of their protective action, including formation of ultrathin coatings on Cu, have been repeatedly discussed in books [2,7,72] and reviews [20,61,63,73–76], so we will not review them here. Although carboxylate OCIs for Cu are less popular than azoles, they are in many cases quite efficient and less hazardous to the environment.

It was shown as early as in [41] by polarization resistance (R_p) measurements that in a solution containing 500.0 ppm NaCl, 100.0 ppm NaHCO₃ and 5.0 mmol/L OCI (pH 8.4 was provided by addition of 1.0 mol/L NaOH or HClO₄), straight-chain ALC with $0 < n_c \leq 9$ are not very efficient in Cu protection. A sharp increase in the efficiency of ALC was found only in the case of sodium undecanoate ($n_c = 10$), but that of dodecanoate ($n_c = 11$) was significantly smaller. However, in contrast to steel protection, ALC with larger n_c showed slightly better protection of Cu up to sodium stearate ($n_c = 17$). The authors suggested that the effects of ALC solubility and micellization were less pronounced in protecting Cu than in the case of mild steel. This is consistent with the Irving–Williams stability series, which is characteristic of transition metal cations interacting with complexing molecules.

α,ω -Dicarboxylates are moderately corrosive ($n_c = 0$, oxalate) or weakly retard Cu corrosion. The corrosiveness of oxalate toward Cu in comparison with mild steel is explained by stronger complexation of oxalate with Cu(II) cations than with Fe(II), which facilitates the dissolution of the protective oxide-hydroxide layer on Cu. The action of α,ω -dicarboxylates on Cu differs from other series by a relatively steady increase in R_p with increasing n_c , although a sharp increase was also observed for tridecanoate ($n_c = 11$). However, there was no sharp decrease in R_p and α,ω -dicarboxylates were effective OCIs even in the case of hexadecanoate ($n_c = 14$). The authors suggested that even at great chain lengths, dicarboxylates were bound to the Cu surface more strongly than to steel.

Later [77], the passivating effect of potassium salts of ALC was studied by immersing Cu (99.999 wt.%) in their solutions containing 1.0 g/L K₂SO₄ and the OCI with a chain length of more than 6 carbon atoms that formed hydrophobic films on the electrode. It was confirmed that increasing the alkyl length provided better protection against corrosion, i.e., it reduced the anodic current density i_a during Cu polarization. It was shown by the EIS method that increasing the alkyl in OCIs enhanced the resistance of the protective layer of

ALC anions on Cu, R_f . The authors attributed the increase in R_f to the formation of a denser and thicker OCI layer on Cu. They believe that such ALC can find wide applications in practice, from cooling systems to Cu passivation in microelectronics.

The adsorption of mono- and dicarboxylates on Cu was extensively studied by in situ reflectance ellipsometry. Adsorption measurements were performed in borate buffer with pH 7.4 on passive Cu after reduction of the electrode surface at $E = -0.60$ V followed by its oxidation for 30–40 min at $E = 0.0$ V. It has been shown that adsorption is sometimes adequately described by the Frumkin isotherm equation [78], but more often by the Temkin equation [32,79–82] and increases with the chain length of their molecules. Thus, in [78] five monocarboxylates were studied whose inhibition efficiency against local anodic dissolution of Cu increased in the same order as the hydrophobicity of the corresponding acid anions ($\log D$): SMeF (2.29) < SFF (2.57) < SPhU (3.68) < SOL (5.10) < SOS (5.65). Interestingly, these anions significantly exceed BTA in the $\log D$ value (1.32), apparently in part because it has lower acidity (pK_a 8.38) than carboxylic acids whose pK_a values range from 3.73 (SMeF) to 4.80 (SOL). As it can be seen from the plots of $(-\delta\Delta)$ vs. $\log C_{in}$ (Figure 4), the best adsorption capacity among them is observed for SOL and SOS that have $(-\Delta G_A^0) = 57.0$ and 62.0 kJ/mol, respectively, for the first monolayer. The other carboxylates are adsorbed more weakly than BTA whose $(-\Delta G_A^0) = 51.0$ kJ/mol. It should be noted that SOS forms a polymolecular film on Cu even at very low C_{in} values.

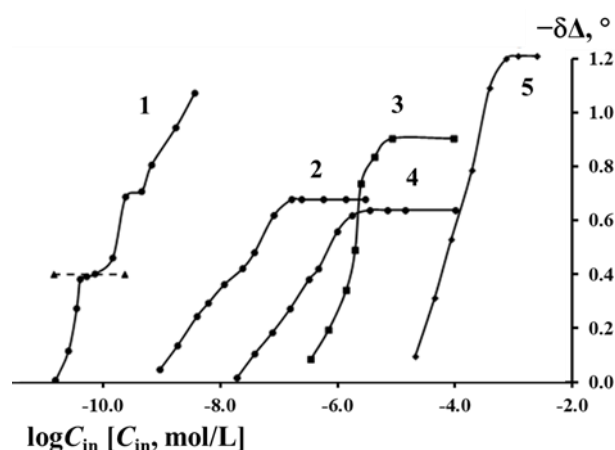


Figure 4. Variation of the ellipsometric angle $(-\delta\Delta)$ measured on Cu at $E = 0.0$ V as a function of the concentrations of SOS (1), SOL (2), SMeF (3), SFF (4), and SPhU (5). The dashed line shows a tentative monolayer (reproduced from [78] with permission; Copyright 2015 Springer Nature).

Comparison of the protective efficiency of a Cu thin coating formed in 2.0 mmol/L BTA solution with similar passivation by SOS or SOL was carried out in a humid atmosphere with daily condensation of moisture on the samples. It showed that after prolonged treatment (1 h) at room temperature and passivation for 5 min at 60 °C, BTA was less efficient than SOS and was not inferior to SOL only in the case of “hot” treatment.

Sodium tridecanoate $\text{CH}_3(\text{CH}_2)_{11}\text{COONa}$ (NaC_{13}) is sufficiently soluble in water to be an efficient passivator of Cu in it [79]. Its adsorption starts at low $C_{in} = 0.01$ nmol/L, with $(-\Delta G_A^0) = 67.0$ kJ/mol, i.e., higher than that of SOS, although its $\log D$ is smaller. It is possible that the first NaC_{13} monolayer has a denser packing. The film it forms on Cu with an increase in its C_{in} is also polymolecular. Corrosion tests with daily moisture condensation on copper kept for 5 min in OCI solution at 60 °C showed that the protective mixture of NaC_{13} with AEAPTS (3:1) at $C_{in} = 8.0$ mmol/L provided 62 days before the first corrosion damage appeared.

The sodium salts of dicarboxylates can form ultrathin protective coatings on Cu even at relatively low molecular weights. This was shown in [80] for sodium succinate and sodium ethylmalonate whose adsorption was studied on Cu in neutral buffer solutions with pH 7.4, and its corrosion inhibition in 0.01 mol/L NaCl aqueous solution. It was found

that the highest ($-\Delta G_A^0$) on passive Cu at $E = 0.0$ V in borate buffer is shown by succinate, and on its reduced surface free of oxides at $E = -0.60$ V, by ethyl malonate. In the first case, the values of ($-\Delta G_A^0$) for malonate, ethyl malonate, and sodium succinate are 47.7, 69.4, and 77.4 kJ/mol, respectively, indicating chemisorption of their anions. Comparison of the monolayer thicknesses on Cu and the sizes of the adsorbate molecules allowed us to conclude that the anions were flatly oriented on the oxidized electrode surface. On a reduced Cu surface, the values of ($-\Delta G_A^0$) are significantly smaller and amount to 38.3, 64.2, and 53.1 kJ/mol, respectively. The succinate and ethyl malonate anions are also chemisorbed here, but this is less likely for malonate. Corrosion tests of Cu in a 10.0 mmol/L NaCl aqueous solution also showed the advantage of sodium succinate and sodium ethyl malonate over sodium malonate. The highest degree of Cu corrosion protection (91.0%) at $C_{in} = 3.0$ mmol/L is provided by ethyl malonate, whereas for sodium succinate and sodium malonate $Z = 83.0$ and 77.0%, respectively.

However, it should not be assumed that the $\log D$ value always completely determines the adsorption and protective properties of dicarboxylates. It has recently been shown [81] that sodium adipate $\text{NaOOC}(\text{CH}_2)_4\text{COONa}$ ($\log D = -4.48$) is better adsorbed on MNZh5-1 Cu alloy than the less hydrophilic ethylmalonate ($\log D = -3.73$). It is possible that when protecting the alloy containing Fe and Ni, the adsorption conditions are more complicated and are affected by the interaction not only with Cu, but also with the alloy inclusions.

The excellent adsorption of sodium succinate on Cu, despite the high hydrophilicity of its anion, aroused interest in its derivatives, in particular a mixture of sodium salts of alkenylsuccinic acids with the number of C atoms in the alkenyl $n_c = 12$ –15 (SKAP-25) [83]. The anions of SKAP-25 components are less hydrophilic than the succinate anion ($\log D = -0.25$ and 1.16, respectively, at $n_c = 12$ and 15). Not surprisingly, this OCI is more efficient in suppressing Cu anodic dissolution in borate buffer containing 0.01 mol/L NaCl. Comparison of the passivation efficiency of Cu with 16.0 mmol/L solutions of SKAP-25, SOL, and sodium tridecanoate in a humid atmosphere with daily moisture condensation on the samples showed that the alkenylsuccinate mixture was the best passivator (Table 2).

Table 2. Results of corrosion tests of Cu samples passivated in 16.0 mmol/L aqueous solutions of sodium salts of carboxylic acids in a humid atmosphere with daily condensation of moisture on the samples.

OCI	Time of Appearance of the First Corrosion Damage (Days) without and After Pre-Treatment		
	without NaCl	0.1 g/L NaCl	1.0 g/L NaCl
NaC_{13}	24 ± 0.5	21 ± 0.5	14 ± 0.5
SKAP-25	72 ± 0.5	18 ± 0.5	6 ± 0.5
SOL	>41	22 ± 0.5	16 ± 0.5

However, if after passivation of Cu the samples were immersed for 10 s in a NaCl solution, i.e., the tests were made more severe, the protective properties of SKAP-25 became weaker than those of NaC_{13} or SOL. Therefore, the protection of Cu by SKAP-25 anions in the presence of chlorides was enhanced by using it with 2-mercaptobenzothiazole (MBT) that forms a hardly soluble complex with Cu(I). It was shown by EIS that even in a 3.5% NaCl solution with very small additions of MBT, SKAP-25 dramatically enhanced its passivation effect on Cu. In addition, this mixture could be more efficient than MBT that is poorly soluble in water.

Dicarboxylic acid salts of porphyrin derivatives, i.e., DMG [82] and depocolin (3,7,12,17-tetramethyl-8,13-divinyl-2,18-porphinedipropionic acid disodium salt) [84], are also noteworthy as CIs for Cu. On oxidized Cu ($E = 0.0$ V) DMG is adsorbed from borate buffer at lower concentrations, $\log C_{in} = -7.75$ to -5.75 , than on steel (Figure 5). The value of ($-\Delta G_A^0$) = 56.0 kJ/mol indicates a strong chemisorption bond of the first DMG monolayer

with the Cu surface. Meanwhile, according to XPS studies, DMG binds to Cu surface cations via the two oxygen atoms of the carboxyl group, while nitrogen atoms do not take part. On increasing C_{in} , the film formed on Cu is polymolecular in thickness. Therefore, it is not surprising that even at $10.0 \mu\text{mol/L}$ ($\approx 6.58 \text{ mg/L}$), DMG stabilizes the passive state of Cu in chloride solutions, although C_{NaCl} is many times higher than C_{in} . The efficiency of passive state stabilization of Cu by carboxylates increases in the series: SFF < BTA < 5-Cl-BTA < DMG. Modifying the Cu surface with DMG, like on Fe, facilitates the adsorption of BTA. This increases $(-\Delta G_A^0)$ and improves the protection of Cu against corrosion, for example, in a humid atmosphere. Depocolin studied by XPS in [84] and similar to DMG in nature is also chemisorbed on Cu, which indirectly confirms the high stability of its monolayer coating, which is not removed from the surface even by ultrasonic treatment of the metal. The thickness of the adsorbed depocolin layer is 1.2 nm, which according to calculations corresponds to the molecule plane angle of 55° with respect to the Cu surface.

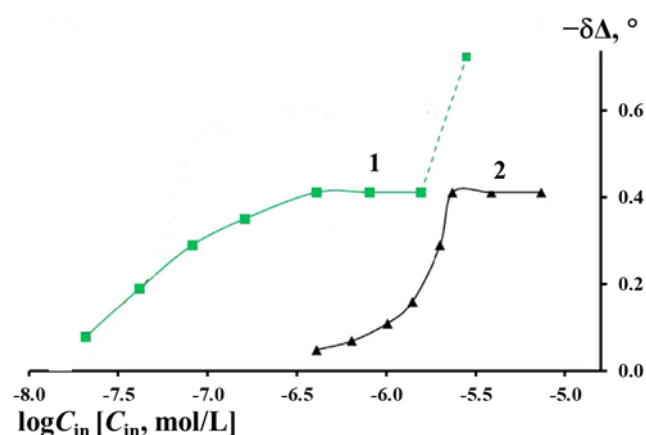


Figure 5. The effect of dimegin on the ellipsometric angle $-\delta\Delta^\circ$ on a passive surface of (1) copper and (2) zone-melted iron in borate buffer solution (pH 7.4) as a function of $\log C_{in}$ (adapted from [82] with permission; Copyright 2015 Elsevier). On curve 1, the section highlighted by a dashed line means that its upper point is nonequilibrium due to the beginning of the formation of a polymolecular coating.

Both carboxylate-type porphyrin derivatives are interesting because they seem to have a certain versatility toward various metals. For example, the adsorption of DMG on Ni from neutral borate buffer solutions was studied [85] and it was shown that it is also described by the Temkin isotherm equation, and the $(-\Delta G_A^0)$ values at $E = -0.65 \text{ V}$ and 0.2 V are 75.3 and 54.8 kJ/mol, respectively. Hence, DMG chemisorption also occurs on Ni, and it is particularly strong on a reduced electrode. The OCI adsorption layer thicknesses were found to be almost the same: 0.6–0.8 nm, and the angle between the plane of their molecules and the metal surface was 45° . Like on other metals, both porphyrin dicarboxylates bind to the Ni surface through oxygen of the carboxyl groups (without participation of the nitrogen atoms in the macrocycle) and stabilize the passive state of Ni by preventing its local depassivation by chlorides.

2.1.3. Zinc

Zinc is used for corrosion protection of steel that is not subject to mechanical stress and for metallizing tanks, steel structures, bridges, etc. It is widely used in various current sources and in other industries, but at least half of overall steel production corresponds to items that are subject to corrosion caused by corrosive atmospheres or aqueous solutions. In this regard, passivation of zinc or Zn coatings is often necessary, but for environmental reasons, its well-known variety—chromatization—now requires replacement and the search for new methods and OCIs is relevant [86].

Carboxylates, like other OCIs, have been investigated less widely on Zn and galvanized steel than on steels or Cu and its alloys, although attempts were made in the past century to use SPhAn and its derivatives for this purpose in neutral solutions [7]. Appar-

ently, K. Aramaki [87] was the first to show that in 0.5 mol/L NaCl solution at $t = 30\text{ }^{\circ}\text{C}$, even a low $C_{\text{in}} \geq 0.03\text{ mmol/L}$ of sodium S-octyl-3-thiopropionate (SOTP) is capable of providing a degree of protection $Z \approx 95\%$. As shown by XPS and FTIR spectroscopy, this is due to the formation on the surface of Zn of an oxyhydroxide film containing a small amount of the chelate whose structure is shown in Figure 6.

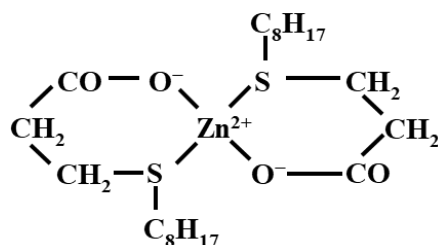


Figure 6. Structure of the chelate complex formed on the surface of Zn in a SOTP solution (reproduced from [87] with permission; Copyright 2001 Elsevier).

It was shown [88,89] that the protection of Zn in 0.5 mol/L NaCl by carboxylate anions, such as HOC_{16}A , can be enhanced by preforming a Ce_2O_3 layer on the electrode. In this case, the protective effect of such a duplex film is higher than that of the Ce_2O_3 layer itself, which slows down only the cathodic reaction. The wetting angle Θ_c of water on a surface covered by this film was larger than in the case of HOC_{16}A adsorption, so partial adsorption of the organic anion through the $-\text{COO}^-$ and $-\text{OH}$ groups on the Ce_2O_3 surface was assumed. In this case, loop-like orientation of the adsorbate particles is possible, which in time adversely affects the compactness of the thin protective film. For this reason, a more hydrophobic ALC—sodium hexadecanoate $\text{C}_{15}\text{H}_{31}\text{COONa}$ (NaC_{16})—was investigated. However, because of its low solubility in water, a water-methanol solvent (1:2) was used, which allowed obtaining a dense hydrophobic layer (with $\Theta_c = 113^\circ$) on Ce_2O_3 in 71 h of electrode immersion in this solution containing 0.1 mmol/L NaC_{16} . This duplex film perfectly protected Zn in 0.5 mol/L NaCl aqueous solution, providing $Z > 99.0\%$. Another way to enhance the protective properties of ultrathin films on Zn was suggested in [89]. It also involved the formation of first Ce_2O_3 on which OHC_{16}A was adsorbed, but with modification with various triethoxysilanes. This stage is carried out in organic solutions, so it will be discussed in the next section of our review.

It has been previously noted [7,21] that stabilization of the passive state of Fe, carbon steels or Cu is relatively easy achieved by many carboxylates, but efficient protection of Zn requires their higher homologues with increased hydrophobicity. For example, the corrosion protection of steel with a coating obtained by with hot-dip galvanizing (100% Zn) and electrochemical deposition of Zn (98% Zn, 2% Al) with decanoic acid was studied in a solution containing 148 mg/L Na_2SO_4 , 165 mg/L NaCl and 138 mg/L NaHCO_3 at $t = 30\text{ }^{\circ}\text{C}$ [90]. According to EIS measurements, addition of the OCI at $C_{\text{in}} = 0.27\text{--}0.77\text{ wt.}\%$ provided in the former case $Z = 83.01\%\text{--}83.59\%$, and $92.83\%\text{--}93.59\%$ in the latter case. It was found by XPS and ATR-FTIR methods that decanoic acid was chemisorbed on Zn through the carboxyl group.

However, even in this case, for example for decanoic, myristic or stearic acids, ethanol solutions of passivators are used most often [91]. In view of this, it is interesting to consider carboxylic acid salts sufficiently soluble in aqueous solutions to ensure the formation of thin protective coatings from them. SFF, the action of which has already been discussed above on other metals, deserves attention in this regard.

SFF anions have high surface activity, since at pH 7.4 their hydrophobicity index is $\log D = 2.57$. Adsorption of SFF from borate solutions with pH 7.4 and 9.1 on pre-oxidized Zn at $E = 0.2\text{ V}$ was studied in situ by reflectance ellipsometry [92]. This method was used to measure the kinetics of Zn oxidation in borate solutions and calculate the thicknesses of stationary oxyhydroxide films, d . It was found that adsorption on them occurs more readily in a slightly alkaline environment where the film is thinner ($d = 1.2\text{ nm}$) than in

a neutral solution ($d = 4.0$ nm). In both solutions, it is described by the Frumkin isotherm with $(-\Delta G_A^0) = 57.8$ and 61.0 kJ/mol, respectively. Such high values of SFF adsorption energy indicate chemisorption of its anions on Zn. The stability of SFF adsorption on oxidized Zn was confirmed by XPS studies. The presence of the CF_3 group in its molecules, which served as a label in the surface analysis, allowed us to establish a nearly vertical orientation of the adsorbed SFF anions with respect to the electrode plane. In this case, they are adsorbed on the surface of oxidized Zn through the oxygen atoms of the COO^- groups.

A study of the adsorption and passivating action of some salts of higher carboxylates on Zn in borate buffer with pH 7.4 [93] showed that SOS was the best of them. It manifests polylayer adsorption on oxidized Zn at $E = 0.2$ V, but the formation of the first monolayer is described by the Temkin equation with $f = 2.6$ and $(-\Delta G_A^0) = 49.2$ kJ/mol, which is lower than on oxidized Cu but higher than on Fe (35.9 kJ/mol). On the oxide-free Zn surface (at $E = -0.9$ V), SOS adsorption is also described by the Temkin isotherm with $(-\Delta G_A^0) = 45.3$ kJ/mol and $f = 1.2$. In both cases, it may be assumed that the OCI is chemisorbed on a Zn electrode. The monolayer thicknesses measured by the ellipsometric method were 0.3 and 0.5 nm, respectively, which, given the length of the SOS anion (more than 2.5 nm), indicates an oblique orientation with respect to the Zn surface. The suppression of the active dissolution of Zn in borate buffer containing 10.0 mmol/L NaCl occurs already at $C_{\text{in}} = 1.0$ mmol/L and is accompanied by an increase in E_{pit} by 0.1 V. Increasing C_{in} by an order of magnitude increases E_{pit} by 0.5 V. The ability of SOS to stabilize the passive state of Zn was confirmed by testing the samples (after their treatment in 16.0 mmol/L solution of the OCI) in a humid atmosphere, where the time to the appearance of the first signs of corrosion (τ_{cor}) increased almost 4.7-fold. The Zn treatment efficiency can be increased by using SOS formulations with AEAPTS as a passivation solution, as previously shown in the protection of steel [70] and AMg6 Al alloy [94].

To conclude the analysis of the formation of OCI carboxylate-type thin films on the surface of metals in aqueous solutions, let us note a relatively new group of compounds, i.e., ionic liquids. In recent years, they have attracted researchers by their environmental safety, stability, low vapor pressure, etc. [95]. In most cases they are investigated in aqueous acid solutions, but recently the possibility of using ionic liquids consisting of salts of imidazolinium cations with carboxylate anions in a chloride solution with a pH of 2 to 8 as OCIs for steel was reported [96]. While imidazolinium plays an important role in corrosion inhibition of steel in acid solutions, in neutral solutions it seems to be due to adsorption of the 4-hydroxycinnamate anion. It is hoped that further research will lead to the development of ionic liquids capable of protecting various metals in neutral aqueous solutions as well.

2.2. Organophosphates

2.2.1. Organic Esters of Phosphoric Acid

A large group of metal CIs are phosphorus-containing organic compounds, which usually include phosphoric acid esters, phosphonic acids, their salts and complexes with metal cations. Salts of organic esters of phosphoric acid have a high surface activity and form thin passive films as a result of chemisorption on oxidized metal surfaces. This, along with low toxicity and useful technological properties (good solubility in water, anti-scale properties, relatively high thermal stability, etc.) makes them interesting as efficient CIs of various metals and alloys. In addition, salts of phosphoric acid esters can be used as inhibiting pigments in various coatings (PEO and sol-gel coatings) [97–99]. However, within the framework of this review, only the anticorrosion protection of metals by thin films formed in the presence of CIs of this class is considered. According to the results of numerous studies of the adsorption and inhibiting properties of alkyl-, aryl-, dialkyl- and diphenyl phosphates with respect to metals in neutral solutions, they are superior in this even to anions of higher carboxylic acids. In this regard, a significant number of works devoted to finding even more efficient OCIs among them, as well as to the study of the

features of the mechanism of their protective action, have been published over the past decade [100–103].

Iron and steels. Sodium dioctyl phosphate (SDOP) is among the most efficient passivators of mild steel in neutral solutions [100,103]. According to [4], it has better inhibiting properties in neutral aqueous solution than its branched homologue, bis(2-ethylhexyl) phosphate (BEHP), which has long been known as an efficient dispersant often used to stabilize the so-called “magnetic ink”.

The inhibiting properties of mono- and diakyl phosphates to a certain extent depend on the hydrophobicity of their anions, which can be quantified by the value of $\log D$ and calculated from $\log P$ taking into account the pH of the solution and pK_a [17]. At pH 7.4, the value for SDOP is $\log D = 2.95$, i.e., the SDOP anion has a high hydrophobicity and, as a consequence, high surface activity. The presence of a phosphate group in the SDOP molecule additionally ensures its high adsorption capacity. This is confirmed by the results of an in-situ study of SDOP adsorption on mild steel in borate buffer with pH 7.4 by the method of reflection ellipsometry [100]. The change in the ellipsometric angle $\delta\Delta$ determined by this method as a function of C_{in} was used to determine the type of the adsorption isotherm [7,20]. The adsorption isotherm built on the basis of $(-\delta\Delta)$ vs. C_{in} and assuming that the plateau of this value corresponds to a coverage degree of the surface by the adsorbate $\Theta \rightarrow 1.0$ is described by the Frumkin Equation (8). If the Frumkin isotherm is plotted in the coordinates $X = \Theta$; $Y = \ln\{\Theta/[(1-\Theta)C]\}$, the point of intersection of the isotherm with the Y axis provides the $\ln B$ value. The adsorption energy of SDOP on steel at $E = -0.65$ V was determined from the value of the B constant (L/mol): $(-\Delta G_A^0) = 32.06 \pm 1.6$ kJ/mol. The adsorption energy of SDOP on steel at $E = 0.2$ V is noticeably lower: $(-\Delta G_A^0) = 26.4 \pm 1.3$ kJ/mol. This indicates a higher adsorption activity of SDOP on the “oxide-free” steel surface than on the oxidized one.

In addition, SDOP can hamper the growth of an oxide film by adsorbing on the steel surface, i.e., it protects the metal by the non-oxide passivation mechanism. This has been proved by the galvanostatic coulometry method [100]. The chronopotentiograms obtained showed no potential delays corresponding to the reduction of iron oxides during the reduction of the passive film on the steel electrode (Figure 7).

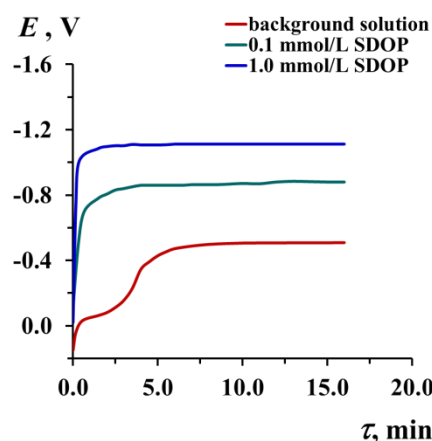


Figure 7. Chronopotentiograms obtained on mild steel by galvanostatic coulometry in a deaerated borate buffer (pH 7.4) without and in the presence of SDOP (at $i = 9 \mu\text{A}/\text{cm}^2$ and $t = 20^\circ\text{C}$) (reproduced from [100] with permission; Copyright 2013 Springer Nature).

The high adsorption activity of SDOP determines its passivating ability in relation to steel in a neutral aqueous solution. SDOP leads to spontaneous passivation of steel and an increase in the E_{pit} value at relatively low concentrations (0.5 mmol/L) [100]. The protective properties of thin films formed by SDOP depend on the temperature of the CI solution, its concentration, and the duration of sample exposure in it. With an increase

in C_{in} , the resistance of steel to the corrosive action of Cl^- increases, as evidenced by an increase in the pitting-resistant range on the anodic polarization curves (Figure 8).

