Triazoles as a class of multifunctional corrosion inhibitors. Review. Part II. 1,2,3-Benzotriazole and its derivatives. Iron and steels¹

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Abstract

This article presents a review of studies (mainly published in 2005–2019) on the adsorption of 1,2,3-benzotriazole (BTA) and its derivatives on iron and various steels from aqueous solutions, as well as their ability to inhibit corrosion in a wide range of solution pH. It examines the effect of these organic corrosion inhibitors on the formation of surface layers, their composition and efficiency of protective action studied using corrosion, electrochemical and other physicochemical methods. Considerable attention is paid to BTA itself, the wide range of corrosive environments in which it can serve as an effective corrosion inhibitor, analysis of the reasons for its successful application in the practice of anticorrosion protection of various steels, as well as the new prospects for its use and increasing the efficiency of anticorrosion protection. The significant advantages of BTA and some of its derivatives for the protection of iron and steel in combination with other organic corrosion inhibitors mainly belonging to the class of carboxylic acid salts are analyzed. A brief discussion is given concerning the prospects of creating nanocontainers with BTA that can significantly increase the protective properties and environmental safety of paint and other coatings on steels. The importance of continuing research in this relatively new and important scientific field is noted. At the same time, it is noted that the prospects of steel protection with mixed inhibitors containing BTA or its substituted derivatives are poorly studied in alkaline and acidic environments, in contrast to neutral ones.

Keywords: *metal corrosion, adsorption, corrosion inhibitors, 1,2,3-benzotriazole and its derivatives, iron, mild steel, carboxylic acid salts, acid solutions, concrete pore solutions, encapsulated inhibitor.*

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I. Introduction

1,2,3-Benzotriazole (BTA), its substituted derivatives and formulations based on them are not only widely known as corrosion inhibitors (CIs) of copper, zinc and their alloys in various environments, but, although on a much smaller scale, are studied and applied to protect other metals. The protection of low-carbon steels is no less important for multifunctional CIs. The vast majority of triazole reviews considered them as CIs of copper and its alloys, which was taken into account in the first part of this review [1]. There are several review articles discussing the inhibition of mild steels corrosion by BTA and its derivatives [2–4], but they mainly analyze acid environments where the efficiency of these compounds is usually low. In contrast to the anti-corrosion protection of copper and its alloys by means of BTA that has been studied for many decades, studies on the inhibition of the corrosion of iron and low-carbon steels began later. V.P. Barannik *et al.* [5] was the first to show that although BTA in an aqueous solution slows down the corrosion of low-carbon steel, it does not suppress it completely. However, its passivation is possible at pH 8.0 in a buffer solution consisting of a weak NH-acid, that is, BTA, and the sodium salt of BTA. Based on this important result, S.A. Balezin *et al.* [6] investigated the dependence of the corrosion rate of Steel 10 on the concentration of BTA in distilled water with additions of NaOH, monoethanolamine (MEA), or ethylene diamine (EDA). The authors concluded that BTA itself does not completely suppress steel corrosion at any C_{in} in water, but in the presence of EDA or MEA in amounts substantially lower than their passivating C_{in} , corrosion on steel samples is not observed. It should be noted that even in a solution of an equimolar mixture of BTA with EDA at $C_{in} = 10$ mM that provides steel passivation, its pH is 10.4, *i.e.* by 0.9 units less than in a similar solution of EDA alone, which also passivates steel. To passivate steel in a neutral solution, for example, at pH 7.15, the authors had to lower C_{EDA} to 1 mM and increase C_{BTA} to 100 mM. Obviously, this fact does not indicate strong passivating properties of BTA with respect to steel in distilled water.

Apparently, K. Nobe *et al.* [7–9] were the first to investigate the inhibitory properties of BTA itself with respect to iron or a Fe–Ni alloy in acid solutions, and later found that its substituted derivatives may be more effective inhibitors of the acid corrosion of iron [10].