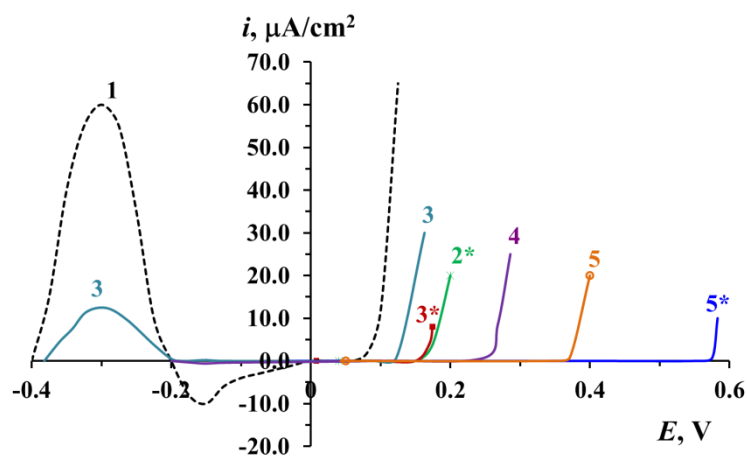


Figure 8. Anodic polarization curves of mild steel in borate buffer (pH 7.4) containing 10.0 mmol/L NaCl without (1) and in the presence of SDOP additives, mmol/L: 2*—0.05; 3, 3*—0.1; 4—0.5; 5, 5*—1.0. The duration of the electrode exposure in inhibitor-containing solutions before the start of its anodic polarization was 15 min (curves 3–5) and 90 min (curves 2*, 3*, 5*) (adapted from [100] with permission; Copyright 2013 Springer Nature).

Since the protective layers formed by phosphoric acid esters on metals are self-assembling, their protective ability should depend on the duration of sample exposure in an OCI solution. An increase in E_{pit} with an increase in the duration of exposure from 15 min to 90 min and a 10-fold decrease in the C_{in} required to transfer steel to a passive state indicates that self-assembly and formation of more perfect protective films on steel occur (Figure 8). Another factor that can significantly affect the passivation of steel in the presence of SDOP is the temperature of the solution. With an increase in temperature to 60 °C, the steel passes into the passive state at $C_{in} = 0.1$ mmol/L. However, in this case, E_{pit} shifts in the negative direction, which is associated with the SDOP ability to hamper oxide film growth by being adsorbed on the steel surface. The concentration of SDOP may be insufficient to maintain a passive state under high temperature conditions and in the presence of Cl^- ; therefore, local depassivation occurs at a more negative potential.

One more factor which has a positive effect on the passivating ability of SDOP is the flow velocity of the environment. A comparative analysis of the anodic polarization curves of mild steel obtained without and with stirring of the electrolyte (using a rotating disk electrode) showed that under the same conditions (60 °C, exposure duration 15 min, $C_{in} = 1.0$ mmol/L) the E_{pit} value increases more than 3-fold to reach 0.77 V. Thus, stirring of the electrolyte enhances the ability of SDOP to prevent local depassivation of steel.

BEHP (see Appendix A: Table A1) with more branched alkyl radicals is slightly less hydrophilic ($\log D = 2.59$ at pH 7.4) than SDOP and has weaker adsorption and passivating properties with respect to Fe and steels [4,20]. At the same time, in the presence of BEHP, thin self-assembling films are also formed on the surface of these metals, preventing their corrosion in aqueous media of various corrosiveness. For example, J. Hu et al. [104] investigated the possibility of inhibition of carbon steel corrosion by BEHP in an environment containing CO_2 and O_2 . The results of corrosion and electrochemical measurements indicated a significant decrease in the corrosion rate of steel in the presence of 500 mg/L BEHP in a 1.0% NaCl solution with 0.02 MPa CO_2 and 3 mg/L O_2 . The efficiency of corrosion inhibition by BEHP depends on the C_{in} and C_{O_2} in the chloride-containing solution. It was shown by the XPS method that the formation of a thick and compact protective layer occurs due to the interaction of BEHP with Fe^{2+} , Fe^{3+} and iron oxides with formation of P-O-Fe bonds.

The structure and protective properties of self-assembling layers obtained on Fe in an aqueous solution of BEHP were studied in more detail by R. Yan et al. [105] using FTIR, XPS and AFM. It was found that the surface phosphate layer has a nodule-like morphology. The authors confirmed the well-known mechanism of chemisorption and formation of a protective film by BEHP, which involves the formation of P-O-Fe bonds between the iron substrate and BEHP molecules.

Monoalkyl phosphates with short alkyl radicals (less than eight carbon atoms) are hydrophilic in comparison with their non-substituted analogs, and therefore have a weaker adsorption activity. At the same time, the simplicity of the synthesis of monoalkyl phosphates and the better solubility in water simplify their practical application. For example, a simple but efficient method for obtaining protective layers of butyl and hexyl phosphates on Fe in an aqueous solution using an excess of alkyl phosphates at the solid-water interface and specific adsorption of phosphate groups of CI were demonstrated [106]. The formation of relatively ordered chemisorbed phosphate layers on the Fe surface were proven by FTIR, energy dispersive X-ray spectrometry (EDS), XPS, and Θ_c measurements. In addition, as noted by the authors, in the case of butyl phosphate ($\log D = -4.31$ at pH 7.4) with a short carbon chain, an increase in the duration of treatment and C_{in} led to an increase in the protective properties of the films. In contrast, the use of hexyl phosphate ($\log D = -3.25$ at pH 7.4) with a longer alkyl, which has lower water solubility and stronger tendency to be accumulated at the solid-water interface, i.e., a higher surface activity, makes it possible to reduce the C_{in} required for efficient anticorrosion protection of Fe in 3.5 wt.% NaCl solution.

Among acidic phosphoric acid esters, phytic acid or D-myo-inositol-1,2,3,4,5,6-hexakisdihydrophosphoric acid, its salts or complex compounds with various metal cations are of special interest (Figure 9) [4].

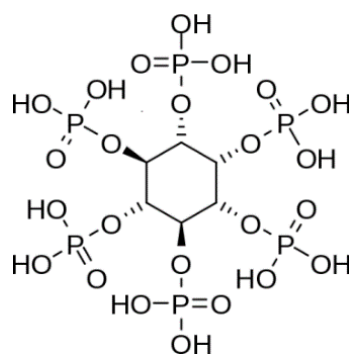


Figure 9. Structural formula of phytic acid.

This ecologically friendly acid of plant origin is an ester of a hexabasic alcohol myo-inositol and six phosphoric acid residues. Phytic acid and its salts can form complexes with metal ions due to its structure, containing 12 acidic groups, and high hydrophilicity ($\log P = -8.47$; $\log D \approx -24.0$ at pH 7.4). As a result, ordered chemisorbed layers are formed on the surface, which protect the metal from corrosion. In the past decade, studies of CI based on phytic acid, its salts and complexes were expanded and interesting features of the mechanism of their protective action toward to various metals were revealed.

The inhibiting properties of phytic acid strongly depend on the pH of the aqueous solution, namely, they are improved with a pH increase. In [107], X. Gao et al. investigated the effect of pH of solutions containing 0.005–0.5 mmol/L phytic acid on its adsorption mechanism on a Fe surface. It was found by FTIR and XPS methods that phytic acid is adsorbed on the metal surface from acid solutions (pH 0.3) mainly in the form of undissociated molecules. The chemisorption of phytic acid molecules on a Fe surface occurs through the oxygen atoms of the phosphate group and is described by the Langmuir isotherm with $(-\Delta G_A^0) = 42.46$ kJ/mol. In neutral solutions (pH 5.3–7.0), phytate ions exhibit a strong chelating ability toward the cations of dissolving Fe. The resulting Fe(II) complexes are

deposited on the metal surface, forming a barrier layer and therefore ensuring its passive state. Despite this, the authors note that the phytate-based barrier layers are not dense, as evidenced by the relatively high current values (10^{-4} A/cm²) in the passive region on the anodic polarization curves obtained in 3.5% NaCl solution. Later, high protective properties of phytic acid on 20SiMn steel were found in weakly alkaline and alkaline (pH 8.9 and 12.3) chloride-containing solutions simulating the concrete pore solution [6,108]. It was found that the film formed in the presence of phytic acid has a three-layer structure. The internal layer adjacent to the metal surface consists of Fe₃O₄ and FeOOH, the middle layer consists of Fe₃O₄, FeOOH, and FePO₄, and the outer layer consists of Fe₃O₄, FeOOH, FePO₄ and complexes of phytic acid with Fe(II).

Salts of phytic acid with ions of many metals have an even greater inhibiting efficiency. In [109–112], the influence of various metal cations Me²⁺ (where Me²⁺ = Ca²⁺, Zn²⁺, Co²⁺ and Ni²⁺) on the protective and adsorption properties of phytic acid in relation to steel in aqueous media was investigated. The coatings obtained in aqueous solutions of phytic acid complexes (PAMe(II)) at pH 6.0 had much higher anticorrosion properties in 3.5 wt.% NaCl solution and chloride-containing concrete pore solution than phytic acid itself [110,112]. The authors believe that the formation of more perfect protective coatings on the steel surface is due to the action of Me²⁺ as crosslinking agents for phytic acid. At the same time, they do not rule out the presence of oxides or hydroxides of complexing cation Me²⁺ in the film. This was confirmed later in [112] by a combination of electrochemical and physicochemical methods. Using PAZn as an example, it was also shown that the PAMe(II) complexes slow down both electrode reactions, i.e., they are CIs of mixed type. The regularities established in these works are important for understanding the structure and mechanism of the formation of protective phytate layers on the Fe and steel surface; however, they cannot be classified as thin films. They are CCs. The CCs obtained in solutions of phytic acid salts with Me(II) were much thicker (more than 15 µm) and denser than the coatings formed in a sodium phytate solution (0.56 µm).

It should be noted the synergism of protection of organic phosphoric acid esters and REM (see Appendix A: Table A1) salts mainly studied on Al, Mg and their alloys. The regularities of inhibition of metal corrosion established for organophosphates with Me(II) cations are also valid for REM complexes that have recently attracted the attention of researchers due to the tightening of environmental regulations. For example, Forsyth et al. [113] noted that diphenyl phosphates (DPhP) of REM provide better corrosion protection for Al alloys than many analogous carboxylates. They believe that the synergism of protection with such salts is associated with the difference in the mechanism of their action. REM cations, primarily Ce³⁺, inhibit the cathodic reaction, while organic anions inhibit the anodic one. Similar studies on steel are described in [114]. The authors showed efficient inhibition of mild steel corrosion in 0.1 mol/L NaCl solution by small ($C_{in} = 0.11\text{--}0.68$ mmol/L) DPhPLa additives. According to electrochemical measurements, it slows down steel dissolution even at low C_{in} , acting as a mixed type CI with predominant inhibition of the cathodic process.

Copper and its alloys. Of organic phosphoric acid esters, mainly phytic acid, its salts and formulations based on them have been studied as corrosion inhibitors of Cu and its alloys over the past decade. It should be noted that the possibility of using phytic acid salts with Ca²⁺ and Mg²⁺ (PACa and PAMg) to prevent the pitting of copper pipes for domestic water was suggested back in the late 1980s by Japanese researchers [4,61]. They demonstrated the advantage of PACa and PAMg over phytic acid or sodium phytate itself in inhibiting the corrosion of not only Cu but also of brass in water [115]. In later works, it was shown that the protective films formed in 1.0 mmol/L PACa solution in 5 h efficiently ($Z = 92.53\%$) prevent Cu corrosion in 3.0% NaCl solution [116]. PACa is a CI of mixed type that slows down both the cathodic and anodic reactions on Cu. Its adsorption on a Cu surface estimated from EIS data and potentiodynamic polarization results under the

assumption that the degree of coverage with phytic acid molecules or anions is proportional to Z (%) is described by the Langmuir isotherm:

$$\frac{C}{\Theta} = \frac{1}{B} + C \quad (9)$$

The $(-\Delta G_A^0)$ value calculated from relationship (5) is 37.3 kJ/mol, i.e., it is close to 40.0 kJ/mol which, in the authors' opinion, indicates the chemical adsorption of PACa. The results of surface-enhanced Raman scattering (SERS) showed that the formation of a film in the presence of PACa occurs due to its chemical interaction with the Cu surface through the $-P-O^-$ and $-P=O$ groups.

In some cases, phytic acid appears to be an even more effective CI for copper than the well-known 1,2,3-benzotriazole (BTA) and its derivatives. For example, it was found [117] that the degree of corrosion inhibition of H62 copper by phytic acid in the model circulating water of a power plant at 45 °C and $C_{in} = 5.0$ mg/L was 94.16%. At the same C_{in} , the anticorrosion efficiency of phytic acid was higher than that of BTA, mercaptobenzoxazole and methylbenzene-BTA by 1.1%, 9.2%, and 0.3%, respectively.

Studies on the adsorption of phytic acid on Cu carried out by electrochemical polarization measurements, EIS and SERS [118,119] showed that it binds to the metal surface through the $-P-O^-$ groups. The adsorption of phytic acid on the Cu surface is described by the Langmuir isotherm with $(-\Delta G_A^0) = 39.96$ kJ/mol, which indicates its chemisorption. A protective film preliminarily formed in a 0.1 mmol/L solution of phytic acid for 6 h provided inhibition of Cu corrosion in 3.0 wt.% NaCl with $Z > 80.0\%$. Analysis of the polarization curves showed that phytic acid acts as a CI of mixed type with predominant inhibition of the cathodic process [118]. Later, the same authors studied the effect of the pH of phytic acid solution on its adsorption and inhibiting properties. It was found that with an increase in pH of 1.0 mmol/L aqueous solution of phytic acid from 3 to 9, the size of its micelles decreased. According to SERS studies, smaller micelles are chemisorbed on the Cu surface only through one $-P-O^-$ group, while the self-assembling layer that is formed is denser, more homogeneous and has better protective properties [119].

Zinc and its alloys. Zinc, primarily in the form of galvanized steels, is widely used as a structural material due to its high corrosion resistance in corrosive atmospheres. This stability is largely due to the protective layer of interaction products of Zn with the converting aqueous solutions of chromates, which were previously used for its passivation. This approach is relatively cheap and efficient in terms of production, but the tightening of environmental regulations in recent decades necessitates the replacement of the carcinogenic passivating solutions of Cr(VI). Considering that the inhibition of Zn corrosion in neutral aqueous solutions is often explained by the chelation reaction between Zn^{2+} and an organic anion with formation of a protective layer with a complex composition on the metal surface [4,7,21], organic phosphoric acid esters can be an efficient alternative to chromates.

For example, SDOP manifests passivating properties not only toward Fe and steels, as noted above, but also toward Zn, although less clearly [4,93]. Addition of small amounts of SDOP ($C_{in} \geq 0.1$ mmol/L) to neutral borate buffer containing 10.0 mmol/L NaCl transfers Zn to the passive state. However, an increase in C_{in} in a wide range (from 0.1 to 50.0 mmol/L) does not lead to a significant increase in E_{pit} (no more than 30.0 mV). At $C_{in} \geq 70.0$ mmol/L, the nature of depassivation changes, namely, instead of a sharp increase in the anodic current when E_{pit} is reached, only small oscillations are observed. After such polarization and removal of a Zn electrode from the solution, it is difficult to distinguish very shallow pits on its surface, which indicates stronger competition between activating Cl^- and the passivating OCI. A further increase in C_{in} to 100.0 mmol/L provides a stable passive state of Zn up to $E_{pit} = 0.5$ V, i.e., the length of the passive region exceeds 1.1 V. Characteristically, at high C_{in} the solution becomes colloidal, and polymolecular adsorption of SDOP can be assumed. Under these conditions, the inhibiting effect is due not only to the strong chemisorption of SDOP on the Zn surface, but also to the barrier properties of the protective film. Thin films formed in the presence of SDOP can enhance

the corrosion resistance of Zn under humid conditions. For example, pretreatment of Zn in a 16.0 mmol/L SDOP solution at 20 °C increases its corrosion resistance twofold as compared to bare Zn in corrosion tests in a heat and moisture chamber [93].

The inhibiting effect of phytic acid, its salts and formulations based thereon was observed not only to the above metals, but also to galvanized steel [120]. For example, in [121] a method was suggested for the passivation of galvanized steel in a molybdate-phytate solution (20.0 g/L Na₂MoO₄, 20.0 g/L phytic acid, 1.0 g/L NaNO₂, 3.0 mL/L 63% HNO₃, 0.2 mL/L 98% H₂SO₄). According to the results of the droplet and immersion mass loss tests, the films obtained in this solution increased the corrosion resistance of galvanized steel better than those obtained in solutions of molybdate or phytic acid alone. This was also confirmed by electrochemical tests (potentiodynamic polarization and EIS) in 0.5 mol/L NaCl solution. In the authors' opinion, the synergistic effect of phytic acid and molybdate is due, first, to the complexation between the reactive groups of phytic acid with the cations of dissolving Zn and adsorption of the resulting complex on the metal surface. Second, it occurs due to the reduction of molybdate to oxides with low valence that can be embedded into the protective layer. A SEM study identified such oxide particles in the film, which was different from those formed by passivation in a molybdate solution alone. Thus, treatment of galvanized steel in a mixed molybdate-phytate solution leads to the formation of a more compact film with high protective properties.

El-Sayed et al. [122] studied ultrathin films formed on galvanized steel by layer-by-layer passivation in 0.5 mmol/L solutions of phytic acid without and with addition of 1.0 mmol/L MnSO₄ and 1.0 mmol/L 2,3-dimercapto-1-propanol (DMP) or 1.0 mmol/L dithio-oxamide (DTOA) at 45 °C. The protective properties of the films were estimated from the results of polarization measurements and EIS in 0.5 mol/L NaCl solution. It was found that the efficiency of phytic acid itself is 3-fold smaller, however, modification of a phytate film, especially that formed in the presence of Mn²⁺, with DMP or DTOA significantly enhances the protection of galvanized steel.

Thus, thin films formed in the presence of acidic organic phosphoric acid esters and their salts can efficiently inhibit the metal corrosion in corrosive media (aqueous solutions with pH ≥ 5.0 and corrosive atmospheres). To provide strong adsorption of their anions on various metals from aqueous solutions, they must contain hydrocarbon radicals, which impart hydrophobic properties to them characterized by log *D* > 0 values. At the same time, a CI should have moderate solubility in water. It should be noted that in the past decade, the study of the mechanism of the protective action of a CI based on organophosphates was carried out not only for the above-mentioned metals, but also for Al, Mg and their alloys [123,124]. For example, some mono- and dialkyl phosphates, namely, dodecyl-, dioctyl-, diphenyl- and dibutylphosphates, are widely used for the passivation of Al and its alloys [102,113,125–128]. To increase the corrosion resistance of Mg and its alloys, the greatest attention was paid to the protective properties of phytic acid and its salts [129,130]. However, in this case, organic phosphoric acid esters, including phytic acid, were mainly studied not as CI or passivators that form ultrathin protective layers, but as the main components of conversion, polymer coatings, and sol-gel protective films [98,131–134].

2.2.2. Phosphonic Acids and Phosphonates

Phosphorus-containing complexons and their complexes with metal cations represent a large group of complex-forming OCIs. Phosphonic acids (PAs) contain basic and acidic donor centers that form at least two cycles on interaction with a metal cation, which ensures a high stability of complex compounds. In this regard, PA anions are often called chelating ligands, and their complex compounds, i.e., phosphonates, are called chelates. The general formula for the simplest dibasic PA is R-P(O)(OH)₂. They can also be polybasic, for example, the structural formulas of the best known ones are shown in Figure 10.

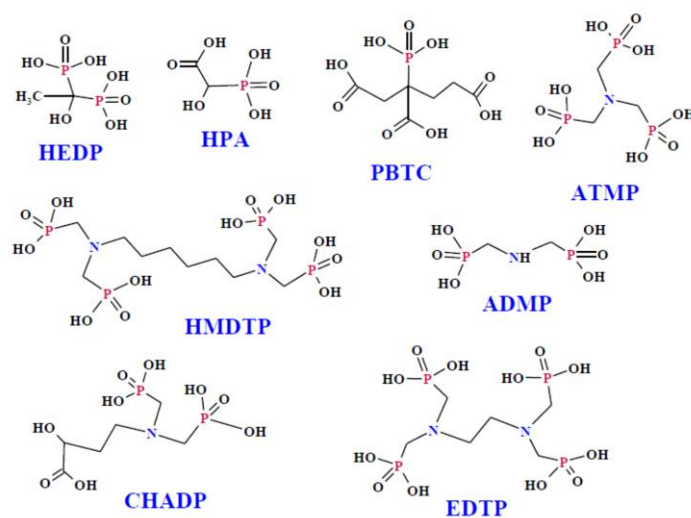
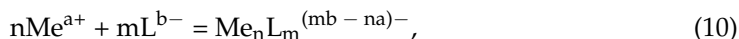


Figure 10. Phosphonic acids: 1-hydroxyethane-1,1-diphosphonic acid (HEDP), amino-tris(methylenephosphonic) acid (ATMP), amino-di(methylenephosphonic) acid (ADMP), ethylenediamine-N,N,N',N'-tetrakis(methylenephosphonic) acid (EDTP), hexaethylenediamine-N,N,N',N'-tetrakis(methylenephosphonic) acid (HMDTP), 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), hydroxyphosphonoacetic acid (HPAA), 1,1-hydroxycarboxypropane-3-amino-di(methylenephosphonic) acid (CHADP).

The high saturation of many PAs with functional groups and the associated ability to form complexes with cations of various metals and to undergo chemisorption on metal surfaces determines their use as efficient OCIs [7]. They are also excellent surface modifiers for various materials used in such different fields as biomedicine, catalysis, optoelectronics, etc. [7,135,136]. However, due to its high reactivity and relatively low toxicity combined with the ability to inhibit scale deposition or dissolve deposits, phosphonate CIs are most widely used for water treatment in circulating cooling systems in order to prevent scale deposition and corrosion [137–142].

Studies on phosphorus-containing complexons and complexonates as CIs began as far back as in the early 1970s. Since then, scientific knowledge about the mechanism of their inhibiting action and the structure of the resulting thin phosphonate protective films expanded significantly. The results of numerous studies of phosphonic acids, phosphonates and compositions based on them as inhibitors of corrosion and scale deposition over the past decade are summarized in a number of works [135–147].

Iron and steel. The mechanism of corrosion inhibition of metals, including Fe and steels, by PAs is due to the complexation between their anions with the cations of the dissolving metal [7,146]. In this case, soluble complexes Me-L may be formed in the near-surface layer:



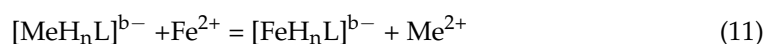
where Me is a cation of the dissolving metal and L is a phosphonate ligand. Hydrophilic phosphonate ligands (for example, HEDP, ATMP), which form readily-soluble complexes in a corrosive medium, can accelerate Fe corrosion and initiate the formation of fine pits on the oxidized surface. However, if $n > m$ in the near-surface layer, PAs are capable of forming hardly soluble polynuclear complexes and act as CIs. This is possible with an excess of complexing cations or deficiency of the ligand, for example, in the case of active Fe dissolution and low concentrations of a complexon. In addition, the compensation of the negative charge of the ligand upon chelation with the metal cation increases the hydrophobicity of the compound and hence its surface activity. Upon accumulation at the metal/solution interface, a hardly soluble complex blocks the Fe or steel surfaces from further dissolution and inhibits corrosion. Unfortunately, corrosion inhibition occurs in a narrow C_{in} range, since an increase in the PA content in the solution results in $n < m$

and the mononuclear complexes that are formed become soluble. Less hydrophilic and more surface-active PAs (for example, HMDTP) whose complexes are poorly soluble or totally insoluble in a corrosive medium are capable of passivating Fe and preventing its depassivation by Cl^- . It is important to note that the described mechanism of action of PAs (“the complexation concept”) does not exclude a beneficial role of adsorption in the inhibition of iron and steel corrosion. However, this concept highlights the need to consider the participation of PAs in complexation processes, taking the features of their chemical structure and the properties of the resulting complexes into account.

In the past decade, studies of the inhibiting action of PAs themselves toward Fe and steels in neutral aqueous solutions were scarce, since this issue has been thoroughly studied previously. Few works deal mainly with the synthesis of new complex derivatives of PAs and expansion of their application field, for example, in acids and highly mineralized media [148–151]. For example, Migahed et al. [150] synthesized new water-soluble phosphonate OCIs, namely (2-hydroxyethoxy)methylbutyl-1-(propylamino)-ethylphosphonate (HMPA), (2-hydroxyethoxy)methylbutyl-1-(undecylamino)ethyl-phosphonate (HMUA) and (2-hydroxyethoxy)methylbutyl-1-(heptadecylamino)ethylphosphonate (HMHA). Quantum-chemical calculations, in agreement with electrochemical measurements, showed a high anticorrosion efficiency of the CIs obtained toward carbon steel in formation water with a total salt content of 12.03 mg/L (pH 6.37). The strongest decrease in the corrosion rate of steel ($Z = 94\%$) was observed in the presence of 15.0 mg/L HMPA. In another work, a comparative analysis of several N-phosphonomethylamino acids was carried out as CIs of carbon steel and scale inhibitors in an aqueous solution containing (g/L) 0.47 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 0.23 $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, 0.11 NaHCO_3 , 0.13 $\text{CaCl}_2 \cdot \text{H}_2\text{O}$, with various pH: 3.7, 7.0, and 8.5 [151]. It was shown that an increase in the number of phosphonic groups in substituted amino acids and an increase in the solution pH significantly enhance their protective efficiency. The authors attribute this to a higher ionization degree of PAs molecules in neutral and weakly alkaline solutions and to an enhancement in their chelating ability. N,N-di(phosphonomethyl)glycine was the most efficient in preventing corrosion and scale deposition in the group of compounds studied.

A much larger number of works have recently been devoted to the study of the adsorption and protective properties of PA complexes with metal cations toward not only Fe or steels but also other metals and alloys. This is not surprising, since the superiority of phosphonates over PAs themselves has long been known [7,146,147]. Modern research methods make it possible to expand the understanding of the mechanism of protective action of phosphonates and to study the structure and composition of thin films formed in their presence on metal surfaces.

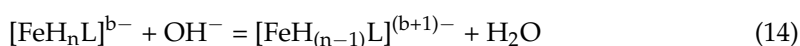
The mechanism of inhibition of Fe and steels corrosion by phosphorus-containing complexonates is rather complicated and depends on their chemical composition [7,146,147]. The formation of a protective film on a Fe (steel) surface by phosphonates can be initiated by the reaction of electrophilic substitution of cations in the inhibiting complex by Fe^{2+} ions formed as a result of the anodic reaction:



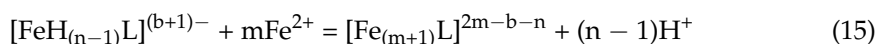
where Me is the complexing cation in the phosphonate. The complementary reaction of oxygen reduction, which generates OH^- and alkalizes the near-electrode layer, promotes the deposition of a hardly soluble hydroxide, $\text{Me}(\text{OH})_2$:



which, along with the adsorption of the CI, provides Fe protection. Alkalinization of the near-electrode layer can also lead to further deprotonation of the complex:



As a result, the formation of binuclear and/or polynuclear complexes with high stability is possible:



Reaction (11) is possible if the K_s values of the resulting Fe(II) phosphonate complexes are higher than the K_s of the inhibiting phosphonate. For example, if the nature of the ligand is unchanged while the Me(II) cation is changed, a non-linear dependence of the CI efficiency on the solubility of the Me(II) hydroxide formed upon electrophilic substitution is observed. This can be explained by taking into account the conditions for the occurrence of reaction (11). The protective properties of Me(II) phosphonates increase with a decrease in the $\text{Me}(\text{OH})_2$ solubility and an increase in the stability of inhibiting complexes until their K_s values exceed the K_s of the Fe(II) phosphonates formed (Figure 11a). In another case, in the series of phosphonates with the same complexing cation, the minimum protective C_{in} (at which a significant inhibition of the metal corrosion rate is observed) increases with increasing K_s , since reaction (11) is kinetically hindered. This is shown in Figure 11b for various zinc phosphonate complexes as an example.