II. Iron and steel

Neutral media. Although the results of the first studies on the passivating ability of BTA with respect to iron and various steels in neutral media were not optimistic, interest in this problem persisted and even increased in the past twenty years. This is largely due not only to the industrial availability of BTA and its widespread use for the protection of copper alloys, but also to the ability of BTA to successfully combine with other well-known inhibitors that are highly effective in protecting ferrous metals. In addition, such formulations can be volatile corrosion inhibitors (VCI), since BTA itself has a relatively low but sufficient volatility (saturated vapor pressure $p_s = 10^{-5}$ mmHg [11]). BTA itself, as a VCI, is very effective for protecting copper, somewhat weaker for brass, but cannot protect steel

or cast iron under relatively drastic conditions of 100% atmospheric humidity and periodic (daily) moisture condensation on samples [12]. However, by combining an effective nitrogen-containing corrosion inhibitor for ferrous metals IFKHAN-8 and BTA, it is possible to achieve improved copper protection under the same conditions, although not without weakening its efficiency toward steel. It is quite logical that BTA and its mixture with octadecylamine (ODA) were one of the first objects of research in the development of a fundamentally new means of vapor-phase metal protection against corrosion – chamber inhibitors (CIN) [13, 14]. The essence of this method is the use of low-volatility inhibitors capable of chemisorption on various metals and alloys and forming ultrathin (nanoscale) layers that provide a long-term protective aftereffect under normal atmospheric conditions. To accelerate the formation of such layers, the product to be protected is placed in a closed space where an elevated temperature (80–120)°C is maintained, which increases the p_s of the CIN and the rate of its interaction with the metal. Even the first studies showed that such a treatment of copper and low-carbon steel with a mixed CI exhibits a synergy of protection and gives hydrophobic properties to the surface being protected. As a result, stable passivity of metals is ensured even under drastic conditions of 100% relative humidity and daily moisture condensation, for 149 days on copper samples and 7 days on low-carbon steel.

Another reason for continuing the studies on the inhibitory effect of BTA toward iron was the desire of researchers to expand the range of physicochemical methods in order to determine the composition and specific features of the formation of protective films on this metal. For example, Chinese researchers [15, 16] developed techniques for iron treatment in order to obtain the optimal signal from surface Raman scattering (SERS). They managed to increase it quite significantly (by 2–3 orders of magnitude) and thus successfully apply SERS to study iron electrodes of practical importance. As an example, the authors cited a study on the formation of a BTA film and its inhibitory effect on the surface of iron. In their opinion, BTA interacts with the surface of iron *via* two N atoms of the triazole ring to form a surface polymer consisting of $[\text{Fe}_n(\text{BTA})_p]_m$ complexes that can suppress the dissolution and oxidation of iron.

The ability of BTA to transfer iron to a passive state at concentration $C_{\text{in}} \geq 4.5$ mM in a borate buffer solution (pH 7.36), which is often used to study the passivating ability of metals, was proved by us [17]. In these experiments, an Armco iron electrode was freed from the oxide film before the addition of BTA; therefore, its spontaneous passivation required a relatively high C_{in} . However, if this solution contained chlorides, for example, 0.01 M NaCl, then even 15 mM BTA did not ensure the stability of the passive state of iron, and local depassivation of the electrode was observed on the anodic polarization curves. At the same time, a small increase in pH to 9.1, which increases the dissociation of the weak NH-acid, increased the activity of benzotriazolate anions in competition with chlorides and, even at $C_{\text{in}} = 1.0$ and 2.0 mM, increased the potential of local depassivation of iron E_{pt} by 0.20 and 0.43 V, respectively.

These studies were supplemented by studying the X-ray photoelectron spectra of the surface of low-carbon steel St3 electrodes exposed for 30 min at the corrosion potential in

borate buffer with pH 7.36 and 9.11 [18]. A film of oxides is present on such an electrode: presumably, FeOOH and Fe₃O₄ with $E_b = 711.6$ with 710.6 eV for Fe2p_{3/2}, $E_b = 56.6$ eV and $E_b = 52.2$ eV for Fe3p. It is rather thin ($d \approx 1.8$ nm), since the peak of Fe⁰ ($E_b = 707.0$ eV) was observed in the spectrum, and hydroxylated, as evidenced by the peak with $E_b = 532$ eV.

Exposure of a steel sample for 30 min in borate buffer with pH 7.36 containing 2 mM BTA led to the appearance of the N1s peak in the spectrum and the disappearance of the Fe⁰ peak (Table 1).

Table 1. Composition and thickness of surface films on St3 steel.