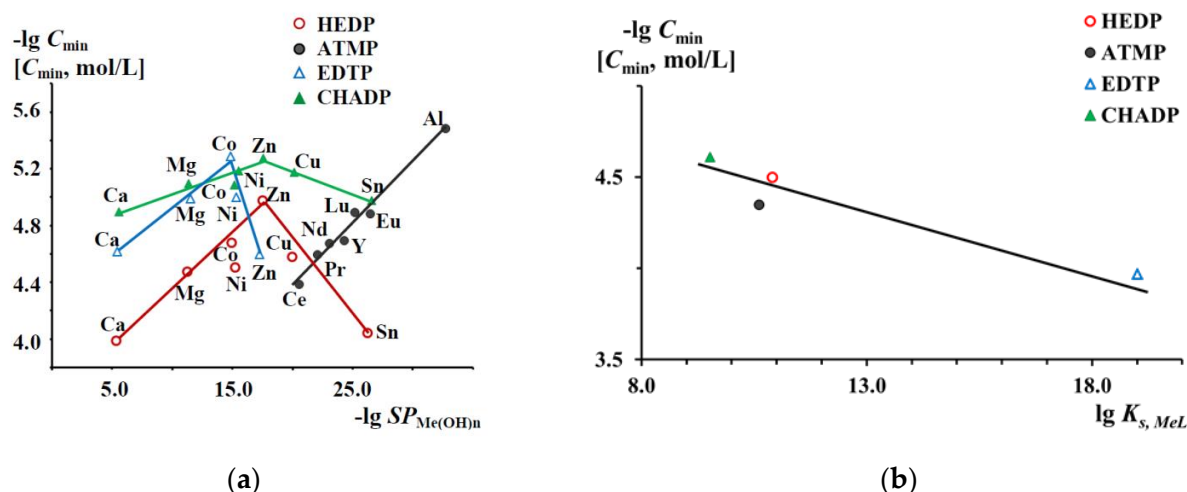
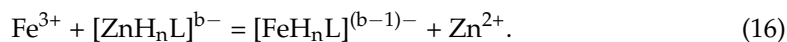


Figure 11. Effect of the solubility product of hydroxides of complexing cations ($SP_{\text{Me}(\text{OH})_n}$) in PA complexes (a) and the stability constant (K_s) of zinc phosphonates (b) on their minimum protective concentration for mild steel in water containing 30 mg/L NaCl and 70 mg/L Na_2SO_4 . The flow velocity of the environment is 0.8 m/s (reproduced from [147] with permission; Copyright 2002 Springer Nature).

The most studied phosphonate CIs for Fe and steel are zinc complexes of PAs, which have low toxicity, high antiscalant and anticorrosion properties [152,153]. According to the mechanism of action of phosphonates described above, inhibition of Fe (or steel) corrosion by zinc phosphonates in aqueous solutions is due to the formation of protective layers on the metal surface, which inhibit both electrochemical reactions and consist of hardly soluble $\text{Zn}(\text{OH})_2$ and hetero- and/or polynuclear phosphonate complexes with the cations of dissolving Fe. This process is apparently initiated by electrophilic substitution of Zn^{2+} by Fe^{2+} cations according to reaction (11) to give complexes with different composition and solubility. The released Zn^{2+} reacts with OH^- generated by cathodic oxygen reduction to form hardly soluble $\text{Zn}(\text{OH})_2$ (reactions 12 and 13), which blocks the metal surface and slows down corrosion. As the rate of Fe dissolution decreases, the deposition of $\text{Zn}(\text{OH})_2$ slows down and the inhibiting complex itself is mainly adsorbed on the surface. It is important that reaction (11) is thermodynamically possible if zinc complexes are either less stable than the similar Fe(II) compounds, or if the difference $\Delta K_s = K_{s, \text{Fe(II)L}} - K_{s, \text{ZnL}}$ is small [7,146,147]. If ΔK_s is significant, then reaction (11), and hence all subsequent reactions (the formation of hydroxides and hardly soluble complexes), become thermody-

namically impossible. However, since in neutral solutions Fe^{2+} may be oxidized to Fe^{3+} , such compounds protect steel according to the following reaction:



Despite the fact that the synergistic effect of the protective properties of zinc salts and PAs has been known for a long time, its studies continue under various conditions for various complexones and metals being protected [154–158]. For example, Yan et al. in a series of works [155–157] investigated the anticorrosion properties of thin films formed on the cold-rolled steel surface in aqueous solutions of HEDP, ATMP, HPAA with Zn^{2+} added as ZnNO_3 . According to the EIS results, a phosphonate layer formed for 10 s in an equimolar solution of HEDP and ZnNO_3 at 90 °C efficiently inhibited steel dissolution ($Z = 93.4\%$) even after 6 h of exposure in 3.5% NaCl [155]. FTIR and XPS analysis of the protective film on a steel surface formed in a solution of the zinc complex of ATMP (AMPZn) showed that it has a layered structure with a thickness of no more than 0.7 μm and consists of heteronuclear complexes of ATMP with Fe(III) and Zn(II) and a certain amount of Zn(OH)_2 [156,159]. The authors note that the presence of hydroxide in the film further enhances its protective properties. The results obtained are in good agreement with the mechanism of action of zinc phosphonates described above (reaction 16). Such films increased the corrosion resistance of steel more efficiently than similar films obtained in an ATMP solution and represented mainly by Fe(III) phosphonate.

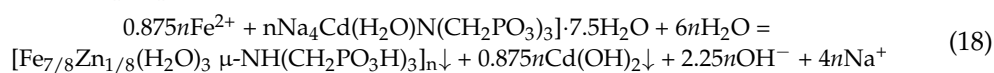
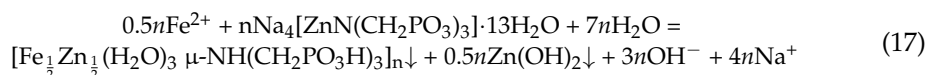
A similar synergistic effect of ATMP with Zn^{2+} (ADMPZn) was observed in the inhibition of mild steel corrosion in a model solution of water-cooling systems containing 60 mg/L Cl^- (pH 7.0) by Prabakaran et al. [160]. It was shown that ADMPZn is a mixed type CI with predominant inhibition of the cathodic process. The changes in the impedance parameters such as charge transfer resistance (R_{ct}) and constant phase element (CPE) confirmed the high adsorption properties of zinc phosphonate. Analysis of the composition and structure of a phosphonate film formed on the steel surface in the presence of ADMPZn by FTIR, SEM, and energy-dispersive X-ray spectroscopy (EDS) showed the presence of mixed ADMP complexes with Fe(II), Fe(III) and Zn(II), as well as Zn(OH)_2 . ADMPZn prevents the adsorption of Cl^- , as indicated by the almost complete absence of chlorides on the steel surface after 7 days of exposure to the model solution.

The protective layers formed in the presence of phosphonates on Fe and steel surfaces are able to efficiently prevent their corrosion even in more corrosive solutions containing high concentrations of Cl^- and/or S^{2-} , for example, in seawater or associated water during oil production [161–163]. For example, Kavipriya et al. observed the inhibition of carbon steel corrosion in seawater ($Z = 70.0\%$) by diethylenetriaminepentamethylene phosphonic acid (DTPMP) with addition of Ni^{2+} [161]. Using FTIR and AFM, they confirmed the formation of a protective film consisting of hardly soluble DTPMPFe complexes and Ni(OH)_2 on the steel surface. The authors of [162] suggested to use HEDP with Ca^{2+} , Mg^{2+} and Zn^{2+} as CIs for AISI304 austenitic stainless steel in 3.5 wt.% NaCl containing 1.0 mmol/L Na_2S . It should be noted that the use of zinc phosphonates in such environments can be limited due to the risk of precipitation of hardly soluble sphalerite or wurtzite. However, phosphonates of metals whose sulfides are not so low soluble are quite applicable for these purposes. It is not surprising that the results of corrosion and electrochemical measurements (potentiodynamic polarization, EIS, mass loss tests) of the inhibiting efficiency of HEDP ($C_{\text{in}} = 50.0$ mg/L) without and together with Ca(II), Mg(II) and Zn(II) chlorides ($C_{\text{in}} = 10.0$ – 30.0 mg/L) in a sulfide-containing solution showed the greatest inhibition of steel corrosion upon addition of Mg^{2+} ($Z = 70.4\%$) or small amounts (10.0 mg/L) of Zn^{2+} ($Z = 85.2\%$).

Studies on the chemical structure of phosphonate CIs is an important direction of research and contributes to a better understanding of the mechanism of their action and is also the basis for obtaining new functional materials with a given structure and properties. Modern research methods make it possible to obtain detailed information on the structural features of the complexes, namely, spatial isomerism, denticity, and the type of ligand

coordination. For example, in the works of Chaousov et al. [164–169] the regularities of the formation of the molecular structure and crystal packing of 62 new coordination compounds of partially and completely deprotonated ATMP with various classes of metal complexing agents (*s*-, *p*-, *d*- and *f*-elements) have been systematically studied by X-ray diffraction method (XSD), EDS, IR and Raman spectroscopy. The main structural types of coordination compounds have been identified and the factors determining their formation have been established.

An important aspect of these studies is the established regularities of the effect of the molecular structure, coordination symmetry, and the nature of the coordination bond in ATMP complexes on their adsorption and anticorrosion properties with respect to steel in aqueous media. For example, it was shown [164,165] that ATMP complexes with Zn^{2+} and Cd^{2+} (ATMPZn and ATMPCd) have different effects on the corrosion-electrochemical behavior of carbon steel in a borate buffer (pH 7.4) depending on the deprotonation degree. The entirely deprotonated ATMPZn and ATMPCd chelate complexes have a higher inhibiting efficiency for steel protection under these conditions than double-deprotonated complexes with a linear polymer structure. At the same time, the minimum protective C_{in} of the cadmium complex is almost five times smaller than that of the zinc complex (0.15 and 0.70 mmol/L, respectively). XPS analysis showed that this is due to the deposition of hardly soluble hydroxides of complexing cations and ATMP(Zn,Fe) and ATMP(Cd,Fe) heteronuclear complexes with strong covalent Fe-O bonds on the metal surface. As a result, the following scheme was suggested for the interaction of phosphonates with Fe^{2+} ions [165]:



The authors of these studies also note that the formation of the reaction products of phosphonates with Fe^{2+} and OH^- on the surface makes a greater contribution to the anticorrosion protection of steel in comparison with the primary blocking of the surface by chemically unchanged OCI molecules. These findings are consistent with the mechanism of action of phosphonates described above.

The effect of the structure of coordination compounds on the composition and protective properties of the adsorption layers formed in their presence on a carbon steel surface was studied using two ATMP complexes with Pb^{2+} with different coordination of the Pb atom, namely, bridging $[\text{Pb}\{\mu^5\text{-NH}(\text{CH}_2\text{PO}_3\text{H})_3\}]$ and chelate $\text{Na}_4[\text{Pb}_2(\text{H}_2\text{O})_2\{\mu^3\text{-N}(\text{CH}_2\text{PO}_3)_3\text{H}_2\}_2] \cdot 10\text{H}_2\text{O}$, as examples, by the same group of scientists [166–168]. The results of electrochemical measurements showed that both complexes insignificantly affect the kinetics of the anodic process. However, subsequent heat treatment at 300 °C of the phosphonate film obtained in a 1.0% solution of the chelate complex leads to a significant increase in its protective properties in a neutral borate buffer but does not affect the properties of the film formed by the bridging complex of ATMP with Pb^{2+} . According to the authors, this is due to the decomposition of chelates upon heating, which leads to secondary inhibition of the steel surface by thermochemical transformation products with a complex composition, including ATMP(Pb,Fe) mixed complexes.

Heteronuclear complexes of phosphonic acids can be more efficient CIs than their mononuclear analogs under the same corrosive conditions. For example, a comparative study of the composition and structure of thin phosphonate films formed in solutions of ATMP, its complexes with Cu^{2+} and Ni^{2+} (ATMPCu and ATMPNi), as well as a new synthesized mixed complex ATMP(Cu,Ni), with subsequent heat treatment at 400 °C was carried out in [169]. The results of polarization measurements in a neutral borate buffer showed a significant inhibition of the anodic dissolution of carbon steel when using a copper-nickel complex, which is characterized by the lowest corrosion currents both in the active dissolution region and in the passive state.

Despite all the advantages of phosphonate CIs, their use can be limited due to the tightening of environmental regulations for the phosphorus content in water. The disadvantages of these CIs also include the possibility of local corrosion, a decrease in efficiency in stagnant zones and in the presence of even small quantities of hydrogen sulfide, and degradation in the presence of oxidizing biocides [135,138,170]. A targeted change in the chemical structure of PAs and phosphonates to give them a high protective ability is one of the main directions in the development of new environmentally friendly and efficient CIs of phosphonate type [146]. It has already been basically discussed above. The second way to increase the efficiency of phosphonate CIs and reduce their protective concentration is to use them in combination with nontoxic and economically available nonoxidative additives, for example, water-soluble polymers, adsorption CIs, or complexing reagents [171–173].

The third direction of research in this area follows from the mechanism of action of phosphonates and involves alkalizing the near-electrode layer to destabilize them and facilitate the precipitation of a hardly soluble hydroxide of the complexing cation. This method was implemented in the combined protection of steel in seawater and was described in [7]. It involved the cathodic polarization of the steel structure to be protected with a “sacrificial” anode and simultaneous addition of small amounts of phosphonate CIs. Recently, this method was applied for anticorrosion protection of bottoms of product storage tanks and tankers in the oil and gas industry [174]. The pH of the near-electrode layer can also be increased by addition of oxidizing additives to a solution. Reduction of such additives generates an excess of OH^- anions [7,146,147]. In [146,175–177], the possibility of enhancing the inhibiting properties of HEDP and ATMP complexes with Me^{2+} toward low-carbon steel in hot (80 °C) highly mineralized water by small additions of NaNO_2 and sodium *m*-nitrobenzoate (*m*-SNB) was shown. It was found that the oxidizer plays an auxiliary role in the formation of a protective film on the steel surface by the main component of the mixture, namely, phosphonate.

When assessing the effect of an oxidizer on the protective properties of phosphonates, it is important that its reduction is not accompanied by formation of hardly soluble compounds as is the case, for example, with chromates, molybdates, etc. The inclusion of such reduction products in the protective layers on a Fe surface complicates the interpretation of experimental data. For example, Zhai et al. [157] used Na_2MoO_4 to increase the anticorrosion properties of films formed in the presence of the zinc complex of HPAA (HPAAZn) on a cold-rolled steel. The EDS and XPS results showed the presence of Mo in the protective layer and formation of the Mo-O-P bond. At the same time, the significant increase in the intensity of the O1s, P2p, and Zn2p peaks and their shift towards higher binding energies in the XPS spectra of steel samples treated in a mixture of HPAAZn and Na_2MoO_4 were ignored. Taking into account the generally accepted mechanism of action of phosphonates, this may be due to the facilitation of the precipitation of hardly soluble $\text{Zn}(\text{OH})_2$ and phosphonate complexes as a result of the reduction of the oxidizer.

The ability of phosphorus-containing complexons and complexonates to form thin protective films on the surface of many metals in aqueous solutions, thereby modifying their surface, has recently attracted the attention of many researchers and opens up new possibilities for their application, for example, to prevent atmospheric corrosion [146,178–181]. Recently, it was suggested to use zinc phosphonates for surface modification of mild steel, which improves the efficiency of subsequent passivation with carboxylates or formulations based thereon [182–184]. The developed method of two-stage treatment of steel for protection against atmospheric corrosion involves the preliminary modification of its surface in HEDPZn or ATMPZn solutions and subsequent passivation in solutions based on carboxylate CIs – SOI or SOS with BTA or trialkoxysilanes (TAS). It has been found that the modifying treatment of mild steel is most efficient at elevated temperatures (60 °C for HEDPZn and 80 °C for ATMPZn), and always increases the stability of passivating films. In this case, the phosphonate films themselves, formed in 8.0 mmol/L HEDPZn or ATMPZn solutions, with a thickness of 6.0 and 5.2 nm, respectively, have weak protective properties in a humid atmosphere. The total thickness of the protective layers after pas-

sivating treatment in solutions of 4.0 mmol/L SOI with 4.0 mmol/L BTA or 4 mmol/L SOS with 4 mmol/L BTA was 25.7–33.0 nm. ATMPZn was found to be more efficient as a modifier than HEDPZn.

These studies also showed the positive effect of NaNO_2 on the efficiency of modification of the steel surface with zinc phosphonates (its mechanism was discussed above). The addition of an oxidizer to the modifying solution of ATMPZn, facilitating the formation of hardly soluble compounds on the steel surface, increased twofold its resistance to local depassivation by Cl^- in a neutral borate buffer and corrosion in an atmosphere of 100% relative humidity. Formulations based on SOS had higher protective properties among passivating solutions. The protective effect of the coatings obtained, estimated by the τ_{cor} value, reached 62 days ($\tau_{\text{cor}} \leq 1$ day for untreated samples) during corrosion tests in a heat and moisture chamber [182]. The formulations of SOS with vinyltrimethoxysilane (VTMS) $\text{H}_2\text{C}=\text{CH}-\text{Si}(\text{OCH}_3)_3$ had better protective properties than those with BTA. The authors attributed this to the formation of a polysiloxane network in the presence of VTMS, which stabilizes and blocks phosphonate protective layers on the metal surface. Polarization, EIS measurements, as well as field tests in an urban atmosphere have shown that the preliminary modification of mild steel surface in 8.0 mmol/L solution of ATMPZn increased the passivating effect of the equimolar mixture of SOS with VTMS (with total $C_{\text{in}} = 8.0$ mmol/L) [183]. The practical prospects of this method of surface treatment in comparison with traditional methods of temporary anticorrosion protection are the possibility of using non-toxic compounds at low concentrations and the extremely small thickness of the protective films (30–60 nm). This solves the problems associated with the depreservation and disposal of the used-up compounds.

An important feature of phosphonate CIs is their ability to form polymolecular self-assembling layers on the surface of various metals, including Fe and steels. The first layer is usually strongly bound to the metal surface, and its structure and properties are determined by the interaction of the phosphonate with the surface. Divalent metal cations usually serve as “bridges” between phosphonate monolayers [135,144]. From the point of view of molecular self-assembly on metal surfaces, the most attention in recent decades was drawn to alkylphosphonic acids ($C_n\text{PA}$) and their salts ($C_n\text{PMe}$) [178,185–187]. On the one hand, such $C_n\text{PAs}$ are more hydrophobic and have high surface activity. However, the formation of thin films by them from aqueous solutions is limited due to low solubility and formation of colloids. At the same time, the use of $C_n\text{PAs}$ with $n_c \leq 12$ or diphosphonic acids with good water solubility at low concentrations makes it possible to obtain their thin layers, including SAMs, even in aqueous solutions [187–191]. For example, it was shown [188] that propylphosphonic acid ($C_3\text{PA}$), together with Zn^{2+} , efficiently ($Z = 90\%$) inhibits the dissolution of carbon steel in an aqueous solution containing 60 mg/L Cl^- . According to the results of FTIR, AFM, SEM and XPS measurements, the inhibiting effect of zinc alkyl phosphonate is due to the formation of a thin film on the steel surface, consisting of mixed complexes of $C_3\text{PA}$ with Fe(III), Fe(II) and Zn(II), $\text{Zn}(\text{OH})_2$, iron oxides and hydroxides.

The effect of sodium salts of $C_n\text{PAs}$ ($C_n\text{PNas}$) with the general formula $C_n\text{H}_{2n+1}\text{PO}_3\text{Na}_2$ ($n_c = 7\text{--}10$) on the anodic dissolution and passivation of mild steel in a borate buffer with pH 7.4 containing 10.0 mmol/L NaCl was studied in [189]. Electrochemical studies have shown that $C_n\text{PNas}$ can inhibit the anodic dissolution of steel under the studied conditions, up to complete passivation of its surface. The passivating effect of $C_n\text{PNas}$ nonlinearly depends on the length of the hydrocarbon radical and enhances in the series: $C_{10}\text{PNa}$ (−0.84) < $C_7\text{PNa}$ (−2.41) = $C_9\text{PNa}$ (−1.37) < $C_8\text{PNa}$ (−1.90). The hydrophobicity of these CIs increases with the alkyl length, judging by the $\log D$ values given in parentheses. This apparently explains the difference in the effect of these OCIs on the anodic dissolution of mild steel. $C_8\text{PNa}$ is more hydrophobic than $C_7\text{PNa}$, therefore its surface activity and adsorption properties are somewhat higher. However, an increase in hydrophobicity can lead to a decrease in the effective C_{in} in the solution due to micelle formation; therefore, the protective ability of $C_9\text{PNa}$ and $C_{10}\text{PNa}$ becomes lower.

C₈PNa has the highest inhibiting efficiency among the studied C_nPNaS [190]. C₈PNa is capable of transferring steel to a passive state, but the formation of a protective film is slow. If exposure of a steel electrode in a borate buffer is short (15 min), steel passivation does not occur even at C_{in} = 4.0 mmol/L C₈PNa, but prolonging it to 2 h leads to spontaneous passivation even at C_{in} = 0.3 mmol/L. At the same time, E_{pit} increases, which indicates the formation of more stable films. This also indicates the self-assembly of the phosphonate film, which requires additional time. Increasing the temperature and stirring the solution accelerate the formation of protective layers on steel by the alkylphosphonate. With an increase in temperature to 60 °C, spontaneous passivation of steel is observed even at 0.1 mmol/L C₈PNa. However, the passive film formed is unstable because the E_{pit} value is smaller than in a solution without a CI. In the authors' opinion, this may be due to the fact that C₈PNa adsorption prevents the growth of an oxide film on the steel surface. The concentration of the phosphonate is too low to withstand the adsorption competition with corrosive Cl[−] since its content in solution is two orders of magnitude higher. With a growth in C_{in}, the lack of steel protection by C₈PNa disappears and E_{pit} increases. This assumption about steel passivation with C₈PNa by the “non-oxide” adsorption mechanism was confirmed by galvanostatic coulometry data [190].

The results of in-situ ellipsometric studies in a neutral borate buffer showed that C₈PNa is adsorbed both on reduced (at $E = -0.65$ V) and pre-oxidized (at $E = 0.20$ V) steel surfaces. The adsorption of C₈PNa is described by the Frumkin isotherm, and the calculated values of $(-\Delta G_A^0)$ are 36.31 and 29.63 kJ/mol, respectively. These results indicate a strong bond of C₈PNa anions with the steel surface and its better adsorption on an oxide-free surface than on an oxidized surface of mild steel. This conclusion is different from the results of previous studies [192,193] on Fe passivation with C₈PA in a borate buffer with pH 8.4. Thus, C₈PNa is able to passivate mild steel even at lower C_{in} than the well-known passivators, namely SOL and SDOP [21,100,103].

The passivation of mild steel in a borate buffer with pH 7.3 by sodium dodecylphosphonate (C₁₂PNa) and the effect of the initial state of the surface, namely the presence of a surface oxide layer, on its adsorption was studied by I.D. Zartsyn et al. [194]. The adsorption of C₁₂PNa was studied on a steel electrode with an air-formed oxide (native surface), as well as by combining the adsorption of the CI with cathodic reduction of the surface. It was found that the minimum i_p values were observed when a C₁₂PNa dispersion was introduced into the solution under cathodic polarization ($E = -0.65$ V) that cleaned the electrode surface from the air-formed oxide. In this case, the authors observed the absence of a potential delay corresponding to the reduction of iron oxides on the steel surface during galvanostatic polarization of the electrode after its exposure at potentials in the passive region. FTIR results showed that the maximum amount of adsorbed phosphonate was observed upon cathodic reduction of the steel surface in the presence of C₁₂PNa in a deaerated borate buffer. At the same time, even after C₁₂PNa adsorption on the native surface, peaks corresponding to the vibrations of the −CH₂ and −CH₃ groups were also clearly visible on the FTIR spectra, though with a lower intensity. This fact allowed the authors to suggest that C₁₂PNa can protect mild steel by the “non-oxide” passivation mechanism, like it was previously proved for SDOP, C₈PNa, and anions of some higher carboxylic acids [21,100,190].

Copper and its alloys. In the past decade, PAs themselves have been little studied as CIs of Cu in aqueous solutions, although it is one of the most important industrial non-ferrous metals. However, taking into account the high adsorption and complexing ability of the phosphonic group, as well as the formation of phosphonate SAMs on the surface of many metals and their oxides, PAs or C_nPA are used to synthesize new compounds or to make inhibiting formulations with well-known CIs of Cu and its alloys, for example, with heterocyclic compounds. For example, Wang et al. [195] synthesized a multipolymer with −OH, −SO₃H, −COOH, and −PO₃H functional groups in the molecule that are often contained in scale and corrosion inhibitors for water treatment in industrial circulation systems. The phosphorus content in the polymer did not exceed

4.0 wt.%, which makes it safe from an environmental point of view. The synthesized polymer at $C_{in} = 8.0$ mg/L efficiently ($Z = 70.22\%$) prevented brass corrosion in water containing (mg/L) 7.35×10^{-2} $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 6.58×10^{-2} NaCl, 4.93×10^{-2} $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 1.68×10^{-2} $\text{Ca}(\text{HCO}_3)_2$ at 45 ± 1 °C, acting as an anodic CI. According to the results of EDS analysis, the protective film formed on the brass surface consisted of Cu(II) and Zn(II) complexes with organic ligands.

Kozlica et al. [196] studied the inhibition of Cu corrosion in 3.0 wt.% NaCl in the presence of C₈PA, 2-mercaptobenzimidazole (MBI), and their binary formulations. Electrochemical studies have shown that MBI is a good CI for Cu, while C₈PA can synergistically enhance its action. The most pronounced synergistic effect of a mixture of MBI with C₈PA was observed at the 9:1 molar ratio of the components ($C_{mix} = 1.0$ mmol/L). The authors obtained interesting results by studying the composition of the surface protective film formed in the presence of this inhibiting formulation. According to quantum-chemical calculations based on the density functional theory (DFT), both investigated CIs are capable of adsorbing on the copper surface. Considering this and the known ability of C_nPAs to form complexes with Cu^{2+} , the results of XPS and FTIR analysis were unexpected as they showed the absence of products of interaction of C₈PA with the Cu surface, neither when used alone, nor in combination with MBI. At the same time, it was found that MBI used alone binds to copper in the thiolate form (both pyridine and pyrrole nitrogen signals are present), while in the presence of C₈PA, the binding mechanism changes and, in addition to thiolate, the film contains the thione form with pyrrole nitrogen. The authors suggested that C₈PA enhances the adsorption of MBI and leads to the formation of a thicker multilayer film with high protective properties. In this case, a decrease in the solution pH upon addition of C₈PA and the presence of Cl^- can lead to the formation of a soluble complex of C₈PA with Cu(II).