Conditions		Composition, %						Thickness, nm			
C_{in}	E , pH	CH	OH	Fe _{ox}	O	N	Fe _m	C_{dif}	OH	BTA	FeOOH
2 mM	E_{cor} , pH 7.36	51.0	25.1	14.8	7.6	2.3	0	2.09	1.80	0.27	–
5 mM	E_{cor} , pH 7.36	37.6	27.2	18.3	8.8	8.1	0	1.07	1.11	0.92	–
5 mM	$E = -0.65$, pH 7.36	48.6	20.5	12.5	6.1	12.2	0	1.36	1.04	1.80	–
5 mM	E_{cor} , pH 9.11	31.2	27.1	21.1	12.7	0.4	7.5	1.26	0.92	0.04	3.51
5 mM	E_{cor} , pH 9.11	45.2	24.7	15.5	8.1	1.2	5.4	1.86	1.42	0.16	3.55
5 mM	$E = -0.65$, pH 9.11	38.8	24.5	18.8	11.2	1.5	5.3	0.93	0.94	0.19	3.91
5 mM	1 M H ₂ SO ₄	40.2	27.5	17.8	9.4	2.3	2.9	1.29	1.41	0.40	4.28

* exposure 17 h.

The presence of an inhibitor in the solution increases the thickness of the oxide (ion etching of the steel surface in the spectrometer estimates $d = 6–8$ nm), and there is a BTA layer with $d \geq 0.35$ nm above it. In the case of an electrode where the inhibitor was pre-adsorbed from a solution with $C_{in} = 5$ mM, the calculated value of the BTA layer reached 0.8–1.2 nm.

If the exposure of the steel electrode was carried out at $E = -0.65$ V, *i.e.* in the absence of an oxide film which was removed from the surface by cathodic polarization for 15 minutes, a thicker BTA film was formed ($d \sim 1.5–2.0$ μm).

Even a long exposure of a steel sample (17 h) in a borate solution with pH 9.11 containing an inhibitor showed the presence of a FeOOH layer with $d \approx 4$ nm, on which BTA was adsorbed in an amount estimated to be no more than 0.2 nm.

The authors estimated the total energy of the system using the RMZ program with a flat arrangement of BTA molecules. In this case, the 5×5 Fe (100) plane turned out to be arranged slightly lower than in the case of vertically arranged BTA where two adjacent nitrogen atoms served as bridges between two iron atoms on the Fe (100) plane. It is assumed that the vertical arrangement of BTA becomes possible with an increase in its C_{in} in solution. Regardless of the solution pH, when BTA interacts with iron cations, deprotonation and aligning of the electron density between nitrogen atoms occurs.

Noteworthy are the results of a study of BTA adsorption on iron and low-carbon steel obtained in a borate buffer solution by the *in situ* ellipsometry method. Since it is used in combination with electrochemical methods and under controlled electrode potential (E), it allows one to evaluate the adsorption on a reduced (at $E = -0.65$ V) and pre-oxidized ($E = 0.2$ V) electrode surfaces. Earlier, this method made it possible to confirm the possibility of adsorption (“oxide-free”) passivation of iron in neutral aqueous solutions [19] and to reveal the features of adsorption of carboxylate class inhibitors on some metals in these solutions [20–27]. The extensive experience of ellipsometric studies accumulated in these works served as the basis for starting studies on the adsorption of other classes of organic inhibitors, including triazoles.

It is not surprising that BTA was the first object in the ellipsometric studies on the adsorption of triazoles on iron [28]. As mentioned above, the ability of BTA in a neutral solution to transfer iron to a passive state was undeniable. The *in situ* method confirmed that BTA was firmly adsorbed on the reduced iron surface, and its adsorption apparently produced a two-layer film. The first monolayer, which is closer to the metal, starts to form even at very small $C_{in} > 0.1$ $\mu\text{mol/L}$ and is characterized by a higher free adsorption energy ($-\Delta G_a^0$) than the second monolayer. BTA is also adsorbed on oxidized iron at $E = 0.2$ V, although at three orders of magnitude greater C_{in} values, *i.e.*, > 0.1 mmol/L. However, even with a slight increase in the solution pH (up to 9.2), its adsorption on the oxidized surface increases, which indicates the important role of the concentration of benzotriazolate anions, C_{BTA} , in the adsorption of the inhibitor. It is possible that BTA is initially flatly oriented on oxidized iron, but with an increase in C_{BTA} , the adsorption layer becomes more densely packed and the orientation of the inhibitor particles on the surface changes.