The effect of Cl^- on the formation of a thin film in the presence of an inhibiting mixture of MBI and C₈PA in 3.0 wt.% NaCl solution was studied in more detail by the same authors later [197]. According to the results of time-of-flight secondary ion mass spectrometry, the Cl^- ions act as a promoter of the $[\text{Cu-MBI}]_n/[\text{Cu-Cl-MBI}]_n$ polymeric film formation and is simultaneously incorporated into it. Along with this, this film has high protective properties because it comprises a lower Cu₂O layer adjacent to the metal surface and a top porous $[\text{Cu-Cl-MBI}]_n$ layer with “straw-like” morphology. In addition, the protective thin film formed in the presence of the synergistic composition of C₈PA and MBI is highly resistant to degradation.

Zinc and its alloys. Despite the fact that the ability of PAs to form strong complex compounds with Zn^{2+} has been known for a long time, there are few works devoted to the study of their effect on the corrosion-electrochemical behavior of Zn and its alloys. For example, Aramaki investigated the effect of HEDP and ATMP salts with Na^+ (HEDPNa and ATMPNa) on the electrochemical behavior of Zn in an aerated 0.5 mol/L NaCl solution [198]. According to electrochemical measurements, both phosphonates at $C_{in} = 3.0$ and 10.0 mmol/L stimulated the anodic dissolution of Zn, shifting its E_{cor} in the negative direction. The author logically related this fact with the formation of soluble complexes of HEDP and ATMP with Zn^{2+} . Later Zhang et al. [199] who studied the functionalization of the surface of ZnO nanowires and monocrystalline ZnO (0001) wafers in an aqueous solution of 3-phosphonopropionic acid (3-PPA) plates observed an increase in the surface roughness of ZnO, as well as the formation of an inhomogeneous film after treatment. In the authors' opinion, this was due to slight acid etching of the ZnO wafer surface during adsorption.

However, as noted above, polybasic PAs can form hardly soluble polynuclear complexes and act as CIs if there is a deficiency of ligand anions or an excess of complexing cations in the near-surface layer ($[\text{Me}^{2+}] > [\text{L}^-]$). In addition, a more complete deprotonation of phosphonate complexes, for example, with an increase in the solution pH, enhances their inhibiting properties because reaction (15) can occur. Taking this into account, the possibility of inhibition of Zn corrosion by HEDPZn in a borate buffer solution (pH 7.4) containing 1.0 mmol/L NaCl and in a humid atmosphere was studied [200]. In this work,

two approaches were used to increase the efficiency of anticorrosion protection of Zn, as mentioned earlier in the section concerning the inhibition of steel corrosion by zinc phosphonates. The first approach involved the joint use of HEDPZn with an oxidizer (*m*-SNB). It was shown that the formulation of HEDPZn with *m*-SNB was a more efficient CI for Zn than its individual components under the conditions studied. An increase in the temperature of the passivating solution, the duration of treatment, and C_{in} facilitates the formation of protective layers by a mixture of HEDPZn and *m*-SNB and increases their stability in a humid atmosphere. The second method involved the layer-by-layer passivation of Zn in a solution of the mixed CI consisting of HEDPZn and *m*-SNB (first layer), and a carboxylate CI, SOI (second layer). This two-stage treatment made it possible to increase the corrosion resistance of Zn under harsh conditions of high atmospheric humidity, increasing the τ_{cor} value 8-fold.

Glover et al. [201] investigated phenylphosphonic acid (PhPA) as a CI for hot dip galvanized steel (HDG) in 5.0 wt.% NaCl solution in a wide pH range (2.0 ± 11.5). The effect of PhPA concentration and solution pH on the inhibition of localized corrosion of HDG was studied in situ by the scanning vibrating electrode technique where the C_{in} in the solution was gradually increased, as well as by mass loss tests. It was shown that PhPA efficiently ($Z = 96\%$) suppresses the local dissolution of steel at $C_{in} = 50$ mol/L in a neutral solution (pH 7.0). Its inhibiting effect is due to the formation of a protective film of PhPZn as a result of additional deprotonation of HPhP[−] anions to give PhP^{2−} upon alkalinization of the near-electrode layer on the cathodic surface areas. The anticorrosion efficiency of the phosphonate film in a neutral solution is much higher than in the acidic (pH 2.0) or alkaline (pH 11.5) solutions. In the authors' opinion, this is due to the insufficient concentration of PhP^{2−} ions at low pH, or to the predominance of soluble zincate anions ($ZnO_2^{2−}$) at high pH, which prevents the formation of a strong and uniform protective film.

Taking into account that C_n PNas are more hydrophobic, surface-active and capable of forming very thin self-assembled films even from aqueous solutions, the adsorption and passivating properties of sodium decylphosphonate (C_{10} PNa) and C_{12} PNa toward Zn in a borate buffer with pH 7.4 containing 1.0 mmol/L NaCl, in atmospheres of high humidity and in a salt spray were studied in [202–205]. The studies were carried out on a reduced Zn surface at $E = -1.1$ V, as well as air-oxidized surface and in solution at $E = 0.2$ V to establish the regularities of zinc passivation by C_n PNas and the effect of the surface oxide. As a result, it was shown that C_{10} PNa and C_{12} PNa are able to passivate Zn, increasing its stability in a chloride-containing aqueous solution and in a humid atmosphere [202,203]. The inhibiting properties of alkyl phosphonates are enhanced with an increase in the alkyl length, C_{in} , and duration of passivation. The protective properties of C_{10} PNa and C_{12} PNa are more pronounced on a reduced Zn surface, and their minimum C_{in} required to transfer the metal to the passive state is 2.0–2.5 times smaller. At the same time, the passivating effect of alkyl phosphonates is characterized by threshold C_{in} values, namely, 5.0 and 2.0 mmol/L on the Zn surface oxidized in solution and 2.0 and 1.0 mmol/L on an oxide-free surface, respectively. An important role in the passivation of Zn by C_n PNas is played by the composition and structure of surface oxide films formed in the atmosphere and in solution. For example, an air-formed oxide layer does not prevent the formation of a passive film by C_{12} PNa on Zn under free corrosion conditions. At the same time, C_{12} PNa does not passivate anodically oxidized Zn at $E = 0.2$ V [203].

The adsorption of C_{10} PNa and C_{12} PNa on “non-oxide” and previously oxidized Zn surfaces was first studied in situ by ellipsometry in a borate buffer with pH 7.4 at controlled potentials of -1.1 and 0.2 V [202,203]. Both alkyl phosphonates exhibit the highest adsorption activity on a reduced Zn surface (Figure 12). The adsorption of a monolayer of C_{10} PNa and C_{12} PNa at $E = -1.1$ V is described by the Temkin equation with high values of $(-\Delta G_A^0)$: 75.9 and 88.70 kJ/mol, respectively. It is clear that the adsorption properties of C_{12} PNa are more pronounced than those of C_{10} PNa. It is logical to associate this with an increase in its hydrophobicity characterized by the value of $\log D$ (at pH 7.4, $\log D$ is -0.84 and 0.22 for the C_{10} PNa and C_{12} PNa anions, respectively).

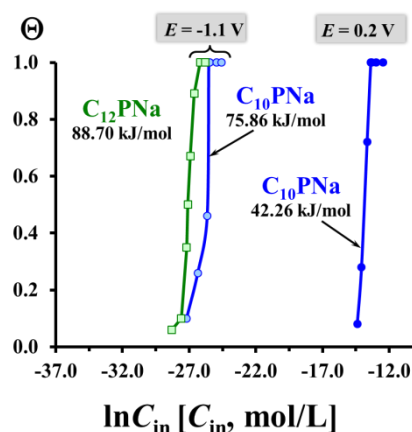


Figure 12. The adsorption isotherms of C_{10} PNa and C_{12} PNa on Zn surface at $E = -1.1$ and 0.2 V (vs. SHE) in borate buffer solution (pH 7.4) (adapted from [202,203] with permission; Copyright 2018 Springer Nature; Copyright 2020 Elsevier).

Based on the results of ellipsometric measurements, it was found that the thickness of the C_{12} PNa monolayer adsorbed on the “non-oxide” surface is 1.7 nm, and the orientation of the molecules in the monolayer corresponds to the model of fully extended (all-trans) alkyl chains. On the Zn surface preliminarily anodically oxidized at $E = 0.2$ V, the adsorption of the alkyl phosphonates studied is hindered due to the formation of a thick oxide-hydroxide layer on it. In this case, it was not possible to obtain the adsorption isotherm of C_{12} PNa.

The results of ex situ XPS analysis of the composition of protective layers formed on the oxidized (in air and in solution) and reduced Zn surfaces in the presence of C_{12} PNa confirmed the conclusions described above [203]. In general, treatment of Zn in a 1.0 mmol/L C_{12} PNa solution for 2 h leads to the formation of a thin protective film consisting of ZnO, $Zn(OH)_2$, and $C_{12}PZn$ complex (Figure 13), regardless of the presence of an oxide-hydroxide layer on the surface and electrode potential. The thickness of the complex layer exceeds the length of the C_{12} PNa molecule, even after ultrasonic washing, which indicates the formation of a strongly chemisorbed polymolecular layer. This layer can be retained by the formation of $-Zn-O-P-O-Zn-O-P-$ surface chain complex. The greatest thickness of the $C_{12}PZn$ layer (7.2 ± 0.2 nm) was observed upon passivation of a Zn surface cathodically pre-reduced at $E = -1.1$ V and a native (air-oxidized) surface under free corrosion conditions. This, along with the smallest thickness of the oxide-hydroxide layer (2.0 ± 0.2 nm), apparently determines the high protective properties of the films. Conversely, the presence of a thick layer of ZnO and $Zn(OH)_2$ (3.0 and 2.8 ± 0.2 nm) and a thin layer of the $C_{12}PZn$ complex (2.7 ± 0.2 nm) in the film formed on the Zn surface anodically oxidized at $E = 0.2$ V determines its weak protective properties that were observed in polarization measurements.

It should be noted that thin films formed in an aqueous solution of C_{12} PNa give hydrophobic properties to the Zn surface (the Θ_c value increases from $72 \pm 3^\circ$ for untreated air-oxidized zinc to $104 \pm 4^\circ$). The combined body of the data obtained indicates a high degree of ordering of the adsorption layers formed in the presence of C_{12} PNa, which provides their passivating effect with respect to Zn even in the absence of an oxide-hydroxide film on the surface and indicates the possibility of “non-oxide” adsorption passivation of Zn by C_n PNas [203].

Ultrathin films formed on Zn in an aqueous solution of C_{12} PNa can increase its corrosion resistance not only in a chloride aqueous solution, but also in a humid atmosphere. The protective properties of phosphonate layers depend on the conditions of their formation. According to the results of electrochemical and corrosion tests, the films formed in the presence of C_{10} PNa or C_{12} PNa on a Zn surface had the best anticorrosion properties when they were obtained from a stirred solution at 40°C for 2 h. However, the resulting phosphonate films are not sufficiently efficient for long-term protection of Zn against corrosion or under more harsh conditions, for example, in a salt spray.

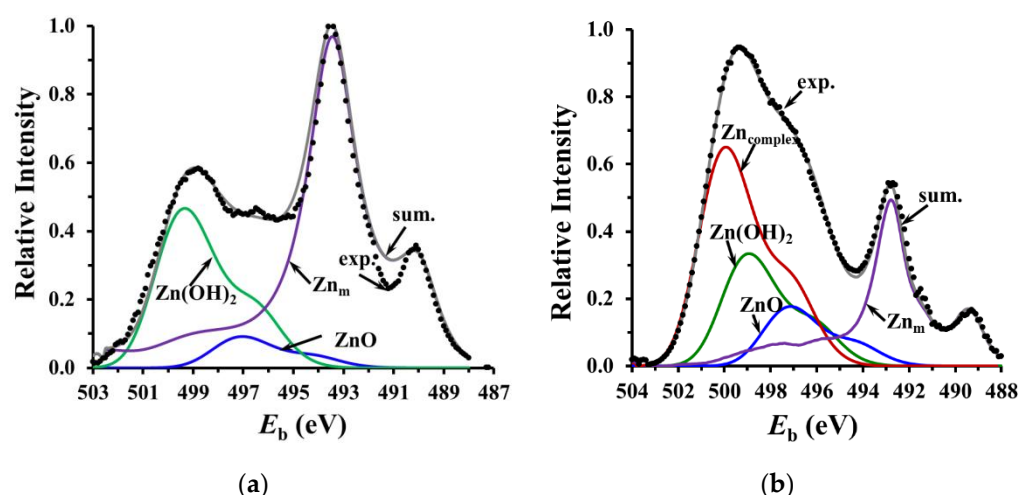


Figure 13. Auger ZnLMM spectrum of a Zn sample exposed for 120 min at E_{cor} in borate buffer (pH 7.4) (a) without and (b) in the presence of 1.0 mmol/L $C_{12}PNa$ (reproduced from [203] with permission; Copyright 2020 Elsevier).

The protective properties of layers formed on Zn in the presence of C_nPNa s can be increased by TAS (see Appendix A: Table A1) using the LbL method. For example, it was shown [204] that the efficiency of anticorrosion protection of Zn in a chloride-containing solution and in corrosive atmospheres is higher in the case of joint use of $C_{12}PNa$ and TAS with various structures (AEAPTS; VTMS and *n*-octyltriethoxysilane (OTES) $CH_3-(CH_2)_7-Si(-OCH_3)_3$) than when individual CIs are used. The nature of TAS and the sequence of their application in the layer-by-layer passivation with phosphonate have a great influence on the protective properties of thin films. For example, AEAPTS containing an amino group in the molecule is most efficient as a first layer enhancing the adhesion of the subsequent alkyl phosphonate layer. It is preferable to apply hydrophobic VTMS and OTES in a second layer capable of blocking possible defects in the film formed by the chemisorbed alkylphosphonate. At the same time, judging by the values of ΔE and τ_{cor} , the protective properties of films obtained by LbL passivation of Zn with $C_{12}PNa$ and AEAPTS are noticeably inferior to the properties of films obtained by treatment in solutions of $C_{12}PNa$ and VTMS or OTES. Moreover, the treatment of Zn in solutions of $C_{12}PNa$ and OTES is most efficient in inhibiting its anodic dissolution in a chloride-containing aqueous solution and corrosion in atmospheres of high humidity and salt fog (Figure 14).

According to the recommendations of ISO 9227, the rainbow chromate conversion coating satisfactorily protects galvanized steel against corrosion if the τ_{cor} value in the salt spray chamber is at least 72 h. Thus, the ecologically friendly method of Zn passivation suggested in [204] can serve as an excellent alternative to a toxic chromate treatment to protect Zn coatings from atmospheric corrosion.

The formation of a thin film on an air-oxidized Zn surface in solutions of $C_{12}PNa$ and TAS promotes its hydrophobization, which, along with strong chemisorption, is an additional factor affecting an increase in its corrosion resistance under atmospheric conditions. However, on treatment of a smooth Zn surface by $C_{12}PNa$ with OTES that is the most hydrophobic of the TAS studied, the Θ_c value does not exceed $124 \pm 2^\circ$. To obtain SHP (see Appendix A: Table A1) coatings on metals, and hence, increase their corrosion resistance, it is necessary to impart a polymodal morphology to the surface. In [205], a method for obtaining SHP coatings on Zn based on laser surface treatment with subsequent layer-by-layer passivation in an aqueous solution of $C_{12}PNa$ and water-alcohol (90% H_2O + 10% C_2H_5OH) solutions of VTMS or OTES was suggested. The polymodal roughness of the Zn surface obtained by laser texturing makes it possible to achieve its superhydrophobization upon layer-by-layer passivation with $C_{12}PNa$ and TAS and increase the protective properties of the thin films they form. The highly developed surface morphology obtained by such treatment provides better adhesion of the first phosphonate

layer. In combination with a stable siloxane network in the top layer, which blocks existing defects in the film formed by the chemisorbed alkylphosphonate, this determines the high protective and hydrophobic properties of the coatings and their stability over time (Figures 15 and 16).

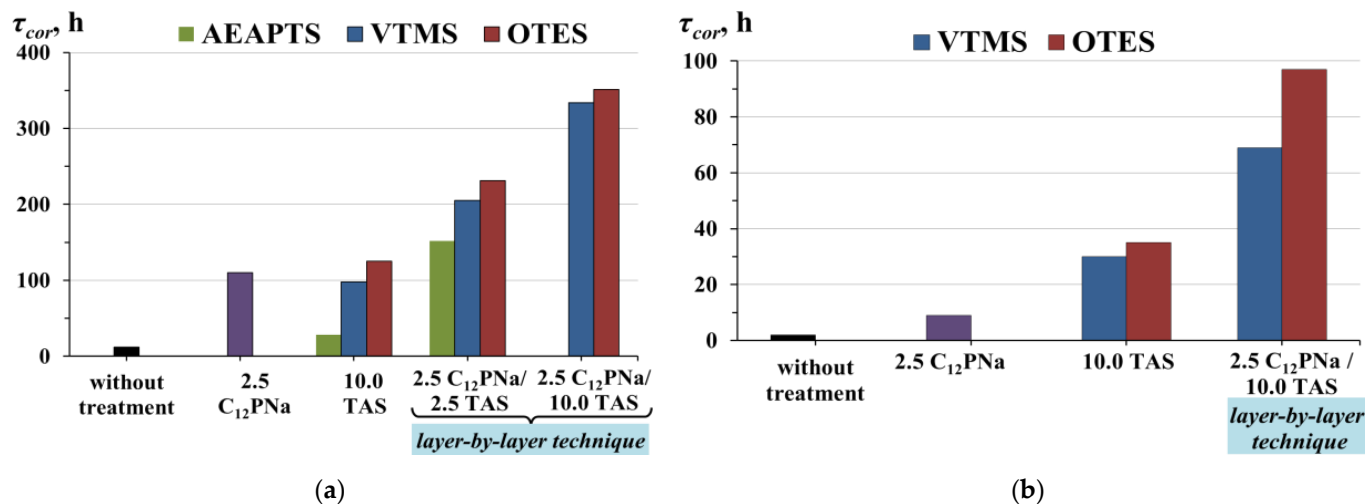


Figure 14. The τ_{cor} value in chambers of (a) heat and moisture and (b) salt spray on Zn samples treated in C_{12} PNa and TAS solutions at 40 °C for 2 h (or 1/1 h in the layer-by-layer treatment). The concentrations of CI solutions are given in mmol/L (adapted from [204] with permission; Copyright 2021 Springer Nature).

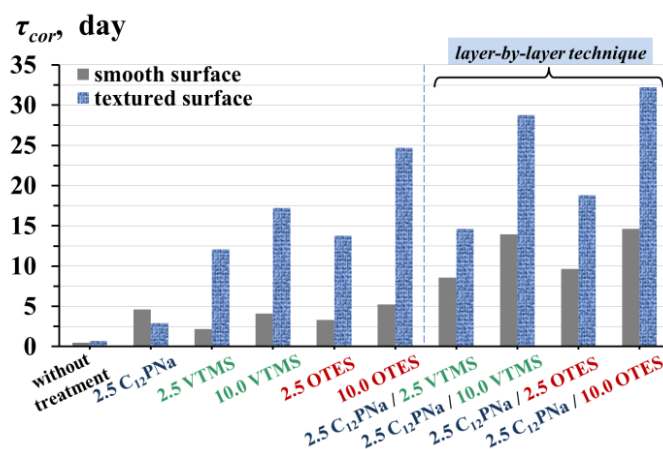


Figure 15. The τ_{cor} value in the heat and moisture chamber on Zn samples passivated in C_{12} PNa and TAS solutions, with and without preliminary laser texturing. The concentrations of CI solutions are given in mmol/L [205].

Thus, the presence of a hydrophilic phosphonic group and a hydrophobic alkyl in the molecules of monoalkylphosphonic acids gives them a diphilic structure, surface activity, and the possibility of self-assembly in the adsorption layer while maintaining sufficient solubility in water. This makes it possible to use their aqueous solutions not only for obtaining thin films with high anticorrosive properties, but also for superhydrophobization of the surface of metals and alloys. In addition, the low hydrophobicity of C_n PAs themselves with $n \leq 12$ ($\log P \leq 3.83 \pm 0.58$) and even more so their anions in neutral aqueous media ($\log D \leq 0.22$) gives certain environmental advantages, since chemical compounds with $\log P < 3.0$ are practically not dangerous with respect to accumulation by the cells of living organisms [206].

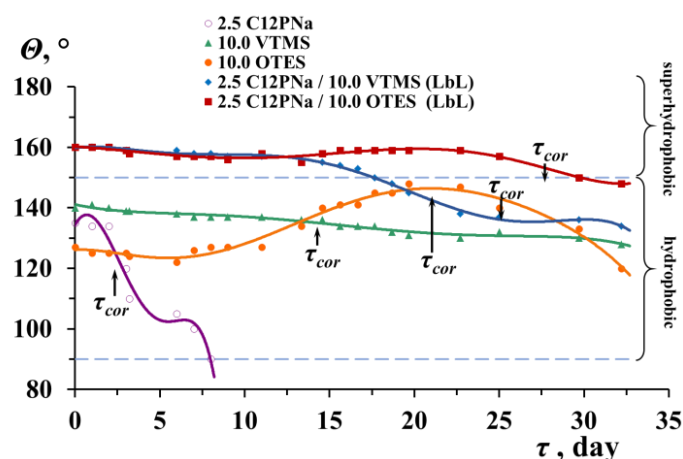


Figure 16. Change in Θ_c with time in the heat and moisture chamber on textured surfaces of Zn samples after layer-by-layer treatment in solutions. The concentrations of CI solutions are given in mmol/L [205].

3. Organic and Water-Organic Solutions

3.1. Carboxylic Acids and Their Salts

The peculiarities of the solvent effect on corrosion inhibition by organic compounds have been repeatedly discussed in the literature [7,27]. The solution of many problems requires the search for OCIs for organic solvents or their mixtures. For example, according to [207], in a mixture of 90.0% gasoline with 10.0% ethanol (GE), the presence of 1.0% water increases the corrosion rate of steel almost 3-fold, although even the mixture itself is more corrosive than gasoline. A small addition of an environmentally safe OCI, ascorbyl palmitate (120.0 mg/L), provided a high degree of carbon steel protection, $Z = 98.6\%$, i.e., reduced its corrosion rate by more than an order. This indicates the prospects of using OCIs to reduce the corrosiveness of GE 10 transport fuel.

However, this section will discuss a narrower but interesting part of the corrosion problems. In organic and water-organic solutions it is possible to form thin protective coatings with very hydrophobic OCIs that are poorly soluble or almost insoluble in water. Note that one very promising area of inhibitor corrosion protection of metals is the superhydrophobization of their surfaces using such solutions. In addition, in these solutions there is an opportunity to study the interaction with the metal surface by carboxylic acids rather than their salts, which is important for understanding its mechanism not only for corrosion inhibition, but also for other purposes.

For example, the authors [208,209] studied the interaction of self-assembling molecules with Fe and Zn as important elements in metallurgy and catalysis. In addition, succinic acid simulates the operation of many adhesives and organic coatings, and Fe and Zn form the basis of the surface of galvanized steel. In this regard, the study of interfacial processes in the interaction of the carboxyl groups of this acid with Zn and Fe substrates provides information about the characteristics of polymer binding and surface properties not only of the metals themselves, but also of galvanized steel. Undoubtedly, the state of the metal surface and the bulk properties of the oxide play an important role in determining the nature of interfacial chemical interactions. It has been shown that carboxylic acids and anhydrides (succinic or myristic acids and succinic anhydride molecules) have the ability to coordination binding to the surfaces of Fe and Zn oxides. Here, acid-base interactions lead to formation of an interfacial dipole and a change in the distribution of charge carriers, which depends on the properties of the adsorbate. Thus, upon adsorption of succinic acid ($\text{COOH}-(\text{CH}_2)_2-\text{COOH}$) on Fe samples with a low hydroxyl fraction ($\text{OH} < 20.0\%$), it was mainly bound to the surface by a single carboxyl group, while if high amounts of hydroxyl ($\text{OH} > 40.0\%$) are present on Zn, the same molecules can be fixated on the surface through both ends. In view of this, the authors studied the effect of oxide resistance,

surface hydroxyl fraction and adsorbates on the Volta potentials of Zn surfaces. They showed that their values grow with increasing oxide resistance and hydroxyl concentration on Zn surfaces. They also found that the presence of contaminants on Zn increases the Volta potential because of changes in dipole moments contributing to its overall magnitude. A high hydroxyl content on the Zn surface increases the deprotonation of adsorbed acid and anhydride molecules. This increases the chemical dipole moment and the shifts of the Volta potential. However, the molecular rearrangement that occurs due to the interaction between organic molecules and the surface additionally affects the molecular dipoles. According to the authors, the decrease in the Volta potential shifts at relatively high hydroxyl fractions is due to the degradation of the dipole orientation due to adsorption of succinic acid by both carboxyl groups, as well as surface dehydroxylation due to hydroxyl consumption occurring upon adsorption of molecules.

Iron and steels. A large number of publications devoted to passivation of these metals using thin layers of OCIs formed from aqueous solutions do not always solve the problem of their temporary protection from corrosion. In this regard, great hopes for the development of new tools and methods in recent decades are associated with a relatively new method—superhydrophobization of metal surfaces, primarily in the interests of mechanical engineering and shipbuilding, power engineering, construction and transport [210]. In this method, higher carboxylic acids, especially the non-toxic and economically available stearic acid (SA), have understandably attracted the attention of researchers. Of course, in addition to the choice of HPA (see Appendix A: Table A1), methods of metal surface preparation to give it a polymodal roughness play a major role in the efficiency and stability of SHP coatings. This has been discussed many times in articles and reviews [8,9,210–218] dealing with the possible applications of SHP coatings. The main difficulties for the development of SHP coatings are expensive materials, low durability of SHP properties, insufficient coating stability, etc.

Well-known methods of metal surface preparation include: immersion in a solution in which reactions of chemical deposition, e.g., of cerium oxide, or selective metal etching take place [8,212–222], electrodeposition [8,223], sol-gel method [224], nanocomposite coatings [225] and templating method [8,226]. A special place is occupied by the creation of polymodal roughness using laser treatment, which in many cases is the most efficient method that positively affects the surface superhydrophobization upon HPA application [227–232]. Although it is beyond the scope of our review to consider the best SHP coating fabrication technologies, we note that optimizing the parameters of such technologies is undoubtedly very important. Note that according to [233], it is sometimes possible to improve the corrosion resistance of a metal or alloy, such as H59 brass, just by using laser ablation of the surface followed by heat treatment. The laser treatment creates hierarchical micro-/nanostructures on the surface, and non-polar C–C/C–H groups are adsorbed on them from the air during the heat treatment. They create air pockets in the roughness grooves and reduce the contact areas of a water drop with the solid surface. As a result, it is possible to achieve superhydrophobization on some areas and improve the corrosion resistance of brass. An interesting work in this regard is [234], in which a nanosecond laser was used to apply a micro-relief with uniform roughness to a stainless steel sheet and the strength of the “lotus effect” was studied using evacuation for a very short period of time. It was concluded that chemisorption of hydrocarbons “on the hydroxylated metal oxide surface occurs much more efficiently in a high vacuum than in an air atmosphere.” We believe that, in view of this, it is difficult to expect long-term preservation of superhydrophobicity when lower hydrocarbons are adsorbed on steel. To develop more durable SHP thin coatings and expand their applications, it is necessary to use HPA whose chemical nature largely determines the stability of superhydrophobicity and protection of the metal or alloy from corrosion. The combination of polymodal roughness and low surface energy of HPA plays a leading role in obtaining stable SHP coatings.

According to [220], the surface energy of monolayer coatings decreases in the series: $-\text{CH}_2 > -\text{CH}_3 > -\text{CF}_2 > -\text{CF}_2\text{H} > -\text{CF}_3$. Not surprisingly, fluorinated organic acids

(e.g., alkylcarboxylic and alkylphosphonic acids) or alkyltrialkoxysilanes are often successfully used to obtain stable SHP coatings [8,9,15,220,227–232].

However, in many cases, a long-lasting SHP effect, and therefore protective effect, can also be achieved with less expensive and more environmentally friendly HPAs. Examples of such compounds are alkylcarboxylic acids, in particular SA. For example, Wang et al. [235] after mechanical stripping and washing a low-alloy steel sample (wt%: 96.30 Fe, 1.34 Cr, 1.33 C, 1.03 Mg) in an ultrasonic bath with ethanol, etched it for 5 min in a 1:1 (*v/v*) mixture of HNO₃ and H₂O₂ solutions. Then the sample was washed in deionized water, dried in an atmosphere of N₂ and exposed for 30 min at 80 °C, which resulted in a polymodal roughness of the steel surface. The sample was then immersed in a solution in *n*-hexane containing 5.0 mmol/L of a SA mixture with N,N'-dicyclohexylcarbodiimide for 24 h. After air-drying, it obtained SHP surface with $\Theta_c = 161 \pm 1^\circ$. The authors made interesting observations of the change in SHP properties upon contact of the samples not only with pure water but also with solutions having a wide pH range from 1 to 14. As the pH is changed from 1 to 5, these properties remain the same and Θ_c increases from $155 \pm 1^\circ$ to $158 \pm 1^\circ$. When the pH is between 6 and 8, the maximum Θ_c value of $161 \pm 1^\circ$ is observed, as it decreases from $159 \pm 1^\circ$ to $151 \pm 1^\circ$ at pH = 11–14.

Later the authors [236] before SA deposition on a sample of S45C carbon steel (in wt%: 0.45 C; 0.24 Si; 0.60 Mn; 0.009 P; 0.018 S and the remaining Fe) after polishing, washing in ethanol, ultrasonic cleaning in deionized water and drying it was dipped for 30 s into a 1:1 (*v/v*) mixture of HF with H₂O₂. The sample was then washed with excess water, dried again, and immersed in ethanol containing 0.05 mol/L SA for 1 h. After thorough washing of the textured sample with pure ethanol and drying, SHP surface with $\Theta_c = 158 \pm 2^\circ$ and a sliding angle of $3 \pm 1^\circ$ was obtained. Potentiodynamic polarization curves of such an electrode showed a reduction in corrosion current i_{cor} by almost an order of magnitude, and the results of tribological measurements indicated reduced friction and wear resistance properties of the SHP steel surface.

One of the popular methods of imparting SHP properties to a steel surface involves its treatment where in the first stage the necessary roughness is given to it by electrochemical deposition of dendrites of another metal. The final stage of the process is to age a galvanized steel sample in an organic solution of a HPA, including SA. An example of such superhydrophobization of galvanized steel will be discussed below [237], here we will also note that the authors [238] demonstrated a method of obtaining SHP Ni films electrochemically deposited on a Cu plate and treated in ethanol containing 3.5 mmol/L SA. There, Ni was deposited as an array of nanocones, and cones of different sizes were formed by varying the electrodeposition conditions. As the cone height increased, Θ_c increased from 148° to 154° . The authors considered a three-phase contact model and reported its calculation to show the relationship between the sliding angles and surface structure.

In [239] a Ni coating was electrochemically applied to the surface of mild steel to reveal the effect of current density (*i*) on the surface morphology, crystal orientation and hydrophobic properties of the coatings. It was found that at $i = 6.0 \text{ A/dm}^2$ and 8.0 A/dm^2 Ni surfaces acquire a micronanostructure, so upon immersion of these samples for 1 h in an ethanol solution containing 0.1 mol/L myristic acid (MA) CH₃(CH₂)₁₂COOH followed by drying for 2 h in hot (60 °C) air, superhydrophobization of Ni was observed. The coating deposited at $i = 6.0 \text{ A/dm}^2$ has a particularly high mechanical stability that is retained even after repeated (10 times) sanding. The corrosion resistance of the samples after MA modification was studied by electrochemical methods: polarization and EIS in 3.5 wt.% NaCl solution. Based on these studies, the authors concluded that superhydrophobization of Ni provides high corrosion resistance of the coating. Previously, MA was successfully used to obtain SHP films on a Fe₃Al intermetallic plate precoated with chemisorbed polyethyleneimine [240]. It was concluded after studying the film structure by SEM and AFM that it is similar to lotus leaves, and the Θ_c of seawater exceeds 150° . The results of EIS measurements in seawater on untreated samples and on those modified by MA showed

that the corrosion rate of Fe₃Al type intermetallide decreased dramatically due to the SHP properties of its surface.

In Chapter 1 of this review the possibility of increasing the stability of the passive state of iron in neutral solutions of salts or in a humid atmosphere by the joint use of higher carboxylates and some TAS (see Appendix A: Table A1) was already considered. This direction of research, apparently initiated by Aramaki et al., was continued as for the superhydrophobization of metal surfaces, in particular Al alloys. For example, in [221,222] samples of AD31 alloy (wt%: Al—97.65–99.35, Fe—up to 0.5, Si—0.4–0.6, Mn—up to 0.1, Cr—up to 0.1, Ti—up to 0.15, Cu—up to 0.1, Mg—0.45–0.9, Zn—up to 0.2) were etched in 10.0% NaOH at $t = 65\text{ }^{\circ}\text{C}$ for 10 s, washed and dipped in ethanol solutions of SA and/or various TAS at $t = 20 \pm 2\text{ }^{\circ}\text{C}$. After this treatment, the samples were dried for 30 min at $75\text{ }^{\circ}\text{C}$, Θ_c was measured and tested in various media (distilled water, 3.0 wt.% NaCl solution, salt spray chamber). It was found that the best results in terms of stability of surface hydrophobization and protection against the appearance of the first centers of corrosion on the alloy were obtained not in the case of treatment with SA, but upon a two-stage hydrophobization of the surface: adsorption first of a TAS, preferably OTES, and then of SA, although the hydrophilic VTMS (see Appendix A: Table A1) also enhances the hydrophobizing effect of subsequent SA adsorption SA (Figure 17). Unfortunately, even in distilled water the layer-by-layer SHP coating saves these properties for only two days. However, in spite of this, hydrophobization of the surface and its passive state are retained for more than a month. Under harsher conditions of salt spray chamber, the coating formed by LbL method from OTES and SA solutions remains the most stable and hydrophobic: after 72 h of testing, $\Theta_c = 101^{\circ}$. Comparing the film thicknesses (d) in Figure 18 shows that even after ultrasonic washing, this coating remains relatively thick ($\approx 8\text{ nm}$). The OTES and SA molecule lengths calculated using the Avogadro program are 1.16 and 2.1 nm, respectively, which suggests a chemical interaction between these chemical compounds that makes it harder than a bilayer coating. Not surprisingly, the first signs of corrosion on the alloy tested in a salt spray chamber appeared after 90 h, which is 30 times longer than without the coating. Neither SA nor OTES offer such protection for the alloy under these harsh conditions.

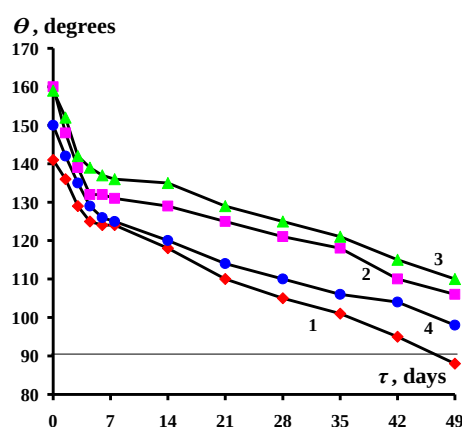


Figure 17. The dependence of the Θ_c value on the exposure time of samples of AD31 alloy in distilled H₂O after layer-by-layer treatment in ethanol solutions containing (in mmol/L): 1—10.0 SA; 2—10.0 VTMS and 10.0 SA; 3—10.0 OTES and 10.0 SA; 4—a mixture of 10.0 VTMS and 10.0 OTES, then 10.0 SA (reproduced from [222] with permission; Copyright 2019 John Wiley and Sons).

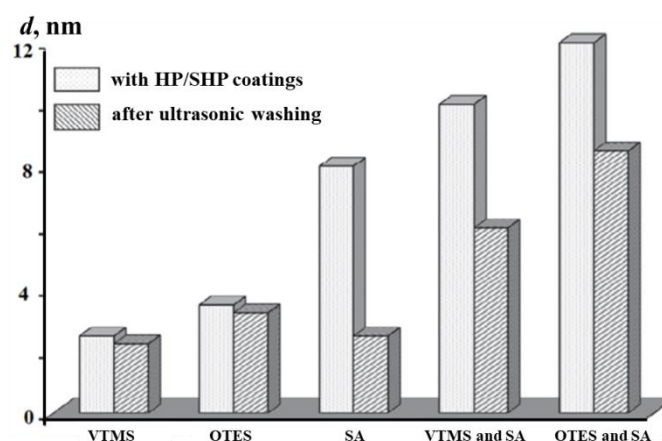


Figure 18. The thickness of hydrophobic (HP) and superhydrophobic (SHP) coatings determined by the ellipsometric method (reproduced from [222] with permission; Copyright 2019 John Wiley and Sons).

Copper and its alloys can also be successfully protected against atmospheric corrosion by passivation treatment with organic OCI solutions. This protection does not necessarily have to be caused by giving their surface SHP properties. In fact, the authors [91] studied the efficiency of corrosion protection of Cu, Zn and brass under conditions simulating urban rain with 0.01 and 0.1 mol/L solutions of a number of fatty acids in ethanol (hexane, decanoic, MA and SA). The duration of the passivating treatment of metals varied from 1 min to 6 days. All the acids studied formed hydrophobic layers with $115^\circ \geq \Theta_c > 90^\circ$. The protective properties of the hydrophobic films were evaluated by polarization curves in water containing, 0.2 g/L NaHCO_3 , 0.2 g/L Na_2SO_4 and 0.2 g/L NaNO_3 with pH corrected by 10.0% H_2SO_4 to pH 5.0. The authors believe that this solution simulates acid rain in a polluted urban atmosphere.

The formation of thin hydrophobic films by alkylcarboxylates proved to be a fast process and 1 min was sufficient to obtain a high protection efficiency for Cu or brasses, and the best results of passivation were achieved using MA and SA solutions. They provided a high degree of protection for Cu and brass, $Z > 95\%$, even at low C_{in} , which was significantly higher than in the passivation of Zn ($Z = 21\%$). Zn protection can be enhanced by a longer passivation in an SA solution. In fact, after 6 days of passivation, $\Theta_c = 128^\circ$, and Z increases to 58.4%.

Later, the hydrophobic surface properties of Cu (99.95%) or Cu40Zn alloy were improved by modifying it with 0.05 mol/L ethanol SA solution with addition of 2.0% α -tocopherol (vitamin E) [241]. The presence of vitamin E contributed to the formation of a more uniform and stable coating as well as an increase in Θ_c on Cu to 143° . Polarization measurements and EIS results in a solution simulating acid rain proved that the corrosion of Cu and Cu40Zn alloy decreased with increasing Θ_c . The authors attributed this to better adsorption of the ester formed by α -tocopherol with SA on the surface of Cu or Cu40Zn alloy in comparison with the mixture components. The non-polar interactions between the alkyls of these molecules due to Van der Waals forces also contribute to the barrier properties of the thin coating and prevent H_2O access to the surface. The degree of protection of the metals increases and exceeds 99%, indicating the suppression of their corrosion.

The authors [242] investigated other SA formulations with heterocyclic OCIs (BTA and 2-MBI). In particular, they immersed Cu samples for 1 h in an ethanol solution of BTA or 2-MBI followed by incubation for 20 min in 0.05 mol/L ethanol solution of SA. In other experiments, samples were soaked for 1 h in an ethanol solution containing 0.01 mol/L BTA or 2-MBI and 0.05 mol/L SA. The morphology of the layers on Cu modified in these solutions varied, ranging from a flower-like structure for SA ($\Theta_c = 114^\circ$) and nanograin-like one for 2-MBI ($\Theta_c = 94^\circ$), to a nanofibrous one for BTA ($\Theta_c = 90^\circ$). After Cu treatment with a mixture of SA with BTA or with 2-MBI, the hydrophobicity of the layer increases

to $\Theta_c \geq 107^\circ$. The highest hydrophobicity was obtained by immersing the samples in a solution of 2-MBI and then in 0.05 M SA ($\Theta_c = 118^\circ$). Corrosion tests in an aqueous solution simulating urban rain (pH 5.0) performed for 2 weeks showed that the BTA layer strongly activates Cu corrosion, while, in contrast, SA and 2-MBI slow it down. The binary formulation significantly reduced the mass loss of Cu samples by 93.0% and the Cu surface retained its hydrophobic properties ($\Theta_c = 92^\circ$) after the testing. The results of electrochemical measurements of Cu electrodes with modified surface in a solution simulating acid rain are in good agreement with the results of corrosion tests.

Above we reviewed examples of the ability of higher carboxylic acids or their salts to efficiently protect Cu from corrosion by forming thin protective coatings on it from aqueous or organic solutions. At the same time, we should also note the numerous attempts to protect Cu surface by means of superhydrophobization by various methods using these compounds. It is logical that at first the attention of researchers was focused on creating on the surface of Cu, as well as other metals, a microstructure with a uniform roughness similar to that common in the nature, in particular on lotus leaves.

Wang et al. [243,244] suggested a one-step potentiostatic electrolysis method to obtain an SHP film on a Cu surface. A Cu tetradecanoate film was obtained in a two-electrode cell in which Cu was the anode and a Pt wire was the cathode. The film was formed for a calculated time at a constant potential of 2 to 10 V in an ethanol solution of tetradecanoic acid at room temperature. Once the Cu sample was removed from the cell, it was washed with ethanol, dried in a nitrogen atmosphere, and studied by Θ_c determination, FTIR, XPS, field emission scanning electron microscopy (FE-SEM), and electrochemical measurements. It was concluded that the SHP properties of the film are due to the flower-like microstructure of the copper tetradecanoate film. The SHP film reduces the current densities upon anodic and cathodic polarization by more than 5 and 4 orders of magnitude, respectively. The air trapped by the coating plays an important role in the protective properties of the Cu tetradecanoate film. It contributes to its isolation, and the film itself contributes to air retention. The coating acquires inhibitory properties, retaining them on Cu and in water containing chlorides.

In [245], an approach to impart SHP properties to the surface of a Cu foil (99.9%) by self-assembly on a porous template of prepolymer of polydimethylsiloxane (PDMS), similar to a lotus leaf, was suggested. To remove contamination, the lotus leaf was washed thoroughly, then a liquid mixture of PDMS and a catalyst was applied, and after 24 h at room temperature, once the porous template had cured, it was removed from the leaf. The porous PDMS template and the Cu foil were washed in an ultrasonic bath with ethanol, HCl, and ethanol again. The template was immersed for 25 min in an ethanol solution, and then the cleaned Cu foil was covered with the FeCl_3 -moistened template and kept vertically for 24 h at a pressure of 7.5 kN/m^2 . Finally, the Cu foil was rinsed with pure ethanol and immersed for 40 min in an ethanol solution containing 6 mmol/L SA serving as an HPA. This treatment produced flower-like microstructures resulting from the self-assembly of Cu stearate, including surfaces similar to a lotus leaf recorded by SEM. The water contact angle on such Cu foil surfaces shows a high degree of superhydrophobization ($\Theta_c = 161^\circ$, sliding angle 3°). Significantly, this superhydrophobicity did not change even after 6 months of exposure of the foil in air.

In [246] a carambola-like CuO film was synthesized on Cu using Cu acetate and a hexamethylenetetramine solution at 90°C . The CuO particles consisting of nanoparticles between 80 and 120 nm thick had a carambola-like shape with a width of 600 nm and a length of 800 nm. The CuO film was endowed with superhydrophobic properties by modification with SA, which corresponded to a SA-modified CuO film. The morphology and chemical composition of the CuO film were characterized by SEM, transmission electron microscopy, XPS and Θ_c determination. The measured Θ_c value of the SA-modified CuO film was 157° . The corrosion resistance and durability of the SA-modified CuO film in 3.5 wt% sodium chloride solution were estimated by EIS. In addition, the corrosion

resistance properties of the SA-modified CuO film were compared with the unmodified pure copper substrate.

However, it soon became clear that a SHP state of a Cu surface can also be achieved in other ways. For example, it was found [223] that in an ethanol solution of 0.038 mol/L CeCl_3 and 0.1 mol/L MA mixture, SHP coatings with $\Theta_c = 161.7 \pm 2^\circ$ can be obtained on its surface by electrodeposition on a copper cathode. Having evaluated the corrosion resistance of the coatings obtained using electrochemical measurements (polarization curves and EIS method) in 3.5% NaCl aqueous solution, the authors concluded that the electrodeposition provides a high degree of Cu corrosion protection. This SHP coating with micro/nanostructures on a cathodic copper substrate was successfully obtained by a fast (30 min) one-step method at a voltage of 20 V between the electrodes. This coating was proved to be a result of the formation of special hierarchical micro/nanostructures and cerium myristate with low surface energy.

Jie et al. [247] have shown that to SHP properties can be given to a brass surface by etching (45 min in 35% HCl + 10% FeCl_3), heat treatment (25 min at $t = 350^\circ\text{C}$), with SA as dissolved in ethanol a hydrophobizing agent. At the same time, the Θ_c of water on a micro-nanostructured brass surface was 153.6° , which ensures its good anticorrosion resistance in 3.5 wt% NaCl solution even for 20 days of tests.

Similarly a SHP coating was obtained on a Cu foil by combining 20 h of its etching in a 10% ammonium solution at room temperature with a thorough rinsing with alcohol and deionized H_2O , followed by drying and calcination for 10 min in air at $t = 350^\circ\text{C}$ [248]. After that Cu, samples were immersed for 3 h in 0.1 mol/L ethanol solution of SA, washed, and dried again. The resulting samples with an SHP surface had $\Theta_c = 157.6^\circ$ and, according to EIS measurements and polarization tests, had good corrosion resistance in 3.5 wt% aqueous NaCl solution. XPS studies of SHP Cu samples confirmed the presence of SA on it and its association with Cu(II), which is the main valence state of Cu in the surface layer.

Considering the stability of SHP metal surfaces under atmospheric conditions, the possibility that acid rains can precipitate on them deserves special attention. In this regard, work [249] should be noted, in which this problem was discussed for marine and industrial environments. It has been correctly noted that superhydrophobicity of metal oxides keeps the surface dry, which prevents corrosion. An acid rain is dangerous because of its ability to dissolve oxide films, so the following Cu surface treatment was suggested. First, a CuO film was formed on a Cu foil in an aqueous alkaline solution containing 0.1 mol/L $(\text{NH}_4)_2\text{S}_2\text{O}_4$ for 10 min, then the sample was washed with water and dried at 180°C . A Cu electrode coated with CuO served as a cathode on which WO_3 was deposited from a 0.5 mol/L Na_2WO_4 solution. Thereafter, the electrode was immersed for 5 s in 0.5% ethanol solution of 1H,1H,2H,2H-perfluorodecyltriethoxysilane and dried at 60°C for 1 h to stabilize the SHP state. The resulting composite film with SHP properties ($\Theta_c = 160 \pm 2^\circ$) provided high acid resistance of Cu and retained an almost ideal micro-/nanostructure after 2 days of exposure to 0.2 N H_2SO_4 . Moreover, polarization measurements on this electrode in a 3.5 wt.% NaCl solution showed that its i_{cor} value is four orders of magnitude lower than for Cu coated with CuO. Although no higher carboxylates were used in the study referred to, it is possible that if they are used to impart superhydrophobicity to such composite films, the acid resistance of the coating can also increase significantly.

Zinc and its alloys have been repeatedly investigated over the past decade in order to identify the specifics of the formation of thin protective films on their surface by carboxylic acids in organic solvents. This mainly concerned the preparation of SHP coatings on Zn or galvanized steel with emphasis on the development of methods to create polymodal surface morphology for this purpose. Among them, a large number of works are devoted to the creation of highly developed ZnO coatings [250–255] with various micro/nanostructures and study of their protective and hydrophobic properties.

Some features of the formation of protective layers on the surface of Zn and its alloys by carboxylic acids in organic solvents have already been mentioned above when considering the adsorption of succinic acid on Fe. The degree of hydroxylation of the metal surface

largely determines the mechanism of dicarboxylic acid binding to it, i.e., through one or two carboxyl groups. Since the surface of Zn is more hydroxylated than that of Fe, the adsorption of succinic acid mainly took place at both ends with formation of a carboxylate. In contrast, the adsorption of OCI on the surface of oxidized Fe occurred at one end, while the carboxyl group at the other end of the molecule remained undissociated [208]. Succinic acid binds in bidentate way to the Zn surface through interaction with $-OH$ groups. In this case, the larger the hydroxyl fraction, the more adsorbate is found on the metal surface. Unfortunately, the authors did not carry out corrosion or electrochemical tests allowing a comparative assessment of the anticorrosion properties of the layers formed by succinic acid on Fe and Zn.

As noted above, monocarboxylic acids with long hydrocarbon radicals, which are more hydrophobic and surface-active than succinic acid, can be efficient CIs of Cu and brass. At the same time, their inhibiting effect toward Zn is less pronounced, for example, when protecting against corrosion under conditions simulating acidic city rain [91]. In this work the authors, who studied the efficiency of the protective action of a number of monocarboxylic acids with the general formula $C_nH_{2n+1}COOH$ (where $n_c = 5, 9, 13, 17$) toward Zn and Cu, showed that it is improved with an increase in the hydrocarbon radical length. However, even when Zn was treated with SA, which leads to hydrophobization of its surface ($\Theta_c = 128^\circ$), the Z value did not exceed 58.4%, while similar treatment of Cu provided $Z > 90.0\%$. The reason for such a difference in the protective properties of SA was shown by the results of SEM studies. The layers formed on Zn surface in an ethanol solution of SA had the morphology in the form of sparse and large plates, in contrast to the denser layers on the Cu surface.

Later, the same authors investigated the possibility of improving the corrosion protection efficiency of Zn with SA using BTA and 2-MBI [256,257]. The results of weight loss immersion tests, polarization measurements and EIS showed that the SAMs formed in the presence of SA formulations containing BTA or MBI had higher hydrophobic and protective properties compared to SAMs of individual OCIs under conditions simulating acid city rain.

Creating a developed morphology on the surface of metals, including Zn, is the basic and main condition for their superhydrophobization. However, examples of superhydrophobization of Zn by carboxylic acids without surface pretreatment also exist. For example, Wang et al. [258] obtained a SHP film on the Zn surface using potentiostatic electrolysis. For this purpose, they treated a Zn foil in 0.1 mol/L ethanol solution of tetradecanoic acid at a constant potential of 30 V for 2 h from a direct current power supply at room temperature. The SHP film formed (with $\Theta_c = 152.5^\circ$) had a petal-like structure and consisted of a zinc tetradecanoate complex. According to the results of electrochemical measurements and EIS, it inhibited the dissolution of Zn in 3.5 wt% NaCl.

On the other hand, in some cases it is possible to do without chemical modification of the surface with OCIs if the necessary polymodal roughness created by micro/nanodimensional structures is provided. For example, in [259] a Zn coating on a Fe substrate was obtained by electrochemical deposition from an aqueous solution containing (in mol/L) 0.01 $Zn(CH_3COO)_2$, 0.1 NaCl and 0.1 HCl, at 1.8 V for 1100 s followed by annealing at 180 °C for 70 min. As a result, stable SHP structures with $\Theta_c = 163 \pm 2^\circ$ and a sliding angle of about 2° formed on the Fe surface. Comprehensive studies using SEM, XRD, EDX, AFM and XPS showed that the Zn coating was represented by Zn micro-/nanoparticles coated with ZnO and had a polymodal dendritic-like morphology, which determines its high hydrophobic, anti-icing (at t down to $-15^\circ C$) and anticorrosion properties in 3.0 wt% NaCl. Later SHP surfaces with a hierarchical micro/nanostructured morphology were obtained in a similar way on Zn substrates by successive stages: etching in an HCl solution, electrodeposition of ZnO from a $Zn(CH_3COO)_2$ -based electrolyte (at 1.25 V for 900 s) and subsequent thermal annealing at 200 °C for 60 min [260]. Such SHP surfaces (with $\Theta_c = 170 \pm 2^\circ$ and a sliding angle of about 0°) exhibited long-term stability, good corrosion resistance, and self-cleaning ability. In addition, the authors demonstrated that it was possi-

ble to rapidly and reversibly switch between superhydrophobicity and superhydrophilicity by alternating UV illumination and dark storage or thermal annealing. Unfortunately, the authors of these works evaluated the protective properties of such SHP coatings based on the results of short-term electrochemical tests but did not carry out long-term corrosion tests, therefore it is not possible to fully assess their anticorrosion efficiency.

At the same time, the results of numerous studies on the formation and properties of SHP films on various metals indicate that both a polymodal surface morphology and its chemical modification with OCIs are necessary to obtain stable SHP films with high anti-corrosion properties. Higher monocarboxylic and fluorocarboxylic acids have been most investigated in the formation of SHP coatings on Zn and galvanized steel. Let us consider only some of the works, classifying them according to the method of surface preparation.

The electrochemical method already mentioned above is a simple, relatively environmentally friendly and fast way to obtain SHP metal surfaces, allowing to adjust the structure of coatings by changing various process parameters, as well as to apply them to arbitrarily shaped surfaces. For example, Jain et al. [261] obtained an SHP coating on Zn in two stages. They electrochemically deposited a Zn layer with a polymodal morphology from an aqueous solution of $\text{Zn}(\text{CH}_3\text{COO})_2$, like it was done in [259,260], followed by treatment in an ethanol solution of SA. Modification of a Zn surface with the resulting needle-shaped and branchy fractal morphology in an ethanol solution of SA gave it SHP properties with $\Theta_c = 156\text{--}166^\circ$ and a sliding angle of $4\text{--}7^\circ$. Such coatings were stable in water under static and dynamic conditions, to mechanical abrasion, and also inhibited Zn dissolution in 3.5 wt.% NaCl.

In [237] a two-step treatment of galvanized steel consisting of the electrodeposition of dendritic Zn structures to obtain a developed surface morphology followed by 24 h of exposure in 0.01 mol/L ethanol solution of SA was suggested. Dendrite-like Zn structures on galvanized steel were obtained by potentiostatic electrodeposition from a sulfate-acetate solution with a low concentration of Zn^{2+} . It was shown that the electrochemical treatment mode of steel surface plays an important role in creating coatings with high protective properties, providing polymodal surface roughness necessary for the heterogeneous wetting mode. The optimal conditions of electrodeposition in terms of preservation of SHP and protective properties of coatings under exposure to a neutral salt spray involved deposition at $E = -1500$ mV (vs. an Ag/AgCl electrode) for 1000 s. This potentiostatic treatment of galvanized steel in a solution with a low Zn^{2+} concentration at a high cathodic overvoltage causes the formation of a zinc deposit under diffusion conditions and growth of dendritic structures on its surface (Figure 19b).