The adsorption studies by the ellipsometric method helped in the development of new effective inhibitors, including those containing BTA, for the protection of ferrous and non-ferrous metals. For example, the IFHAN-40 inhibitor was created on the basis of sodium phenylundecanate $\text{C}_6\text{H}_5(\text{CH}_2)_{10}\text{COONa}$ (FUN) and BTA. It is strongly adsorbed on reduced and oxidized surfaces of zone-melted iron or low-carbon steel, copper, zinc, and aluminum alloy D16 [29, 30]. When creating this inhibitor, it was taken into account that BTA slightly prevents local depassivation of steel by chloride anions, but its use in a mixture with FUN significantly increases the adsorption of the inhibitor on the oxidized electrode surface (Figure 1). It was also noted that FUN is better adsorbed on oxidized iron than on the reduced surface, while BTA and IFKHAN-40 show the opposite behavior. However, the high value of $(-\Delta G_a^0) = 48.7 \pm 2.4$ kJ/mol, which is significantly higher than that for FUN, $(-\Delta G_a^0) = 33.1 \pm 1.66$ kJ/mol, suggests that IFKHAN-40 is chemisorbed on oxidized iron as well. Indeed, if only 2.6 $\mu\text{mol/L}$ IFKHAN-40 is added to borate buffer after stabilization of the iron electrode surface at $E = 0.2$ V, which ensures a monolayer surface coverage in 3 hours, the solution is replaced by a pure borate buffer, then ellipsometric angles Δ do not change for 5 hours. This indicates that the inhibitor is not desorbed, which is in favor of our assumption about the chemisorption of IFKHAN-40.

Figure 1. Dependences of the change in the ellipsometric angle ($-\delta\Delta$) on the logarithm of the concentration of the inhibitor (a) and isotherm (b) on the oxidized surface of iron at $E = 0.2$ V in borate buffer solution (pH 7.4): 1 – an equimolecular mixture of FUN and BTA; 2 – FUN; 3 – BTA [30].

The polarization curves of St3 steel showed that it is spontaneously passivated at $C_{\text{IFKhAN-40}} = 0.2$ mmol/L, and the local depassivation potential E_{pt} increases by 0.13 V, though C_{NaCl} is 50 times higher. At $C_{\text{in}} = 4$ mmol/L, the protective effect $\Delta E = E_{\text{pt}}^{\text{in}} - E_{\text{pt}}^{\text{bg}}$ reaches 0.52 V. The FUN itself at $C_{\text{in}} = 1$ mmol/L provides $\Delta E = 0.2$ V, whereas higher additives practically do not increase ΔE .

Addition of BTA to less effective corrosion inhibitors than FUN, for example, sodium benzoate [31], can not only to provide corrosion protection for several metals, but also to enhance the protection of low-carbon steel. Such synergistic effects have different explanations, though they are not always indisputable. However they open prospects for decreasing the concentrations or replacing environmentally unsafe substances.

In addition, the possibility of measuring *in situ* adsorption of various organic inhibitors or their mixtures on metals, including iron and mild steel, made it possible to better understand the specificity of their protective effect and improve the methods of their application. In fact, we noticed [30] that the values of $(-\Delta G_a^0)$ on oxidized iron for the mixture and FUN are rather close, in contrast to the similar value for BTA. It was suggested that FUN plays a major role in the formation of an adsorption film by an equimolar mixture of these inhibitors, and the association of its components is the reason for the increase in $(-\Delta G_a^0)$ of the mixture. To obtain information on the interaction of the mixture components in the adsorption layer, we used the fact that the adsorption of the mixture and its components is formally described by the Frumkin equation:

$$BC = \left[\frac{\theta}{1-\theta} \right] \exp(-2a\theta) \quad (1)$$

where $B = [1/55.5] \exp(-\Delta G_a^0 / RT)$ is the adsorption constant associated with the free energy of adsorption $(-\Delta G_a^0)$ and a is the attraction constant characterizing the interaction between the adsorbate particles.