Subsequent modification of the Zn surface with a developed morphology in ethanol solution of SA leads to the formation of a thick adsorption layers on it (Figure 19c). Such coatings have hydrophobic properties, but the Θ_c angle does not exceed 150° . Additional washing of samples in ethanol with simultaneous sonication for 5–10 s leads to removal of the physically adsorbed SA layer, as a result of which the surface acquires SHP properties with $\Theta_c = 156^\circ$. The SEM images of the Zn surface after the ultrasonic treatment (Figure 19d) clearly show a large number of leaf-like structures. This, even in comparison with the dendrite-like Zn deposits without SA treatment, indicates a change in the microstructure and additional development of the surface layer. The coatings obtained by this method on galvanized steel by prolonged treatment (up to 148 h), preserving SHP properties, increase its corrosion resistance under corrosive conditions of neutral salt spray almost 27-fold and prevent local dissolution in 0.5 mol/L aqueous solution of NaCl.

It is sometimes possible to obtain polymodal surface roughness of galvanized steel already during zinc plating on a steel substrate. For example, it was demonstrated [262,263] that varying the current density and duration of Zn electrodeposition on steel surface allows the creation of hierarchical micro/nanostructures for further SHP in ethanol solution of SA or perfluorooctanoic acid. The SHP Zn coatings obtained in this manner had self-cleaning properties and long-term stability in air and in NaCl solutions. In addition, the

films formed by SA showed high efficiency ($Z = 97.75\%$) in inhibiting the corrosion of galvanized steel in 3.5 wt.% NaCl, as judged by polarization measurements and EIS.

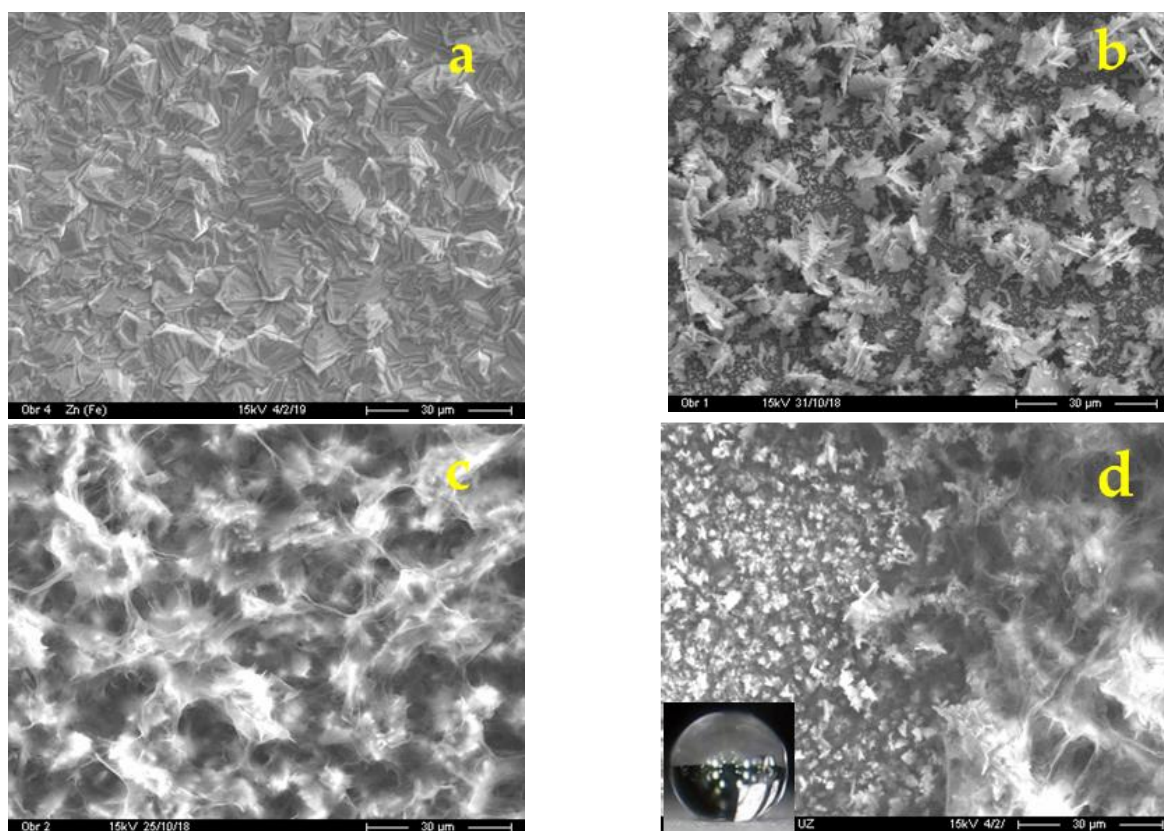


Figure 19. SEM images of zinc-coated steel (a) without treatment, (b) with electrochemically deposited dendritic structures, (c) after modification with SA, and (d) partially sonicated surface region. (Adapted from [237] with permission; Copyright 2021 Elsevier).

Another simple, cheap and efficient way to build micro-/nanostructures on a surface of Zn or galvanized steel is the hydrothermal method. It involves Zn treatment in aqueous solutions at high pressure and temperature, resulting in the formation of a ZnO layer with diverse morphologies (nanorods, nanosheets, etc.) on the surface. The properties of these nanostructures depend on the pH of the solution, the duration and temperature of treatment, and pressure in the system. Subsequent treatment of a Zn surface enriched with oxides and having a polymodal morphology with OCIs leads to its superhydrophobization, a decrease in friction, as well as an increase in corrosion and wear resistance [264,265]. For example, Li et al. [264] obtained SHP films on steel with electrodeposited Zn coatings. For this purpose, they grew ZnO nanosheets by the hydrothermal method in a high-pressure autoclave in a mixed water-alcoholic ammonia solution at 105 °C for 24 h. It is important to note that according to SEM studies, the Zn coating thickness before and after the hydrothermal treatment does not change, which indicates the formation of a very thin ZnO film. To prepare a SHP surface, galvanized steel with ZnO nanosheets was immersed in 0.01 mol/L ethanol solution of pentadecafluorooctanoic acid at room temperature for 11 days. XPS and EDS results confirmed that the carboxylic acid adsorbed on the metal surface. The surface of galvanized steel coated with thin SHP films was characterized by $\Theta_c = 158^\circ$ and a sliding angle of about 6° , as well as excellent self-cleaning properties. In addition, it was experimentally proved in that work that the SHP properties of such coatings are preserved during long-term storage in air, on exposure to high temperatures (200 °C), upon immersion in water, and in adhesive tape peeling tests. Unfortunately, the authors of this study did not perform corrosion tests. However, it can be assumed that such SHP films would also increase the corrosion resistance of galvanized steel.

Chemical etching is one of the simplest methods of creating polymodal surface roughness of metals. As shown by Chen et al. [266], it can be used to achieve superhydrophobization even in an aqueous solution of SA. They suggested a simple and environmentally friendly way to create SHP surfaces of Zn and Al by simply immersing them in an aqueous solution of a mixture of HCl and SA. In this way it was possible to combine the steps of creating a rough metal surface and modifying it with an OCI with low surface energy. According to the results of polarization measurements and EIS, the resulting SHP films on the Zn and Al surface increased their corrosion resistance in 3.5 wt.% NaCl. They were resistant to condensation and freezing and retained SHP properties in aqueous solution over a wide pH range (1 to 14). In another work, Li et al. [267] treated hot-dip galvanized steel in 0.05 mol/L ethanol solution of SA to obtain an SHP surface. To obtain a polymodal surface morphology, a galvanized steel sample was etched in an aqueous $\text{Cu}(\text{NO}_3)_2$ solution. In this case, they varied the concentration of $\text{Cu}(\text{NO}_3)_2$ solution ($C_{\text{Cu}^{2+}} = 0.05\text{--}0.2$ mol/L) and the etching time (5–45 s) to find the optimal conditions for obtaining the SHP films. SEM/EDS, XRD, FTIR and XPS results showed that tiny spherical particles composed of hierarchical micro/nano structures formed on the galvanized steel surface upon etching. The authors suggested that this is due to a galvanic substitution reaction between Zn and $\text{Cu}(\text{NO}_3)_2$ with deposition of ZnO-coated copper agglomerates (Cu/Zn^{2+}) on the metal surface. Subsequent modification of such surface in SA solution led to the formation of a film consisting of zinc ($\text{Zn}[\text{CH}_3(\text{CH}_2)_{16}\text{COO}]_2$) and copper ($\text{Cu}[\text{CH}_3(\text{CH}_2)_{16}\text{COO}]_2$) stearates. The SHP film formed was characterized by a high value of $\Theta_c = 164.3 \pm 2^\circ$ and efficiently inhibited the corrosion of galvanized steel in 3.5 wt.% NaCl ($Z = 96.6\%$).

Differential etching or autooxidation of Zn in a mixture of dimethylformamide and water allows the production of ZnO nanorods or nanowires at low temperatures (50–65 °C) [268–271]. This process forms a highly ordered and densely packed layer of ZnO micro/nanostructures with predictable morphology, e.g., with an adjustable diameter and uniform length. For example, Wan et al. [270] obtained an SHP coating (with $\Theta_c = 155^\circ$) on Zn to reduce friction and improve wear resistance by a simple two-step treatment. First, they grew a ZnO film consisting of homogeneous and well-packed nanorods by immersion of a Zn foil in 4.0% aqueous solution of N,N-dimethylformamide at 50 °C for 24 h. The ZnO nanorods were 2–3 μm long and about 100 nm in diameter. Subsequent modification of the Zn surface with nanoscale roughness in an alcohol solution of SA led to the formation of densely packed carboxylate SAMs, which was confirmed by FTIR results and Θ_c measurements. The preparation of SHP films that have not only high anticorrosion properties but also low friction coefficient and wear resistance is very important in terms of the feasibility of their practical application.

3.2. Organophosphates

Organophosphates are remarkable representatives of organic substances capable of self-assembly on the surfaces of many metals and their oxides. They modify the surface, giving it a number of valuable (anticorrosion, anti-icing, self-cleaning, adhesive, etc.) properties [178,185,186,272,273]. The main requirements for modifiers used to obtain dense, well-ordered, homogeneous SAMs formulated in [185,272] are as follows:

- the anchoring group should firmly bind to the substrate surface, and the reaction should occur as fast as possible;
- the chemical bonds formed upon interaction of the anchoring group with the groups on the surface should be stable under the conditions where the surface-modified material is operated and stored;
- the length of the hydrocarbon chain which determines the compactness of the SAM should be at least 8 carbon atoms;
- the hydrocarbon radical should not contain any substituents or double/triple bonds (especially near the head group) to form a densely packed SAM.

In addition, the properties and stability of SAMs are greatly influenced by the conditions of their preparation (the modifier concentration, the nature of solvent, the temperature

and duration of treatment and drying, the method of preparation) and the initial state of the modified surface (the presence and composition of an oxide-hydroxide film, surface morphology) [202,203,274–279].

3.2.1. Organic Esters of Phosphoric Acid

It is known that salts of organic esters of phosphoric acid have a high surface activity and form thin self-assembling films on metal surfaces, preventing their corrosion in corrosive environments [4,104,105,185,280]. Due to the relatively good solubility of many phosphates, they are used mainly in aqueous solutions, what is their advantage. In this regard, over the past decade, there have been practically no works on the preparation of their thin films in organic solvents for the protection of Fe, Cu, or Zn in neutral aqueous solutions or under atmospheric conditions. In addition, SAMs formed in aqueous solutions of organic esters of phosphoric acid have higher protective properties than those obtained in organic solvents. Yan et al. studied in detail the effect of the solvent on the formation mechanism, structure, and anticorrosion properties of thin films formed on Fe in aqueous and alcoholic solutions of BEHP (see Appendix A: Table A1) [105]. Using FTIR, XPS, and AFM, it was shown that BEHP molecules are adsorbed and self-assembled on a Fe surface regardless of the solvent. However, the mechanism of its binding to the surface and the structure of the SAMs formed are significantly different. In water, phosphate is chemisorbed on a Fe substrate due to the formation of P-O-Fe bonds, and the surface phosphate film have a nodule-like morphology. In an alcoholic solution, BEHP molecules are adsorbed on the Fe surface both through electrostatic interaction and through chemical covalent bonding. As a result, a SAM with an island-like morphology is obtained. In the authors' opinion, physically adsorbed molecules are gradually organized into large domains due to van der Waals forces between 2-ethylhexyl groups with subsequent formation of P-O-Fe bonds. Thin films formed in water are more compact and more firmly bound to the surface, which determines their better protective properties according to electrochemical tests. In addition, the time-consuming mechanism of self-assembly of the layer in alcohol also explains the more pronounced dependence of its protective properties on the exposure time of Fe in a solution of BEHP.

3.2.2. Phosphonic Acids and Phosphonates

Higher C_n PAs with $n_c \geq 12$ ideally meet the above requirements for the formation of stable and well-ordered SAMs. The presence of two $-P-OH$ groups in C_n PAs molecules promotes their chemisorption with formation of a strong coordination bond [186,272,273,281], for example, as a result of nucleophilic substitution of a hydroxyl with an organic anion on the metal surface [7]. The binding of a C_n PA with the surface can be mono-, bi-, and even tridentate due to the formation of a hydrogen bond between the phosphoryl oxygen and the surface hydroxyls [185,272,273]. The structure of the functional group of a C_n PA determines the properties of the modified surface. For example, non-polar $-CH_3$ groups give it hydrophobic and anticorrosion properties, while polar groups ($-OH$, $-COOH$, $-NH_2$) facilitate the adhesion of organic coatings. Intermolecular interactions (due to van der Waals forces), orientation and ordering of molecules in SAMs contributing to its stability occur due to the spacer group, which is usually represented by a long alkyl chain. Such phosphonate SAMs are capable of providing a reliable barrier to the penetration of moisture and corrosive ions [185,186,272]. In addition, as noted by some researchers, SAMs formed by C_n PAs are more strongly bound to an oxidized metal surface and are characterized by higher density, ordering and stability compared to SAMs formed from higher carboxylic acids or silanes [272,281,282]. These specific features of higher C_n PAs, along with low toxicity, allow them to be used as efficient and environmentally friendly surface modifiers of materials and as OCIs [283–286]. However, their use in aqueous solutions is difficult due to their low solubility. They are often applied from organic solvents such as alcohols, tetrahydrofuran (THF), dimethylformamide, chloroform, etc. The preparation of SAMs from organic solvents has both advantages and drawbacks. Due to the good solubility

in organic solvents, more concentrated solutions of C_n PAs can be used, which increases the rate of layer formation and shortens the duration of surface treatment. In addition, the simultaneous undesirable corrosion destruction of the metal, which is observed in aqueous solutions, is reduced [185,287]. However, the use of organic solvents, especially on industrial scale, is unsafe from a technological and environmental points of view.

Iron and steels. Studies of the formation of SAMs by C_n PAs began as early as in the 1990s of the past century [274,288], and the peak in the number of publications occurred in the first decade of the 2000s. In the past decade, knowledge about the mechanism and features of SAMs formation on the surfaces of various metals, including Fe and steels, has been expanded.

The length of the hydrocarbon radical, as well as the presence of unsaturated bonds and substituents in it, have a great influence on the packing density of C_n PA molecules in SAM and, consequently, on its permeability and hydrophobicity. Abohalkuma et al. [289,290] demonstrated this by the example of SAMs of phosphonates with different hydrocarbon part of the molecules: C_{12} PA, undecenyl phosphonic acid $CH_2=CH-(CH_3)_9-PO(OH)_2$ (UPA), styrene-co-styrophosphonic acid, and fluorodecylphosphonic acid ($FC_{10}A$). They obtained phosphonate films on oxidized surfaces of carbon and stainless steels (304 and 316 L) in methanol solutions of phosphonates with $C_{in} = 5.0$ and 50.0 mmol/L, varying the duration of treatment from 15 min to 48 h. The results indicate the formation of well-ordered phosphonate SAMs on steel surfaces (with $\Theta_c > 95^\circ$). The most hydrophobic layers characterized by $\Theta_c = 128 \pm 1^\circ$ formed in the presence of $FC_{10}A$. An increase in the duration of SAM formation up to 24 h increased the density and, consequently, the hydrophobicity of SAM, judging by the Θ_c values. At the same time, an increase in C_{in} had an insignificant effect on the Θ_c value. The efficiency of corrosion protection of steels with phosphonate films was estimated by measuring the linear polarization resistance in a solution containing NaCl and Na_2SO_4 [289] and by electrochemical potentiodynamic polarization and cyclic voltammetry in 0.1 mol/L $NaClO_4$ [290]. According to polarization resistance measurements, adsorption of $FC_{10}A$ not only provided the highest hydrophobization of the surface but also efficiently prevented general and pitting corrosion of carbon steel. The lowest corrosion rate (less than 0.15 mm/year) was observed after prolonged treatment for 4 and 24 h due to the formation of more compact self-assembled layers. In contrast, films formed on steel in a solution of styrene-co-styphos acid, despite the presence of a large hydrophobic part in its molecule, were not resistant to the action of a corrosive aqueous solution and did not provide steel protection against corrosion. The authors believe that the reason for this was the lack of a well-ordered SAM structure.

The SAMs formed in the presence of UPA with an allyl radical deserve special attention. They did not possess hydrophobic properties ($\Theta_c = 86 \pm 3^\circ$) and, while inhibiting general corrosion, were nonefficient in preventing pitting. However, subsequent irradiation of the films with UV light ($\lambda = 254$ nm) increased the Θ_c value. The effect of post-treatment with UV light or gamma rays on the hydrophobic and protective properties of films formed in the presence of UPA on carbon steel was studied in more detail by the same authors later [291]. They varied the treatment duration in the case of UV irradiation (30 and 60 min) or the absorption dose of gamma irradiation (2 and 20 kGy). The Θ_c measurement and AFM results showed that longer (60 min) UV irradiation and gamma irradiation with a higher absorption dose (20 kGy) are most efficient. This post-treatment leads to an increase in the protective properties of the phosphonate layer. In the authors' opinion, this is due to an increase in its compactness owing to the polymerization of UPA at its double bond. This is indicated by an increase in the Θ_c value and a decrease in the roughness parameters of the steel surface. Unfortunately, the authors do not provide evidence of the disappearance of the $-CH=CH_2$ group in the film as a result of polymerization, for example, by FTIR or XPS methods.

Roy et al. also studied the effect of treatment duration and alkyl length on the anticorrosion properties of phosphonate SAMs obtained on 304 L stainless steel in 5.0 mmol/L ethanol solutions of C_n PA (where $n_c = 4, 8, 10, 16$) [277]. Based on the results of cyclic voltam-

metry in an aqueous solution containing 0.2 mol/L Na_2SO_4 and 5.0 mmol/L $\text{K}_4[\text{Fe}(\text{CN})_6]$, they found that 8 h of steel exposure in C_nPAs solutions is optimal. Longer exposure times led to degradation of the adsorbed layers and deterioration of their protective properties. The inhibiting efficiency of C_nPAs increased with the length of the hydrocarbon radical. In this work, the possibility of reducing (at least twice) the duration of steel treatment in a solution of C_{16}PA using simultaneous high-frequency ultrasonic radiation was also shown.

Among higher C_nPAs , octadecylphosphonic acid (C_{18}PA) attracts particular attention of researchers as a modifier of various metal surfaces [275,279,283,292–294]. Being strongly bound to the surfaces of metals and their oxides by covalent bonds, it forms compact adsorption films due to the van der Waals forces between the long alkyls of its molecules. In concentrated solutions of C_{18}PA and/or after slow evaporation of a solvent, such as ethanol, self-assembling bilayers with a thickness of 3.4–5.0 nm can form [294]. Unfortunately, we failed to find any information about the results of direct corrosion tests of Fe or low-carbon steels with a passivating C_{18}PA film in the literature. However, studies on the formation of C_{18}PA adsorption layers on stainless steel are known [279,283,295,296]. Stainless steel is a well-known biomaterial used in medicine (cranial and orthopedic plates for fractures, dental implants, spinal rods and joint prostheses), therefore, its corrosion protection is of great practical importance. Steel treatment is necessary to increase its corrosion resistance and biocompatibility without losing its physico-mechanical properties. For example, the surface modification of dental orthodontic stainless steel in 10.0 mmol/L ethanol solution of C_{18}PA was used to suppress the elution of Cr and Ni ions in aqueous solutions (pH 1.4–6.9), which is the cause of allergic reactions [283]. It was shown that the concentration of Cr and Ni ions for steel samples with a SAM of C_{18}PA decreased on average 2–3 times, depending on the type of solution, after 1–4 weeks of testing at 37 °C with continuous stirring. Traces of these ions were not found at all in saline with pH 6.9. These results may indirectly indicate a decrease in the corrosion rate of stainless steel coated with thin phosphonate films in aqueous solutions.

The surface modification of SS316L austenitic stainless steel in 1.0 mmol/L ethanol solutions of C_nPAs with $n_c = 3$ –18 was studied in [295]. All C_nPAs form SAMs on the steel surface, thereby giving it hydrophobic properties ($\Theta_c = 90$ – $108 \pm 1^\circ$), as it was proved by XPS, AFM, infrared reflection absorption spectroscopy (IRRAS) and Θ_c measurements. In this case, the Θ_c value increases with an increase in the length of the alkyl in the C_nPA molecule and reaches the largest value for C_nPA with $n_c \geq 12$. In addition, analysis of IR spectra showed that with an increase in the length of the hydrocarbon chain, the angle between them and the normal to the surface (tilt angle) decreases. This indicates a high ordering of the layer with an all-trans conformation of alkyls in C_nPA with $n_c \geq 12$. Such films were found to be stable for 30 days in acid (1.0 mmol/L HCl, pH 3) and neutral (Milli-Q water and saline, pH 7.4) aqueous solutions and for 7 days under dry heating (120 °C), judging by the Θ_c values and IR spectra. Only an alkaline solution (pH 11) caused the degradation of the monolayers. Considering the known inhibiting properties of phosphonate SAMs, these results indicate their utility for a variety of applications, even under rather harsh conditions.

The stability of the properties of alkylphosphonate films under the conditions in which the metal is operated determines the possibility and success of the practical application of the modified material. In this regard, post-treatment of the grafted layer, for example, the drying temperature and duration or UV/gamma irradiation, as mentioned above, can have a positive effect. For example, M.S. Lim et al. [279] showed that the stability of a SAM obtained on SS316L steel in 1.0 mmol/L solution of C_{18}PA in THF significantly increased after heat treatment. The treatment was carried out for 0.5–1.0 h at 100–120 °C. AFM, FTIR and Θ_c measurements showed that thermally treated films (with $\Theta_c = 97^\circ$) remain nearly unchanged and retain their hydrophobic properties after washing with methanol, THF or water, as well as after immersion for 3 h in a stream of deionized water ($\Theta_c = 91 \pm 1^\circ$). In contrast, the steel surface with a SAM without heat treatment became hydrophilic

already after 60 min ($\Theta_c = 77 \pm 1^\circ$). In the authors' opinion, a layer of physically adsorbed molecules of $C_{18}PA$, which is held on the metal surface by weak hydrogen bonds, is formed after exposure in the modifying solution. Thermal post-treatment leads to chemisorption of $C_{18}PA$ due to the formation of strong mono- or mixed mono/bidentate bonds.

The protective properties of self-assembling films formed in the presence of $C_{18}PA$ on a stainless steel surface, as well as their stability in flowing natural waters, were also studied in [292]. It should be noted that the authors sprayed a 10.0 mmol/L ethanol solution of $C_{18}PA$ 5 times on steel samples with intermediate drying for 1 h at $80^\circ C$ to obtain an alkylphosphonate layer. The advantage of this method of $C_{18}PA$ deposition over the immersion method was demonstrated by them and other researchers [275–297] on CuNi and NiTi alloys. The results of polarization resistance measurement and EIS showed high protective properties of the layer formed by $C_{18}PA$ in natural river water (pH 7.8) and in seawater (pH 8.2). In this case, a change in the flow rate of the media (from 0 to 2.4 L/min) had an insignificant effect on the efficiency of steel protection by phosphonate films.

Copper and its alloys. In recent years, more and more works on the study of the surface modification of Cu or its alloys with C_nPAs have appeared. Special preliminary preparation of the Cu surface is often required for the successful grafting of C_nPA . For example, in [298], Cu samples were oxidized in 5.0% H_2O_2 solution before 24-h treatment in 1.0 mmol/L ethanol solutions of $C_{12}PA$ and 1-pyrrolyl-10-decanephosphonic acid ($C_{10}PN$). The results of XPS, PM-IRRAS and AFM showed that this increases the surface roughness (from 3 to 50 nm) and changes its morphology. The surface layer in the form of small, randomly oriented grains of different sizes (150–350 nm) and shapes consists of Cu(II) compounds (CuO and $Cu(OH)_2$). The studied C_nPAs are chemisorbed on such surface in a tridentate way, as evidenced by the disappearance of the peaks of the $-P=O$ and $-P-OH$ groups and the appearance of $-P-O-Cu$ vibrations in the PM-IRRAS spectra. Phosphonate SAMs hydrophobize the Cu surface, increasing Θ_c from 13° to $114 \pm 2^\circ$. Unfortunately, the authors did not investigate the corrosion resistance of Cu with a grafted phosphonate layer.

However, these studies were carried out by other authors [299]. They studied the composition, structure, and protective properties of a thin film obtained in 1.0 mmol/L ethanol solution of $C_{12}PA$ on the surface of oxidized Cu in a similar way. Based on XPS and PM-IRRAS measurements, the authors confirmed the tridentate bonding of $C_{12}PA$ molecules with the Cu surface. The Cu surface coated with a phosphonate SAM had a high corrosion resistance in 0.5 mol/L NaCl and excellent tribological characteristics, namely very low friction coefficient value ($\mu \approx 0.12$) and a 100-fold increase in anti-wear life compared to oxidized Cu without a SAM.

Another way to increase the wear resistance and lifetime of Cu was suggested by Wan et al. [300]. To improve the chemical interaction of C_nPA molecules with a metal substrate and thereby obtain densely packed phosphonate SAMs, they immersed a Cu plate for 2 h in a hot ($75^\circ C$) 1.0 mol/L NaOH solution. The Cu surface textured by chemical etching was covered with a Cu_2O layer. Further treatment of oxidized Cu was carried out in 10.0 mmol/L ethanol solutions of $C_{12}PA$ or $C_{18}PA$ for 24 h with subsequent drying in air. It was shown that modification of the textured Cu surface with C_nPAs resulted in a decrease in the friction coefficient and a significant lifetime increase. At the same time, films formed in the presence of $C_{18}PA$ with a long alkyl are more resistant against tribological deformation and provide low coefficients of friction for a longer period of time. In the authors' opinion, this is due to the formation of more compact and ordered layers of $C_{18}PA$ due to stronger interaction between the hydrocarbon radicals in the SAM.

The specific features of adsorption and inhibiting action of $C_{18}PA$ toward Cu, as well as the effect of the surface oxide on them were recently studied by Zhao et al. [301,302]. In [301], thin films of $C_{18}PA$ were obtained on a non-oxidized Cu surface by the immersion method, while varying the treatment duration from 1 s to 24 h. The results of AFM and IRRAS analysis showed that the thickness of the $C_{18}PA$ layer increases with the modification duration. A monolayer with a thickness of ~ 2.5 nm was formed in 1 min, while a multilayer

film with a thickness of ~30.0 nm was formed in 1 h. It was firmly bound to the Cu surface due to the formation of complexes of C₁₈PA with Cu⁺.