A similar case was analyzed in [32], in which the authors theoretically described the joint adsorption of surface-active components of a solution on a metal electrode if the concentration of one of the components in the solution is constant. Let the subscript 1 refer to BTA, 2 to FUN, and 3 to their mixtures, then the effective attraction constant depends on a_1, a_2, a_3 as follows:

$$a_1^* = a_1 + \left\{ (1 - 2a_3)^2 \theta_2 / [1 + (1 - 2a_2)\theta_2] \right\} \quad (2)$$

In the limiting case where $\theta_2 = 1.0$ (a monolayer of FUN is formed), from Equation 2 the effective attraction constant a_1^* is calculated, which describes the adsorption of BTA. Since these constants for BTA and FUN are determined from individual adsorption isotherms ($a_1 = 1.44$ and $a_2 = 1.5$), and the interaction between the components of the mixture $a_3 = 1.3$ is determined from the adsorption isotherm of the mixture, then $a_1^* = -1.12$. A negative value indicates that repulsion occurs between the BTA particles in the mixture.

Similarly, it is possible to determine a_2^* characterizing the interaction between the FUN anions in the presence of a constant concentration of BTA: $a_2^* = -1.4$. The resulting negative value indicates that repulsion in the mixture occurs between the FUN molecules as well. For the mixture itself, the value of a_3 is positive and it can be assumed that this is caused by attraction precisely between the BTA and FUN anions. In this case, one can expect enhanced adsorption of BTA when it does not occur directly on oxidized iron but on a preformed monolayer of FUN.

Indeed, if a FUN monolayer is preliminarily deposited at $E = 0.2$ V on the surface of oxidized iron, and then the inhibited solution is replaced by a pure buffer to which BTA is sequentially added, then its adsorption isotherm on the FUN sublayer can be obtained. Its comparison with the adsorption isotherm of BTA on oxidized iron showed that BTA on the monolayer of FUN starts to be adsorbed at lower concentrations, while the curve is shifted by three orders of magnitude to the left along the concentration axis. The dependence of the change in the ellipsometric angle Δ on C_{BTA} is also adequately described by the Frumkin equation with values of $-\Delta G_a^0 = 36.56 \pm 1.83$ kJ/mol and $a = 1.3 \pm 0.16$. It is noted that the values of $(-\Delta G_a^0)$ calculated for the mixture and BTA on a monolayer of FUN are close to each other. This may indirectly indicate that upon adsorption of a mixture of FUN with BTA, anions of FUN induce BTA adsorption.

Corrosion tests of St3 plates showed that they are treated with a mixture or layer by layer, the times until the first signs of corrosion appear are in the same range (156 ± 18 , 164 ± 24 hours, respectively). This fact shows the possibility of redistributing the components of the mixture on the surface of the electrode; it follows from our analysis of the attraction constants, and indicates the ability of the components of the mixture to undergo self-organization.

The results of the above work laid the foundation for a whole series of studies in which other anions of carboxylic acids were used as modifiers of the surface of iron or low-carbon steel, which significantly improved the adsorption of BTA and the protective properties of the nanoscale coatings. For example, a protoporphyrin derivative [2,4-di(1-methoxyethyl)-deuteroporphyrin IX disodium salt], *i.e.* dimegin [33], can be successfully used as such a modifier of the surface of the zone-melting iron:

Anodic polarization curves of iron in borate buffer containing 10 mmol/L NaCl showed a high surface activity of dimegin. Even in the presence of 1 $\mu\text{mol/L}$ dimegin, the passivation current density decreases from 83 to 72 $\mu\text{A/cm}^2$ and E_{pt} increases by 0.030 V. At $C_{\text{in}} > 10 \mu\text{mol/L}$, the free corrosion potential increases, the passivation current density decreases to 14 $\mu\text{A/cm}^2$, and E_{pt} reaches 0.25 V. This behavior of iron in the presence of dimegin is associated with its adsorption on the electrode surface and possibly forms complex compounds with iron cations. Indeed, a study of the adsorption of dimegin on a passive, *i.e.* pre-oxidized iron at $E = 0.2$ V from a borate buffer with pH 7.4 confirmed that changes in the ellipsometric angle ($-\delta\Delta$) as a function of the logarithm of dimegin concentration allowed us to obtain the adsorption isotherm adequately described by the Temkin equation:

$$\theta = (1/f) \ln(B_{\text{max}} C) \quad (3)$$

where f is the energy heterogeneity factor of the surface characterizing the change in the enthalpy of adsorption with its coverage. The value calculated for dimegin, $-\Delta G_a^0 = 43.3$ kJ/mol, significantly exceeds that of BTA, $-\Delta G_a^0 = 19.2$ kJ/mol, the adsorption of which can also be described by the Temkin isotherm. The value of the other adsorption characteristic, $f = 1.0 \pm 0.12$, indicates a rather low sensitivity of dimegin adsorption to the inhomogeneity of the surface energy of a passive electrode of zone-melted iron. (For BTA adsorption on the same electrode, $f = 3.6 \pm 0.7$).

A high value of $(-\Delta G_a^0)$ indicates the possibility of dimegin chemisorption on oxidized iron, and the multicenter nature of its molecule allows us to expect a successful combined use of dimegin with other corrosion inhibitors. In view of this, it is logical to study it together with BTA in the design of ultrathin protective films on metals.

The surface of passive iron was modified by adsorption of dimegin at $E=0.2$ V, then the solution was replaced with the pure buffer without shutting off the potentiostat. After replacing the solution, the ellipsometric surface parameters, *i.e.*, angles Δ and Ψ , did not change for 2 hours, which indicates the absence of dimegin desorption and the correctness of our assumption about its chemisorption. To measure BTA adsorption, its concentrate was added in portions to a pure borate buffer, and then the variation in angle Δ , *i.e.* the $\delta\Delta$ value, were measured over time. When it reached a constant value, it was considered as a criterion for the equilibrium adsorption of BTA, and the dependences of $\delta\Delta$ on $\log C$ were recalculated into an isotherm. All isotherms obtained at different degrees of surface coverage of passive iron with dimegin at $E=0.2$ V were adequately described by Equation 3, and their characteristics are presented in Table 2.

Table 2. Adsorption characteristics of BTA with varying degrees of surface coverage of oxidized iron with dimegin, θ_{DMG} .

θ_{DMG}	f	$(-\Delta G_a^0)$, kJ/mol
0.00	3.6 ± 0.7	19.2 ± 0.9
0.27	5.1 ± 0.3	38.7 ± 1.9
0.50	5.0 ± 0.5	45.1 ± 2.2
0.70	4.9 ± 0.5	44.6 ± 2.2
1.00	4.7 ± 0.8	39.9 ± 2.0

From the ellipsometric data on the adsorption of dimegin on oxidized iron, its almost flat location $|\delta\Delta \sim 0.41^\circ|$ corresponding to a thickness of ~ 0.9 nm follows. The thickness of the adsorbed BTA layer increases if it is formed on oxidized iron whose surface is preliminarily covered with dimegin, at least partially. For all investigated coverages with dimegin, the thickness of the adsorbed BTA layer lies in the range of 1.0–1.2 nm. It is possible that the increase in the thickness of the BTA adsorption layer is due to the tendency of water-soluble porphyrins to be associated with electron-donor molecules [34], in our case to BTA, and form BTA–dimegin associates. Preliminary chemisorption of dimegin clearly improves the subsequent adsorption of BTA, which is characterized by a larger value of $(-\Delta G_a^0)$. The strengthening of the BTA bond with the electrode surface may be due to the possibility of formation of its associates with chemisorbed anions of dimegin.

It is significant that the adsorption characteristics of BTA depend on the degree of filling of the electrode surface with dimegin. The increase in f in the BTA adsorption

isotherm upon transition to the modified surface is reasonable, since adsorbed dimegin occupies only a small fraction, $\theta_{\text{DMG}}=0.27$, of the total surface (Table 2). At $\theta_{\text{DMG}}=0.50$, $(-\Delta G_a^0)$ acquires a maximum value and even exceeds the same value for dimegin on passive iron itself. Here, the tendency of f to decrease with a further increase in θ_{DMG} begins to appear; this tendency is confirmed by a decrease in $(-\Delta G_a^0)$. This indicates a weakening of BTA adsorption, therefore it may be assumed that the surface not covered with porphyrin can somehow facilitate BTA adsorption.