The same group of researchers studied the effect of the surface oxide and the deposition method on the protective properties of thin films of C₁₈PA [302]. Phosphonate SAMs were obtained on non-oxidized and preoxidized Cu surfaces by the immersion and Langmuir-Blodgett methods. To obtain an oxidized Cu surface, the samples were kept for 20 min in ultrapure water, which led to the formation of a thin cuprite layer. Self-assembled phosphonate films were obtained in 1.0 mmol/L ethanol solution, and Langmuir-Blodgett layers were prepared in a solution of C₁₈PA of the same concentration in chloroform. The anticorrosion properties of C₁₈PA films were investigated under simulated indoor atmospheric conditions (with a relative humidity of 80% and 100 ppb formic acid) using IRRAS and EIS. Grazing incidence X-ray diffraction was used to characterize and determine the corrosion products. Moreover, nano-FTIR, which is a scattering-type scanning near-field optical microscopic (s-SNOM) technique combining AFM and IR spectroscopy, was used to determine the size, chemical nature of the corrosion products and their distribution on the metal surface. It was shown that phosphonate SAMs with the best protective properties are formed on the surface coated with a Cu₂O layer, regardless of the preparation method. Such nanosized (~2.5 nm) films prevented Cu corrosion for 216 h of exposure to the atmosphere without the formation of any corrosion products. The corrosion products on a bare Cu surface were Cu₂O and Cu(OH)(HCOO), while a new corrosion product, Cu₂(OH)₃(HCOO), was found on the surface modified with C₁₈PA. The authors suggested that its formation is associated with local alkalinization of the near-surface layer of the electrolyte as a result of acceleration of the cathodic reaction.

Modification of metal surfaces with C_nPAs to give them anticorrosion, wear resistant, hydrophobic and other valuable properties is used not only for Cu, but also for its alloys. Cu alloys are widely used in practice and have good decorative properties. However, their use without special means of corrosion protection is not always possible. For example, the surface of cupronickel easily subject to corrosion and biofouling in aqueous media, which creates difficulties for its use in shipbuilding. In [303], it was suggested to modify the surface of a CuNi alloy (55.0% Cu, 45.0% Ni) in 1.0 mmol/L solution of C₁₈PA in THF to solve this problem. The stable and well-ordered phosphonate films obtained on the oxidized alloy surface exhibited high corrosion resistance.

Mioč et al. [275] investigated the effect of the temperature and treatment duration, as well as the drying temperature on the protective properties of SAMs of C₁₈PA on a CuNi alloy (67.3% Cu, 31.0% Ni). These parameters significantly affect the efficiency and durability of corrosion protection with C_nPAs, as we repeatedly noted above. Phosphonate films were deposited onto a pre-oxidized surface of the CuNi alloy (for 24 h at 80 °C) by immersion in 10.0 mmol/L alcohol solution. The authors varied the duration of C_nPAs adsorption (20 and 72 h), solution temperature (25 and 40 °C), and drying temperature (5 h at 25, 50 and 80 °C). The results of Θ_c measurements and FTIR showed that well-ordered and hydrophobic SAMs were formed on the alloy surface in all the cases. However, electrochemical studies in 3.0 wt.% NaCl revealed a significant difference in the protective properties of the layers obtained under various conditions. An increase in the temperature of the inhibiting solution (up to 40 °C) and drying temperature (up to 80 °C) enhanced the protective properties of the films, which efficiently ($Z = 97\%$) inhibited the corrosion of the CuNi alloy for 14 days. The authors attributed this to an increase in the bond strength of C₁₈PA molecules with the metal surface and an increase in the film thickness.

Later, the same authors studied the stability of SAMs of C₁₈PA on a CuNi alloy in flowing natural waters [292]. However, in contrast to the previous work, the alkylphosphonate layer was obtained by spraying an inhibiting solution. This method is more practical and allows one to obtain protective layers that are not inferior in protective properties to those obtained by the immersion method [296]. The results of electrochemical, EIS and polarization measurements showed that films formed with C₁₈PA efficiently prevent the corrosion of the CuNi alloy in river and sea waters. The most pronounced effect of the

flow rate of the corrosive medium on the stability of phosphonate films was observed in seawater, while their protective efficiency in river water practically did not change.

Recently, the scope of application of Cu and its alloys modified with C_n PAs has been expanding. For example, in [304], a SHP surface was obtained on an oxidized Cu mesh using C_{18} PA for self-cleaning and oil/water separation. The Cu mesh was preliminarily oxidized by immersion for 30 min in an aqueous solution of 1.0 mol/L NaOH and 0.05 mol/L $K_2S_2O_8$, as a result of which its surface was covered with micro- and nanosized $Cu(OH)_2$ particles. This surface morphology made it possible to quickly (1 s) obtain SAM in 0.2 mmol/L solution of C_{18} PA in THF, which was characterized by the value of water Θ_c of approximately 158.9° and an oil Θ_c of 0° . The surface of the mesh with a grafted phosphonate layer had a self-cleaning property and could be reused for separating gasoline/water and diesel oil/water mixtures.

In [305], modification of a Cu surface by C_n PAs with terminal carboxyl groups (1H, 2H, 2H-perfluorooctanephosphonic, 6-phosphonohexanoic and 16-phosphonohexadecanoic ($COOH-C_{16}$ PA) acids) was used to increase the adhesion of an epoxy layer. It was shown by a set of physicochemical methods that, depending on the length of the spacer between the $-COOH$ and $-PO_3H$ groups, surface layers with different thickness and morphology were formed, which is associated with a denser packing of molecules in the SAM. In this case, $COOH-C_{16}$ PA was the most efficient adhesion promoter.

Zinc and its alloys. Despite the numerous works on the study of the formation mechanism, structure, and properties of SAM formed by C_n PAs, there are few studies of their inhibition of corrosion of Zn or its alloys, and the available studies mainly concern the modification of the ZnO surface [281,293,306,307]. In addition, the authors studying the formation of SAMs with C_n PAs on a Zn surface often carry out no direct corrosion or electrochemical tests. This does not allow evaluating the protective properties of the layers formed.

Hotchkiss investigated the nature of the binding of C_8 PA, C_{18} PA, and tridecafluorooctylphosphonic acid (C_8PF_{13}) to the surface of ZnO deposited onto silicon or gold substrates, as well as the structure of the SAMs formed and the degree of their ordering [281]. Comprehensive studies by XPS, IRRAS, AFM methods and Θ_c measurements have shown that C_n PAs form homogeneous well-packed monolayers. They bind to the ZnO surface predominantly in a tridentate fashion, and their alkyl chains are predominantly in all-trans conformation. It should be noted that pretreatment of ZnO with oxygen plasma activated the surface and provided more reliable binding of C_n PAs to it. By using Cassi's equation and the Θ_c values obtained, the coverage of ZnO surface with C_n PAs molecules was calculated to be 2.9, 3.7, and 4.9 molecules per nm^2 for C_8 PA, C_8PF_{13} , and C_{18} PA monolayers, respectively. It can be seen that the SAM of C_{18} PA is packed most densely, apparently due to longer alkyls in the molecules and, as a consequence, greater stabilization of the monolayer due to van der Waals interactions between the chains.

The keen interest in the modification of ZnO is due to its electronic and photonic properties, which makes it possible to use it in sensors, light-emitting diodes (LEDs), lasers, transistors and solar cells. Phosphonate SAMs can be used to modify the interface in organic solar cells in order to improve the work function between the organic active layer and various metal oxides. In this respect, the report about the fast method for deposition of C_n PA molecules on the surface of metal oxides, including ZnO [306], is of interest. In this method, a solution of pentafluorobenzyl phosphonic acid was deposited onto ZnO substrates heated to 25–150 °C by spraying for 60 s. This method for preparing an ultrathin coating leads to a change in the work function of the oxide, and the degree of surface coverage with phosphonic acid is comparable to or even greater than in the case of the more traditional immersion method (with exposure for 1 h). The surface coverage and the shift of the work function improved with an increase in the substrate temperature. It is important that the rapid action of the sprayed modifier results in smaller etching of ZnO than immersion in the solution. These results confirm the advantage of the spraying

method, which we already mentioned when considering the modification of the surface of Cu and its alloys with C_nPAs.

The surfaces of conductive transparent metal oxides, such as ZnO, modified with C_nPAs are of particular interest, since they can be an alternative to transparent electrodes in optoelectronic devices. Ostapenko et al. [307] studied the stability and orientational ordering of SAMs formed by PhPA on various ZnO single crystals using thermal desorption spectroscopy (TDS), XPS, near-edge X-ray adsorption fine structure spectroscopy, and quantum-chemical DFT calculations. It was shown that the phosphonate layers on all types of ZnO single crystals remain stable up to 550 K. However, at higher temperatures, the C-P bond cleavage and dissociative desorption occur. This is evidenced by the appearance of two desorption peaks in the TD spectra. According to quantum-chemical DFT calculations, they refer to protonated and deprotonated chemisorbed PhPA molecules, which can be tri- and bidentate bonded with ZnO.

The directed functionalization of the ZnO surface by chemical attachment of organic acids to it is of great practical importance. The use of C_nPAs molecules containing terminal functional groups can be especially useful for creating bifunctional thin films and is the basis for an efficient and inexpensive method for adapting the surface properties of nanoparticles. In [293], the structure of SAMs obtained on ZnO nanoparticles in solutions of C_nPAs with different terminal functional groups, namely C₁₈PA, 12-phosphonododecyl-phosphonic acid (PC₁₂PA), and COOH-C₁₆PA, in THF was studied. Depending on the nature of the terminal group, the surface can acquire hydrophobic (–CH₃ group) or hydrophilic (–COOH or –PO(OH)₂ groups) properties. It was found that C_nPAs bind in bi- and tridentate way to the surface of ZnO nanoparticles to form SAMs that are stable in the environment (1 year) as well as upon washing with a solvent and in an acid-base bath. At the same time, it was shown by SEM and solid state nuclear magnetic resonance (SS-NMR) methods that the –COOH group does not bind to the surface. Using PC₁₂PA, it is possible to form multilayer films with precisely controlled thickness and sequence of layers, which expands the scope of possible applications of such modified particles. Thus, the work function of ZnO nanoparticles can be controlled by directed surface modification by adjusting the film thickness and type of C_nPA.

The successful modification of a ZnO surface with C_nPAs to give it a number of valuable properties suggests that they can be used for the same purpose for Zn alloys. This was demonstrated by the example of treatment of the surface of ZnAl alloys (0.5%, 5.0%, and 55.0% Al) with a 1.0 mmol/L ethanol solution of C₁₈PA using physical methods (XPS, SEM, and PM-IRRAS) [308]. It was shown that C₁₈PA can be used for temporary corrosion protection and as promoters of adhesion on ZnAl alloys with Al ≥ 5.0% covered with a passive layer rich in aluminum oxyhydroxide. In contrast, its surface was covered with a mixed layer of Zn and Al oxides when the Al concentration in the alloy was smaller than 5.0%. In this case, a precipitated layer rather than a SAM was formed on the surface.

The studies on the adsorption of C₁₈PA and the stability of SAMs formed in its presence were continued by the same authors on an alloy with a low content of Al and Mg (Zn—98.0%, Al—1.0%, Mg—1.0%), i.e., metals whose oxidized surfaces are more hydroxylated than that of Zn [309,310]. They varied the composition of the surface oxide layer using various plasma treatments for the preliminary preparation of the alloy surface. It was found that the composition of the oxide layer strongly affected the properties of phosphonate SAMs. The most ordered and stable SAM of C₁₈PA solution was formed in an aqueous on the surface enriched by Mg and Al oxides compared to the surface rich in ZnO. It is important that such films cause a significant inhibition of oxidation-reduction reactions on the alloy surface in a borate buffer (pH 8.4).

Thus, the successful modification of various metal surfaces with C_nPAs in organic solvents to impart valuable properties to them makes it possible to use them to increase the corrosion resistance of metals in neutral aqueous solutions. In addition, taking into account the high reactivity and hydrophobicity of molecules of higher C_nPAs and their ability to form stable self-assembling layers on metal surfaces, they can also be used to

obtain superhydrophobic thin coatings. Although there are reports on the realization of this possibility on Al [311], Mg [312], Ni [313] or TiO₂ [314] using C_nPAAs ($n_c = 8, 10, 14, 18$), we could not find publications on the superhydrophobization of the surface of Fe, Cu, Zn or their alloys by these compounds.

4. Vapor-Gas Phase

4.1. Volatile Corrosion Inhibitors

Volatile corrosion inhibitors of metals (VCI) are substances or their mixtures having a saturated vapor pressure $p^0 \geq 10^{-6}$ mm Hg [2]. They are able to evaporate spontaneously, reach the metal surface in the form of vapors, adsorb on it and form protective layers usually indistinguishable to the naked eye. Metal protection by such very thin (nanoscale) layers increases in time and they can be fully considered as self-assembling protective layers, which have a noticeable aftereffect, i.e., protection is maintained even after removal of the VCI from the surrounding space. The valuable advantage of VCIs is their ability to penetrate into hard-to-reach cracks, gaps and form very thin protective layers by adsorbing on a metal from the vapor-gas phase. Other important advantages of VCIs over other types of CIs should also be noted: very low consumption, compatibility with other methods of anticorrosion protection, ability to slow down and even suppress a corrosion process on metals that has already started. The technology of VCI application is also very simple, namely, it is not necessary to apply them on a metal surface, and depreservation of even large items consists only of removal of a VCI carrier, for example silica gel impregnated with it (linasil) and a barrier material such as paper or a polymeric film containing a VCI. The high economic efficiency of application of VCIs and a wide choice of methods for its application have made the practical use of this method popular for protection against atmospheric corrosion, especially during assembly, transportation and storage of metal items (temporary protection) [315–318]. The range of VCI applications is much wider than temporary protection, as discussed in more detail in another review [319].

Although the use of NH₃ and volatile amines to protect the internal surfaces of steam-power plants and pipes against corrosion has been known since the 1920s, VCIs have become widespread since the 1940s when Shell patented the use of amine nitrites for this purpose [2]. The chemical structure of VCIs determines not only their protective ability, but also the value of p^0 . The latter determines the ability to form adsorption layers of different thicknesses on the surface being protected. When protecting against corrosion of precision metal products, such as bearings, electrical or radio equipment and especially electronic equipment, which is usually performed in moderately corrosive environments, the ability of VCIs to form adsorptive nanoscale protective layers is especially attractive.

Since most complex items consist of different metals and alloys, so-called versatile VCIs have been developed. They can be not only individual chemical compounds (*m*-nitrobenzoate of hexamethylenimine, some azoles, dialkylaminoketones) but also mixtures, for example, with BTA, that are efficient in inhibiting the corrosion of non-ferrous metals with those VCIs which reliably protect only ferrous metals (mainly amines).

To form thin protective coatings on various metals from the vapor-gas phase with VCIs it is necessary that they be volatile, but for a number of reasons discussed repeatedly in monographs and review articles [2,320–328], their high volatility, with rare exceptions, is not only unnecessary but may even be harmful. It creates the need to meet high requirements for the barrier material to prevent the risk of environmental pollution, fires and harmful effects on human health, and modification of the physicochemical properties of non-metallic materials. In this regard and because of the tightening of the environmental requirements, efficient VCIs of the class of heterocyclic amines, such as β -aminoketones, which are capable of suppressing the corrosion of many metals and alloys [319], are not currently used in practice.

Another class of VCIs that are generally less volatile than those of the amine type, is represented by salts of organic acids. They have long been known as VCIs [2], although the acids themselves are usually inefficient in this function, as the example of benzoic acid

shows. Apparently, BTA is the only weak NH-acid widely used in practice, including its application as a VCI ($p^0 \approx 10^{-5}$ mmHg or 10^{-3} Pa) that perfectly protects Cu and its alloys. BTA is less efficient in protecting Zn or Fe [2,73–75,326]. However, the possibility of complete suppression of the corrosion of D16 Al alloy by its vapors in a humid atmosphere with periodic condensation of moisture on the tested samples is interesting [2]. BTA is often used as part of mixed VCIs, particularly together with amines, because it increases the pH of the medium, which itself contributes to the improvement of its protection properties toward carbon steels [329,330]. Among BTA derivatives, 5-Cl-BTA deserves special attention as it can be a more efficient OCI than BTA not only for Cu [32,64,73,76], including its use in an acid solution simulating acid rain with pH 2.4 [331], but also for other metals [65,66,73,75,329]. We were unable to find the volatility characteristics of 5-Cl-BTA, but there is no doubt that it is less volatile than BTA, and it seems to be better suitable as a chamber OCI, as it will be shown in the next section.

An important property of the best VCIs is their ability to undergo chemisorption on the metals and alloys being protected. Chemisorption of some of them and its irreversibility creates the possibility of a relatively long protective aftereffect, which is especially important when the tightness of packaging is broken [332]. Indicative in this regard are the results of tests of VCIs under severe conditions of 100% relative humidity of air and periodic condensation of moisture on samples [2,322]. Efficient protection of metals from corrosion under such harsh conditions is possible only using VCIs capable of forming nanolayers on metals that are strongly bound to the metal surface. They are difficult to desorb into the water that condenses on metal surfaces, thereby maintaining their passive state. This possibility is realized in VCI chemisorption, as it is more irreversible. However, it has long been known that chemisorption occurs slowly, which is why the authors [332] emphasized the importance of increasing the temperature to accelerate it for the preservation of metal products. They drew attention to the fact that the action of VCIs in the fight against atmospheric corrosion differs from the conditions of application of film-forming OCIs such as octadecylamine $C_{18}H_{37}NH_2$ (ODA) in heat power engineering. ODA molecules adsorbed on steel at elevated temperatures are not only strongly bound to the surface but also densely packed in the film, which gives it hydrophobic properties. However, more than 60 years ago, Rosenfeld et al. [333] did not observe ODA to have a protective effect in tests under conditions simulating the condensation of atmospheric moisture on the surface of low-carbon steels. In addition to the idea of increasing the temperature to form a passivating film on the metal to be protected from the gas–vapor phase [332], another way to hinder VCI desorption should be noted.

In our laboratory, an efficient VCI based on an azomethine, namely N-benzylbenzylidenimine, was developed and then an attempt was made to modify it by joint application with (3-aminopropyl)-triethoxysilane (APTS) [334,335]. APTS is a volatile compound, though its volatility is low ($p^0 = 1.5 \cdot 10^{-6}$ mm Hg at 25 °C) and comprises an amino group that gives it basic properties. Hydrolysis of its alkoxy groups by water vapor transforms APTS into a silanol whose molecules interact with each other to form siloxane bonds. As a result of condensation, they can form reticulated polyorganosiloxane structures. Since N-benzylbenzylidenimine comprises a double bond, it can be incorporated into these structures on the surface of metals and, at least, reduce its own volatility. In this regard, the ability of silanes to undergo chemical transformations on interaction with water vapor seemed to us attractive for the purposeful construction of protective nanoscale coatings from the vapor-gas phase on the surface of metals.

To perform polarization measurements, a Cu, Zn, or Armco steel electrode was placed for 12 h in a desiccator with vapors of an OCI to be analyzed. Then it was transferred into an electrochemical cell filled with a borate buffer solution (pH 7.4) containing 5.0 mmol/L NaCl. Having measured the initial electrode potential (E_{in}), anodic polarization was switched on without waiting for a stationary corrosion potential of the metal to be established. On the anodic polarization curves (due to the protective action of the oxide and adsorption film of OCI formed on the electrode in contact with the dry atmosphere) there

was no area of active dissolution and E_{pit} was recorded (Table 3). Exposure to vapors of the compounds studied did not change the E_{in} of the metals but increased the E_{pit} . The difference between E_{pit} and E_{in} in the absence of an adsorption film of an OCI was 0.28, 0.06, and 0.46 V for steel, Cu and Zn, respectively. After the electrode contacted APTS vapors, it increased to 0.31, 0.15 and 0.76 V, for steel, Cu and Zn, respectively. Exposure of the electrode to vapors of both studied compounds significantly increased the E_{pit} of all metals, which indicates a greater efficiency of the protective films formed than in the vapors of the mixture components. The protective effect of the adsorption film is the strongest on Cu where this difference reached 1.30 V. The protection of steel by the film formed jointly by APTS and N-benzylbenzylideneimine vapors also increases significantly, reaching 0.66 V. The joint action of these vapors on Zn leads to an increase in the protective effect compared to that of the individual components, although to a smaller extent.

Table 3. Values of potentials of metal electrodes immersed in borate buffer containing 5.0 mmol/L NaCl (E_{in}) and pitting potentials (E_{pit}) determined from the anodic polarization curves.

Pre-Exposure (12 h) of Electrodes in the Vapour of	Armco Steel		Cu		Zn	
	E_{in} , V	E_{pit} , V	E_{in} , V	E_{pit} , V	E_{in} , V	E_{pit} , V
Without exposure	−0.06	0.22	0.10	0.16	−0.96	−0.56
APTS	−0.06	0.25	0.10	0.25	−0.96	−0.20
N-benzylbenzylideneimine	−0.06	0.32	0.10	0.28	−0.96	−0.20
APTS + N-benzylbenzylideneimine	−0.06	0.60	0.10	1.40	−0.96	−0.13

From the above results it follows that the adsorption films formed jointly with APTS from the gas-vapor phase on various metals protect them from the corrosive effects of the environment even in aqueous solutions. This is much more efficient on Cu and steel than after treatment of their surfaces with the mixture components. The reason for the strengthening of the azomethine adsorption film may well lie in the hydrolysis of the adsorbed APTS and its further transformations with involvement of N-benzylbenzylideneimine. It is logical to expect that the adsorption films are not limited to a monolayer, so the authors studied the process of formation of such a film in the gas-vapor phase by ellipsometric method, observing it for 7 days (Figure 20). The film thickness formed in N-benzylbenzylideneimine vapor together with APTS increased most quickly. After about 5 days it reached 5.3 nm and the film growth stopped.

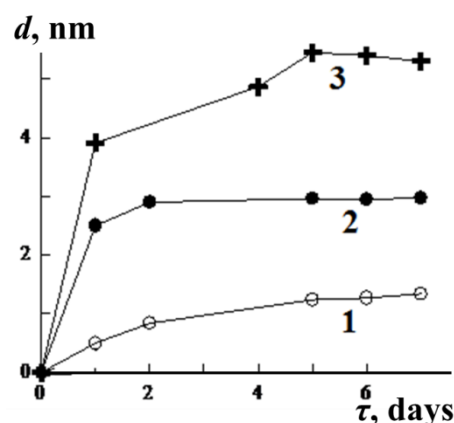


Figure 20. The growth kinetics of VCI films on the surface of steel: 1—N-benzylbenzylideneimine, 2—APTS, 3—N-benzylbenzylideneimine with APTS (reproduced from [334] with permission; Copyright 2011 Springer Nature).

The thickness of the film formed by N-benzylbenzylideneimine vapor reached ≈ 1.0 nm but stabilized after 2 days. After 7 days the cell was opened, the remaining VCIs was removed, and their desorption from the metal surface was observed for 5 days. It was found

that APTS was practically not desorbed within 5 days, and in the case of the film formed in the vapors of both VCIs, only 0.9 nm was desorbed, which does not reach even 20% of the total film thickness. Hence, the combined use of VCIs with volatile silanes can prolong the protective effect of metals. Moreover, as shown in [332], it expands the range of metals that can be protected by adsorption films under harsh conditions of daily moisture condensation on their surfaces.

This direction was further developed in [336], where the LbL adsorption of VCIs and volatile silanes was studied. It was found to form thicker films on the surface of various metals (St3 steel, SCh-18-20 cast iron; M1 copper; L63 brass; Zn0 zinc and aluminum alloys: D16, AD31, AMg3, AMg6, and V95) than the films that the VCIs formed individually. Studies on the protective ability of nanoscale layers of VCIs and volatile silanes on the metal surfaces were carried out according to GOST9.054-75. Before testing in the chamber of heat and moisture, the samples were kept for one day in VCI and silane vapors, then they were placed inside polyethylene film packages that were sealed and hung up inside the chamber. The samples were inspected daily and the time until the first corrosion damage appeared on the samples was recorded.

The adsorption studies of VCI and silanes were carried out by ellipsometric method on St3 mild steel and D16 Al alloy. Considering that increased atmospheric humidity leads to rapid hydrolysis of APTS and loss of its volatility [337], it was replaced by silanes that hydrolyze more slowly than it does. These compounds include volatile vinyltriethoxysilane and VTMS (see Appendix A: Table A1). As in earlier works [334], N-benzylbenzylideneimine served as a VCI example in many experiments. Figure 21 shows the growth kinetics of films upon adsorption and desorption of a VCI and VTMS on D16 Al alloy.

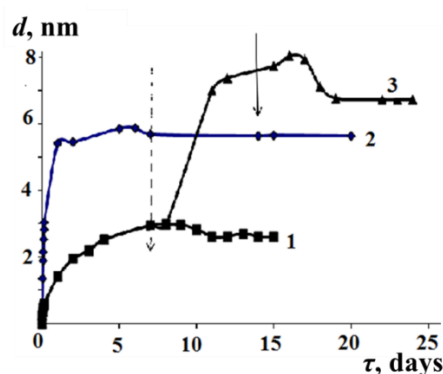


Figure 21. The growth kinetics of VCI and VTMS films on the surface of aluminum alloy D16: 1—VCI, 2—VTMS, 3—VCI + VTMS. The dashed arrow shows the moment of desorption initiation of individual substances and the moment of introduction of the second component into the cell; the solid arrow marks the moment of desorption initiation in the case of layer-by-layer application of VCI and VTMS (reproduced from [336] with permission; Copyright 2017 Springer Nature).

The results of ellipsometric studies have shown that layer-by-layer adsorption of VCI and VTMS allows one to obtain thicker films on steel or Al alloy than films formed by adsorption of any of these volatile compounds. Layer-by-layer application of such films makes it possible to provide more efficient corrosion protection for metals than the VCIs themselves. This was confirmed by the drip method and by tests in the chamber of heat and moisture, as well as under conditions of 100% humidity with periodic condensation of moisture on metal samples.

In this review, corrosion and electrochemical aspects of the formation and properties of thin coatings formed by OCIs on various metals are discussed, supplemented by in situ ellipsometric measurements and, to a lesser extent, other physical and chemical methods of surface examination. Other important aspects of the formation of thin coatings by organic compounds cannot be considered in a single review. In this regard, a review

by Pujari et al. [273], devoted to the modification of metal oxide surfaces by depositing carboxylates, phosphonates, silanes and other monolayers of organic compounds, should be noted. In this article, the focus is on obtaining stable modifications of oxide surfaces, namely covalent binding of monolayers. In particular, the vapor phase deposition of high-quality silane monolayers, almost uncontaminated by siloxane and other particles, is of interest. The examples of chemisorption of organic compounds on a hydroxylated oxide surface given in the review are also noteworthy.