A similar pattern was observed upon combined use of sodium flufenamate (SFF) and BTA [35, 36]. The adsorption of SFF and BTA on oxidized St3 surface is described by Equation 3 with $-\Delta G_a^0 = 28.5$ and 19.2 kJ/mol, respectively. The mixture of SFF and BTA begins to be adsorbed at C_{in} more than 4 orders smaller than its components, and its adsorption isotherm also obeys the Temkin's equation with $-\Delta G_a^0 = 62.2$ kJ/mol, *i.e.* 3.2 times higher than the similar value of BTA. It is also possible to sequentially adsorb SFF anions on low-carbon steel and then BTA, in order to increase the adsorption energy of triazole and, accordingly, increase the protective properties of such nanoscale adsorption layers whose total thickness does not exceed 5 nm. It is significant that the method of sequential adsorption can be performed from very dilute solutions of individual inhibitors.

It turned out that the dependence of BTA adsorption on the degree of coverage with pre-adsorbed SFF passes through a maximum. In fact, if SFF preliminarily forms a monolayer on the surface of steel, BTA cannot be adsorbed on it at all. However, the adsorption of BTA is enhanced and reaches an optimum when the preliminary coverage with SFF is $\theta = 0.33$ – 0.50 , in which case 52.0 – 58.7 kJ/mol is reached. It can be assumed that the attraction between the vertically oriented SFF anions and BTA parts is facilitated in the case of triazole adsorption on an unoccupied surface of oxidized steel due to the lateral interaction of their aromatic rings.

The form of the dependence of the protective effect of BTA on the degree of surface coverage with pre-adsorbed SFF is confirmed by the results of corrosion tests in a humid atmosphere with forced daily condensation of water on the steel surface (Table 3). The best result was obtained after a “two-stage” treatment where first the adsorption of SFF provides $\theta = 0.33$, and then the surface is treated with a BTA solution. In this case, the time before corrosion (τ_{cor}) is more than 10 days, while at $\theta = 0.5$ it is 2 times shorter.

The ability of BTA to enhance the protection of low-carbon steel in neutral aqueous solutions with salts of not only monocarboxylic but also dicarboxylic acids has long been known. Mercer, Thomas *et al.* [37] found a synergy of protection for sodium sebacinate and BTA, also for cast iron and galvanized steel. In [38], these studies were continued and the synergism of steel protection in 0.02 M NaCl solutions and from local depassivation was proved.

The two-stage treatment of steel with inhibitor solutions can have a beneficial effect if the modification stage is carried out in a highly diluted (20 μM) solution of copper sulfate [39].

Table 3. The influence of the passivation method and the solution composition on the protective properties of the adsorption films toward St3 in a humid atmosphere (100% relative humidity of air) with daily condensation of moisture on the samples.

Aqueous solution of inhibitor and its concentration, mmol/L	Time until the first signs of corrosion, days
SFF (1–3)	3.8 ± 0.3
BTA (3)	1.4 ± 0.2
SFF+BTA (3)	5.8 ± 0.2
First layer: SFF with $\theta = 0.10$ Second layer: BTA (3)	9.0 ± 0.4
First layer: SFF with $\theta = 0.33$ Second layer: BTA (3)	10.4 ± 0.3
First layer: SFF with $\theta = 0.5$ Second layer: BTA (3)	5.0 ± 0.3
4 mM BTA	0.16 ± 0.0
4 mM AKS	1.5 ± 0.01
4 mM BTA+4 mM AKS	3.0 ± 0.3
First layer 20 μM CuSO_4 Second layer 4 mM BTA+4 mM AKS	9.5 ± 0.3
First layer 5 μM HEDPCu Second layer 4 mM BTA+4 mM AKS	35 ± 0.5
First layer 10 μM HEDPCu Second layer 4 mM BTA+4 mM AKS	40 ± 0.5
First layer 20 μM HEDPCu Second layer 4 mM BTA+4 mM AKS	50 ± 0.4

In this case, the time until the first signs of corrosion on steel appear after passivating treatment with an equimolar solution of BTA and sodium alkyl carboxylate (SAC) increases more than 3-fold (Table 3). However, a two-stage treatment is much more effective where, at the first stage, copper sulfate is replaced by copper hydroxyethylidene diphosphonate (HEDPCu), which sharply increases the efficiency of subsequent passivation even at lower modifier concentrations [40]. Even with 5 μM HEDPCu, after passivation with the same passivator, τ_{cor} in subsequent corrosion tests reaches 35 days (Table 3). If the modifying

treatment of steel is carried out with a 10 or 20 μM HEDP solution, then in the same tests, τ_{cor} reaches 40 or 50 days, respectively. Obviously, such a strong protective effect is largely due to a stronger bond of BTA and, possibly, SAC, with copper than with iron or steel.