4.2. Chamber Corrosion Inhibitors

The use of organic VCIs for temporary protection against atmospheric corrosion, especially in a humid atmosphere and under periodic condensation of moisture on the surfaces of the metals and alloys to be protected, causes the need for reliable packaging of products. However, this condition is not always possible to fulfill, for example, during the transportation of a metal product the tightness of the barrier packaging can be broken, so it is highly desirable and sometimes necessary to give preference to VCIs that can be strongly chemisorbed on metals due to which the thin nanoscale coatings formed by them from the vapor-gas phase have a protective aftereffect [322]. Above we considered the possibility of reducing the risk of rapid desorption of VCI molecules through its combined use with silane, which is hydrolyzed by water vapor and forms a siloxane mesh upon condensation of silanol molecules. It not only sharply reduces the volatility of silanes, but also prevents the desorption of the VCI. However, there is another way to reduce inhibitor desorption, which also takes into account the important fact that chemisorption is a relatively slow process. In order to speed it up, the temperature of the medium from which adsorption occurs can be increased, which also increases the p^0 . Consequently, this simple technique opens up the possibility of using VCIs with a low p^0 value, i.e., low-volatile OCIs. Under normal conditions, it will desorb more slowly from the metal surface, and the protective aftereffect will be longer in case of package leakage. Taking into account the long-known ability of many efficient OCIs to undergo partially irreversible chemisorption, a method for metal protection by low-volatile OCI vapors was developed [338,339]. It is based on the fact that the metal products to be protected are placed in a closed volume (chamber) whose temperature can be elevated to create favorable conditions for relatively rapid formation of a thin coating on metals by OCI vapors with a significant aftereffect. From the environmental point of view, chamber OCIs also give certain advantages due to the fact that they are only present in the working chamber.

Indeed, ODA, in contrast to its behavior at ambient temperatures, can form a thin protective coating on the surface of St3 low-carbon steel in 1.0 h at 120 °C. To give this chamber OCI protective properties toward non-ferrous metals, ODA was also studied in a mixture with BTA (at a weight ratio of 1:1) [338]. In view of the possible hydrophobization of St3 steel surface after exposure to vapors of these OCIs and cooling the samples to room temperature (after 1.0 day), the Θ_c value was measured on their surfaces. The first signs of corrosion appeared on the samples after different periods of time (τ_{cor}), depending on the duration of chamber treatment (τ_{ct}) and the chemical nature of the OCI vapors. At the optimum temperature, $t_{ct} = 120$ °C, and $\tau_{ct} = 0.5$ h the value of τ_{cor} on St3 steel samples exposed in a humid atmosphere with daily condensation of moisture on the surface increased in the series (hours): without a chamber OCI (0.5) < BTA (1.0) < ODA (96) < BTA + ODA (168). Even daily condensation of moisture on steel samples after their treatment in chamber OCI vapors cannot quickly destroy the protection of steel by the adsorption coating. Thus, the coatings indistinguishable to the naked eye formed in 30 min of contact with ODA vapors or its mixture with BTA increase τ_{cor} 384 or 672 fold, respectively. Apparently, surface hydrophobization is an important factor in steel protection, as it follows from the increase in Θ_c in the case of ODA up to 85°, and in the case of its mixture up to 97°. The treatment with vapors of BTA itself nearly did not affect the Θ_c value.

The efficiency of the protective properties of chamber OCIs as well as the technology of the treatment itself often depends on the metal being protected. For example, chamber

treatment of Zn can be carried out at $t_{ct} \leq 100$ °C and, as shown by accelerated corrosion methods as well as electrochemical and ellipsometric studies, a thin protective film with a long protective aftereffect is formed on the surface of this metal in the vapor of the new OCI [340]. So, if the $\gamma = \tau_{cor}^{in} / \tau_{cor}^0$ value, where the upper indexes refer to samples that underwent chamber treatment and without it, is used as a protection criterion, then after $\tau_{ct} = 1$ h of treatment by vapors of the new OCI comprising a mixture of carboxylic acids (MCA) at 60, 80 and 100 °C, γ reaches 700, 2850 and 3500, respectively. This means that the passive state of Zn can be maintained for up to 70 days after such treatment, despite the daily condensation of moisture on the samples.

The mixture of BTA with ODA well proven in the protection of steel, and given that BTA is the OCI for Zn, is of great interest. It was found that in this case, treatment for 1 h with vapors of this mixture, like on steel, leads to better hydrophobization of the Zn surface than in the case of ODA or BTA alone [341]. In fact, the Θ_c value increases to 114°, 112° and 85°, respectively, at 90 °C, and to 120°, 110° and 96° at 120 °C. However, the best protection is observed for BTA, judging by the value of $\gamma = 16$, which is slightly higher than that of the mixture, $\gamma = 12$, and 2 times higher than that of ODA. Unfortunately, these results show that neither the mixture of ODA with BTA itself, nor its components have a sufficient passivating effect for reliable temporary protection of Zn. In this regard, the authors studied the possibility of mixing MCA with BTA or urotropin, but the best results obtained, although significantly ahead of the mixture of ODA with BTA in the protection of Zn, were noticeably inferior to those of MCA itself.

The development of a technology for the inter-operation protection of Cu by chamber treatment in vapors of OCIs with low p^0 capable of chemisorption on the surfaces of various metals is an important goal because Cu is often used for the manufacture of assemblies and parts of metal products. It has been shown above that although BTA acting as a chamber OCI had a protective effect, it was insufficient for reliable temporary protection of Zn. In this regard, the authors [342] studied this mixture and its components as a chamber OCI, assuming that in this case they would be more efficient in protecting Cu. The authors evaluated the protective aftereffect for copper samples treated in hot vapors of OCIs by corrosion tests in a humid atmosphere with daily condensation of moisture on the surface. Indeed, an hour-long treatment of Cu with a mixture of ODA and BTA vapors at 100 °C much better improves the corrosion resistance of Cu than that of Zn in a humid atmosphere (Figure 22). The passive state of Cu lasts for 50 days in these tests, which is more than three times longer than after treatment with ODA or BTA vapors.

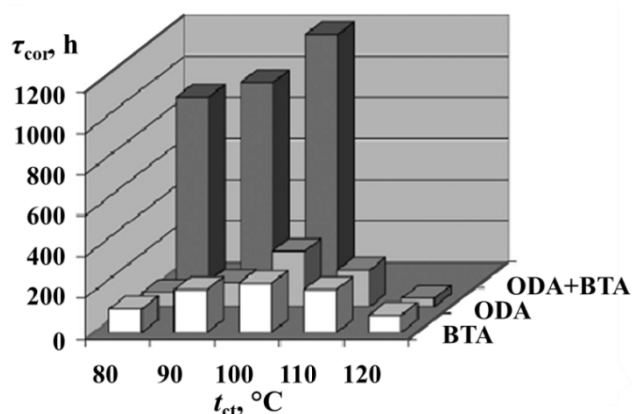


Figure 22. Influence of the temperature of the chamber in which Cu samples are treated for 1 h with OCIs vapor on the time until the first signs of corrosion appear on them in a humid atmosphere with daily condensation of moisture on the samples (reproduced from [342] with permission; Copyright 2018 John Wiley and Sons).

The results of ellipsometric measurements of film thicknesses on Cu before and after its chamber heat treatment are interesting. In fact, the d of the air-formed oxide on Cu is

1 nm, while after 1 h of sample treatment at 100 °C in the absence of OCI it increases to 4.5–5.0 nm. The thickness of the adsorption films formed on the oxide in the presence of OCI vapors depended on the temperature and was 1.0–2.5 nm in the case of BTA, 3.0–4.5 for ODA, and 2.5–5.5 nm for the ODA + BTA mixture. All the OCIs studied slowed down the oxide growth during the heat treatment, so its thickness did not exceed 1.5–2 nm. In contrast to steel and Zn, the Cu surface became hydrophobic after 1 h of chamber treatment not only upon treatment with vapors of ODA or its mixture with BTA ($\Theta_c \approx 115^\circ$), but also of BTA itself ($\Theta_c \approx 100^\circ$).

An attempt to find a chamber OCI of the triazole class that would be more efficient than BTA itself was made in [343]. For this purpose, the properties of thin films formed on Cu at 100 °C by the chamber method from vapors of BTA, 1*H*-1,2,4-triazoles and their substituted derivatives were studied by a set of physicochemical and corrosion methods. It was shown that after treatment of Cu with vapors of these OCIs for $\tau_{ct} = 1.0$ h, a nanosized hydrophobic film is formed on it, which inhibits the growth of oxides. However, they, first of all BTA and its substituted derivatives, stabilize the passive state of Cu, i.e., increase the protective aftereffect. Since it was found that treatment of Cu for $\tau_{ct} = 1.0$ h with OCI vapors at 100 °C is not a time sufficient to form an equilibrium adsorption OCI films on it, longer chamber treatment with vapors substituted BTAs was performed. This allowed the authors to conclude that 5-Cl-BTA is the most efficient chamber OCI upon prolonged exposure of Cu in its hot vapors (1.0 day). This is evidenced by the fact that Cu passivity is retained for a longer time in tests in the salt spray chamber ($\tau_{cor} = 49$ h) than after a similar treatment with BTA or tolyltriazole.

Further studies of Cu chamber treatment with 5-Cl-BTA vapors was continued in [344]. It was shown that the presence of 5-Cl-BTA vapor in the chamber causes the formation of an OCI complex with Cu(I) on the Cu surface, the protective properties of which are significantly superior to those of the oxide. It slows down the formation of Cu₂O, and its thickness increases slightly up to a temperature of 100 °C in the chamber (even at 60 °C, the Cu surface is covered with a monolayer of the 5-Cl-BTA complex). It was shown that its protective effect is much higher than that of copper oxide, which is due to the presence of a film of the 5-Cl-BTA complex up to 4 nm thick. In addition, it appears to have low defectiveness if the chamber temperature is varied from 40 to 100 °C. This significantly increases Cu resistance to general corrosion and local depassivation, which is clearly shown by anodic polarization curves. A further increase in t_{ct} up to 110 °C leads to an increase in heterogeneity of surface layers and a decrease in their protective properties.

The high protective aftereffect of the protective thin coating formed by treatment in 5-Cl-BTA vapor at 100 °C for 1.0 h was evaluated under natural conditions in an urban industrial atmosphere. Cu samples were placed on a rack inside a booth with louvered walls, which was located at the Moscow corrosion station. The first signs of corrosion on Cu samples not subjected to chamber treatment with 5-Cl-BTA vapor appeared 3 weeks after the beginning of the experiment. After 14 months (at the time the article was sent to print), the authors did not observe any signs of corrosion on Cu samples treated with 5-Cl-BTA in a chamber, despite their weekly inspection. Thus, this method can be recommended for temporary protection of Cu products for up to 1 year.

Using a set of methods, as well as electrochemical and corrosion measurements, the possibility of using chamber treatment of Al alloys with vapors of low-volatile OCIs for temporary protection against atmospheric corrosion was studied. For example, the authors [345–347] formed thin adsorption coatings on AMg6 Al alloy for 1.0 h by the chamber method in the vapors of some amines, heterocyclic compounds, carboxylic acids, and their salts. They also evaluated the protective effect of 20 compounds and 4 carboxylic acid salts in the treatment of samples of AMg6 alloy, varying the t_{ct} from 80 to 160 °C. Corrosion tests were performed at 100% humidity and daily condensation of moisture on the samples. The vast majority of potential chamber OCIs were rejected by the results of treatment at 100 °C due to their low efficiency in protecting the alloy. The most promising

chamber inhibitors included three carboxylic acids: oleic acid, neodecanoic acid and carboxylic acid A, whose salt with triethanolamine also deserves attention (Table 4).

Table 4. Effect of the temperature of formation of adsorption films on the results of corrosion tests.

Chamber OCI	Protection Time (Day) at t_{ct} (in °C)			
	80	100	120	140
without chamber OCI	5	5	6	10
carboxylic acid A	9	11	30	50
oleic acid	9	9	18	24
neodecanoic acid	10	18	18	33
Salt of carboxylic acid A and triethanolamine	9	12	27	22

Although the optimum t_{ct} seems to be 140 °C, at which the presence of carboxylic acid A vapors increases the passive state retention in corrosion tests by a factor of 5, 120 °C may also be sufficient. One-hour treatment of the alloy with the vapors of the mentioned acids at these temperatures creates thin adsorption coatings on AMg6 alloy which have a long protective aftereffect but do not hydrophobize the surface. However, there is no doubt that in further studies, more efficient chamber OCIs will be created on their basis.

Recently, Chinese researchers [348] studied the possibility of corrosion protection of AA6061 Al alloy by films formed from the vapor-gas phase of the known mixed OCI containing ODA and BTA. This complex OCI can form coatings on alloy surfaces by self-assembly and thus improve corrosion protection compared to the adsorption of the components alone. In their experiments, alloy samples were placed in the top part of a 0.5-L glass vessel, at the bottom of which 0.5 g of ODA, BTA, or a mixture of both was sprayed. Direct contact of the samples with ODA was not allowed. Experiments were performed at 25 and 50 °C; the duration of exposure of samples to OCI vapor was 48 h. Since the authors assigned an important role to the assembly sequence of ODA and BTA in the formation of various complex SAMs, several combinations of such experiments were performed. It was found that the corrosion resistance and hydrophobic effect of complex films formed by sequential assembly was higher than that of simultaneous assembly. The authors concluded that the SAM of ODA-BTA gives the alloy not only the best corrosion resistance, but also a greater hydrophobic effect. The reason for this is that the ODA adsorbed on the alloy has long alkyls that are oriented perpendicular to the surface. In the next step, the adsorbed BTA molecules are arranged between the long alkyls of the ODA, which can improve the barrier properties of the coating.

Self-assembly of chamber OCIs plays an important role in the protection of other metals, in particular Mg alloys. In fact, the authors [349] studied the properties of nanoscale coatings formed by 5-Cl-BTA from the vapor-gas phase on MA8 alloy (composition, mass%: 96.84–98.55 Mg; 1.3–2.2 Mn; <0.3 Zn; <0.1 Al; <0.1 Si) and found that with increasing time of exposure of samples in air, their protective effect is improved, i.e., a self-assembly ability is shown. Before chamber treatment, the samples (or electrodes) were carefully polished, degreased and dried, then placed in sealed glass vessels of 0.5-L capacity containing a 0.5 g weighed portion of 5-Cl-BTA. The vessels were placed in a desiccator heated to the required $t_{ct} = 20$ –180 °C for different $\tau_{ct} = 5.0$ –360 min. After removing the vessel from the cabinet, the samples were kept at room temperature for 24 h, or even longer in some experiments.

The protective aftereffect of coatings formed with 5-Cl-BTA was estimated by the τ_{cor} value of samples of MA8 alloy in a humid atmosphere with daily condensation of moisture on them. It was found that after treatment for 1 h even at $t_{ct} = 100$ °C OCI the OCI vapor had no effect, but as t_{ct} was increased to 110, 120, 140 and 150 °C, the τ_{cor} value increased 4.0, 6.0, 8.0 and 18.0-fold, respectively. With a decrease in τ_{ct} from 1.0 h to 30 min at 150 °C, the τ_{cor} value decreases 1.5-fold. The choice of optimum conditions of chamber treatment of MA8 alloy (at 150 °C for 1 h) is confirmed by measurements of Θ_c , which indicates that surface hydrophobicity appears at $t_{ct} = 100$ °C and slowly increases from $\Theta_c = 90^\circ$ to 102° at 150 °C. The above-mentioned ability of 5-Cl-BTA to undergo self-assembly allows τ_{cor} to

be to additionally increased twofold by 96 h of ageing of samples already treated under optimum conditions, i.e., the first corrosion signs under severe conditions of moisture condensation appear after 18 h. The results of XPS studies led the authors to the conclusion that the protective aftereffect of 5-Cl-BTA vapor on MA8 alloy results from the formation of nanosized chemisorbed OCI films on the oxide-hydroxide layer.

Ishizaki et al. [15] were apparently the first to study the adsorption of higher carboxylic acids (SA (see Appendix A: Table A1) and isostearic acid (ISA)) as well as *n*-octylphosphonic acid (C₈PA) and 2-(perfluorohexyl)ethyl phosphonic acid CF₃(CF₂)₅-CH₂CH₂PO(OH)₂ (PFEP) from the vapor phase at elevated temperature (423 K) on AZ31 Mg alloy. The duration of exposure of the alloy samples in OCI vapors was 372 h, i.e., more than 15 days. The corrosion resistance of the untreated and modified alloy with SAMs was evaluated by EIS results measured in 5.0 wt% NaCl solution. The Nyquist plots were similar, but with different diameters of the semicircles, indicating differences in the corrosion rates of the alloy. Judging by the capacitive loops, the protective properties of alloys modified with SAMs of phosphonic acids are higher than those of the alloy modified by SA or ISA. Measurements of Θ_c values showed that the hysteresis of Θ_c on the alloy surface modified with a carboxylate SAM is much larger than in the case of phosphonate SAMs. Although SA and ISA have the same carboxyl groups that are attached to the surface of the magnesium alloy, their packing density in the adsorption layer is significantly different. XPS studies showed that the packing density of C₈PA molecules is higher than that of PFEP. The XPS O1s peaks indicate that a combination of mono-, bi-, or tridentate binding of phosphonic acid SAMs to the oxide or hydroxide surface of the Mg alloy is likely to occur. The chemical stability of the SAM-modified magnesium alloy was investigated using Θ_c measurements. The chemical stability of the magnesium alloy modified by SAMs of phosphonic acids was much higher than in the case of SAMs formed from the alkanic acid. The molecular density of C₈PA and PFEP on the magnesium alloy would be higher than that of SA and ISA. The authors suggested that the use of SAMs for creating an inorganic monolayer with a phosphonic acid group would be an efficient strategy to improve the anticorrosion properties of various technical materials.

Considering the preparation and properties of thin protective coatings formed on various metals from the vapor-gas phase, it is impossible to ignore one of the very promising modern methods that solve the problem of improving the efficiency of passivation of metals [350]. It consists in the superhydrophobization of a metal surface, which we have already discussed in Section 3, because it is often successfully used to form thin coatings from organic or water-organic solutions. Recently, this method was applied in nanosecond laser treatment of MA8 alloy to create a surface layer with hierarchical roughness [351]. Laser treatment was performed under laboratory conditions at 40%–50% humidity and 20–25 °C. After the laser treatment, the alloy samples were thoroughly washed with deionized water to remove different particles from their surface, then “Bioforce” UV-cleaner was used for 40 min to improve the adsorption of fluorotrimethoxysilane CF₃(CF₂)₇CH₂O(CH₂)₃Si(OCH₃)₃ used as HPA (see Appendix A: Table A1). The superhydrophobization of the surface of alloy samples was carried out in HPA vapor in a sealed cell at $t_{ct} = 105$ °C. For all laser treatment modes used, the subsequent adsorption of HPA molecules on the surface with a laser texture led to its superhydrophobization with very high $\Theta_c = 170.7$ – 171.5° and the lowest roll-off angle of 2.5° . The corrosion rate of the alloy in 0.5 mol/L NaCl solution strongly depends on the laser treatment mode. In addition, using different laser parameters to provide the best hydrophobic and anticorrosion properties, the authors first analyzed the effect of heating the sample during long-term laser treatment on the electrochemical properties, morphology, wettability and complex element composition of the surface layer formed on metal strips. They also concluded that capillary repulsion of corrosive medium from the hydrophobic walls of pores and cracks minimizes the contact of the solid with the liquid. Negatively charged hydrophobic surfaces repel Cl[−] anions, while HPA molecules block the active surface centers, which prevents chloride adsorption.

5. Conclusions

1. Protection of metals in humid atmospheres and aqueous solutions with pH 5.0–9.0 can be achieved by formation of thin coatings on their surfaces due to the adsorption of OCIs and by more complex chemical interactions with the metal to be protected. In a discussion on the formation of such coatings from aqueous solutions, the important role of the chemical structure of OCIs was shown for salts of carboxylic, phosphonic and dialkylphosphoric acids as an example. Promising OCIs should be capable of chemisorption and self-assembly on the surfaces of metals (Fe, Cu, Zn). In situ adsorption ellipsometry measurements in combination with XPS and FTIR studies played a major role in their selection. It was found possible to increase the efficiency of metal protection by carboxylate anions not only in formulations with oxidants, but also with other OCIs, sometimes using the layer-by-layer method. Especially interesting is the combination of carboxylates with triazoles known for their efficient protection of Cu and Zn, or trialkoxysilanes due to their conversion to a siloxane mesh that prevents the desorption of OCIs. Polybasic phosphonic complexons and water-soluble alkylphosphonic acids inhibit the corrosion of Fe, Cu, and Zn because of their high complex-forming properties in neutral media due to the formation of thin passive films. Thus, the diphilic structure of monoalkylphosphonic acid molecules (C_n PAs) with $n_c \leq 12$ gives them surface activity and capability of self-assembly in the adsorption layer while maintaining solubility in water. While possessing efficient passivating properties, they are less hydrophobic than alkylcarboxylates and dialkylphosphates with the same alkyl length. The low hydrophobicity of C_n PAs anions allows them to be used for the superhydrophobization of the Zn surface in neutral aqueous solutions, which is an advantage in ecological terms. The lower homologues of phosphonates can become efficient OCIs for metals and alloys in combination with oxidizers, triazoles and trialkoxysilanes, including the use of the layer-by-layer method.
2. In organic (mainly alcoholic) and aqueous-organic solutions, higher carboxylic acids are used for hydrophobization and superhydrophobization of the metals surface. Although the combination of a polymodal surface roughness with a low surface energy of a hydrophobizing agent is important to obtain stable superhydrophobic coatings, the review pays great attention to various methods of using higher alkyl carboxylic acids (stearic, myristic) as very affordable hydrophobizing agents. The advantage of two-stage hydrophobization of the surface, for example, of AD31 Al alloy, is noted: first, by adsorption of a trialkoxysilane, preferably n-octyltrimethoxysilane, and then stearic acid. Higher C_n PAs with $n_c > 12$ that form stable and highly ordered layers on the surface of Fe, Cu, and Zn, can also be used to obtain thin superhydrophobic coatings from organic solvents. Noteworthy is the use of C_{18} PA for imparting anticorrosion, wear-resistant, hydrophobic and other valuable properties of various metals. Thus, a superhydrophobic surface was obtained on an oxidized Cu mesh for self-cleaning and separation of oil and water using C_{18} PA. Successful modification of various surfaces of metals with solutions of C_n PAs in organic solvents to impart valuable properties to them allows their application for increasing the corrosion resistance of metals in neutral media. Taking into account the high reactivity and hydrophobicity of higher C_n PAs along with ability to form stable SAMs on metals, they can also be used to obtain thin superhydrophobic coatings.
3. The specific features of the formation of thin protective coatings from the vapor-gas phase are closely related to the long-known volatile corrosion inhibitors (VCIs) and a relatively new type of protection against atmospheric corrosion of metals, i.e., chamber OCIs. The advantages and drawbacks of VCIs are briefly discussed. To increase the protection of metals in the vapor-gas phase, it is necessary to increase the duration of the protective aftereffect, i.e., the stability of thin protective coatings formed by VCI chemisorption. One of these methods involves the combined use of a VCI with a volatile trialkoxysilane, for example, the use of N-benzylbenzylidenimine with

(3-amino-propyl)triethoxysilane to protect steel, Cu, Zn, and an Al alloy. Layer-by-layer deposition of such films provides more efficient protection of metals than VCIs themselves. It has been confirmed by various tests, including 100% humidity conditions with periodic moisture condensation on the samples. Another method, taking into account the slowness of OCI chemisorption on metals, involves increasing the temperature of the medium from which adsorption occurs. It opens up the possibility of using it as a chamber OCI for treating metal surfaces in a chamber containing a compound even with a relatively low volatility under normal conditions. Examples of efficient protection of low-carbon steel, Cu, Al (AA6061) and even Mg alloys (AZ31, MA8) by this method are considered. The implementation of superhydrophobization of a Mg alloy surface by treatment in hot (105 °C) fluorotrimethoxysilane vapor deserves special attention.

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Appendix A

Table A1. List of most frequent abbreviations and symbols.

Symbols			
Θ_c	water contact angle	C_{in}	concentration of corrosion inhibitor
K_s	stability constant of complex	$(-\Delta G_A^0)$	standard free energy of adsorption
pK_a	acidity constant	R_{ct}	charge transfer resistance
Θ	degree of surface coverage	CPE	constant phase element
d	film thicknesses	R_p	polarization resistance
Z	degree of protection	R_f	resistance of the protective layer
τ_{cor}	time to the appearance of the first signs of corrosion	$\log P$	logarithm of the distribution coefficient of the substance in the water–octanol system (for neutral molecules)
Δ	ellipsometry phase shift angle	$\log D$	logarithm of the distribution coefficient of the substance in the water–octanol system (for anions)
E_{in}	initial potential	i_a	anodic current density
E_{pit}	pitting potential	i_p	passivation current density
E_{eq}	equilibrium potential	t_{ct}	temperature of chamber treatment
E_{cor}	corrosion potential	p^0	equilibrium saturated vapor pressure
t	temperature	τ_{ct}	duration of chamber treatment

Table A1. Cont.

Abbreviations			
Basic terms			
CI	corrosion inhibitor	SHP	superhydrophobic
OCI	organic corrosion inhibitor	HPA	hydrophobizing agent
VCI	volatile corrosion inhibitor	REM	rare earth metal
CC	conversion coating	LbL	layer-by-layer
Corrosion inhibitors			
SB	sodium benzoate	PA	phosphonic acid
SAn	sodium anthranilate	HEDP	1-hydroxyethane-1,1-diphosphonic acid
SPhAn	sodium phenylanthranilate	ATMP	amino-tris(methylenephosphonic) acid
SMeF	sodium mefenamate	ADMP	amino-di(methylenephosphonic) acid
SFF	sodium flufenamate	EDTP	ethylendiamine-N,N,N',N'-tetrakis(methylenephosphonic) acid
SPhU	sodium 11-phenylundecionate	HMDTP	hexamethyldiamine-N,N,N',N'-tetrakis(methylenephosphonic) acid
MBP	3-(4'-methylbenzoyl)propionate	PBTC	2-phosphonobutane-1,2,4-tricarboxylic acid
HOC ₁₆ A	hydroxyhexadecanoic acid	HPAA	hydroxyphosphonoacetic acid
C _n A	carboxylic acid	CHADP	1,1-hydroxycarboxypropane-3-amino-di(methylenephosphonic) acid
ALC	alkyl monocarboxylate	DTPMP	diethylenetriaminepentamethylene phosphonic acid
SOI	sodium oleate	<i>m</i> -SNB	sodium <i>m</i> -nitrobenzoate
SOS	sodium N-oleilsarcosinate	C _n PA	alkylphosphonic acid
DMG	dimegine	C ₈ PA	octylphosphonic acid
NaC ₁₃	sodium tridecanoate	C ₁₈ PA	octadecylphosphonic acid
NaC ₁₆	sodium hexadecanoate	C _n PMe	salt of alkylphosphonic acid
SOTP	sodium S-octyl-3-thiopropionate	C ₈ PNa	sodium octylphosphonate
SKAP-25	mixture of sodium salts of alkenylsuccinic acids	C ₁₀ PNa	sodium decylphosphonate
SA	stearic acid	C ₁₂ PNa	sodium dodecylphosphonate
ISA	isostearic	UPA	undecenyl phosphonic acid
MA	myristic acid	FC ₁₀ A	fluorodecylphosphonic acid
BTA	1,2,3-benzotriazole	3-PPA	3-phosphonopropionic acid
5-Cl-BTA	5-chloro-1,2,3-benzotriazole	PhPA	phenylphosphonic acid
MBT	2-mercaptobenzothiazole	TAS	trialkoxysilane
MBI	2-mercaptobenzimidazole	AEAPTS	[3-(2-aminoethylamino)propyl]-trimethoxysilane
SDOP	sodium dioctyl phosphate	APTS	(3-amino-propyl)-triethoxysilane
BEHP	bis(2-ethylhexyl) phosphate	VTMS	vinyltrimethoxysilane
PAMe(II)	complex of phytic acid with Me(II)	OTES	<i>n</i> -octyltriethoxysilane
DPhP	diphenyl phosphates	ODA	octadecylamine
-	-	THF	tetrahydrofuran

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