These studies were further developed using phosphonate metal complexes as a modifier [41–43]. In these works, at the first stage low-carbon steel was processed in a solution of the most environmentally friendly zinc phosphonates: zinc hydroxyethylidenephosphonate HEDPZn or zinc nitrilotrismethylenephosphonate NTPhZn (Table 4).

Table 4. Test results of ultrathin protective coatings on steel by the electrochemical method in a borate buffer with pH 7.4 containing 1 mM NaCl (ΔE) and in a humid atmosphere with daily moisture condensation on the samples (τ_{cor}). The duration of each treatment is 10 min.

Composition of the aqueous treatment solution, mmol/L	ΔE , V	τ_{cor} , days	Coating thickness, nm
8 AKS	0.29	11.5 $\pm$ 0.2	—
8 SOI	0.59	13.5 $\pm$ 0.2	—
8 NaNO ₂	0.27	7.0 $\pm$ 0.2	—
8 BTA	0.29	2.5 $\pm$ 0.2	—
4 SOI+4 BTA	0.52	10.5 $\pm$ 0.2	13.7 $\pm$ 2.5
4 AKS+4 BTA	0.56	9.0 $\pm$ 0.2	22 $\pm$ 0.5
8 mM HEDPZn	0.10	3.0 $\pm$ 0.1	6.0 $\pm$ 1.5
8 mM HEDPZn – 1st treatment 4 mM SAC+4 mM BTA – Passivation	0.64	33.0 $\pm$ 0.3	25.7 $\pm$ 0.2
8 mM HEDPZn – 1st treatment 4 SOI+4 BTA – Passivation	0.38	18.0 $\pm$ 0.2	—
8 mM HEDPZn+8 mM NaNO ₂	0.19	4.0 $\pm$ 0.1	—
8 mM HEDPZn+8 mM NaNO ₂ – 1st treatment 4 mM SAC+4 mM BTA – Passivation	0.66	39.0 $\pm$ 0.3	—
8 mM NTPhZn	0.13	6.0 $\pm$ 0.1	5.25 $\pm$ 0.75
8 mM NTPhZn – 1st treatment 4 mM AKS+4 mM BTA – Passivation	0.46	36.0 $\pm$ 0.3	—
8 mM NTPhZn – 1st treatment 4 mM SOI+4 mM BTA – Passivation	0.58	24 $\pm$ 0.3	33.0 $\pm$ 2.5
8 mM NTPhZn+8 mM NaNO ₂	0.24	7.0 $\pm$ 0.2	—
8 mM NTPhZn+8 mM NaNO ₂ – 1st treatment 4 mM SOI+4 mM BTA – Passivation	0.54	31.0 $\pm$ 0.3	—
8 mM NTPhZn+4 mM VTMS – 1st treatment 4 mM SOI+4 mM BTA – Passivation	0.91	69.0 $\pm$ 0.5	—

Composition of the aqueous treatment solution, mmol/L	ΔE , V	τ_{cor} , days	Coating thickness, nm
The same, but before corrosion tests for 5 sec, the samples were placed in 0.1% NaCl		25.0±0.5	–

It is easy to see that one-stage passivation (without modifying the steel surface) in the best case (for steel treatment in a 8 mM SOL solution) allows one to achieve $\Delta E=0.59$ V in electrochemical experiments, and to provide complete corrosion protection for $\tau_{\text{cor}}=13.5$ days. In this case, partial replacement of SOL by BTA which is not such an effective passivator for steel keeps high both values: $\Delta E=0.52$ V and $\tau_{\text{cor}}=10.5$ days. Treatment with 8 mM HEDPZn or NTPhZn solutions, which modify the steel surface by phosphonate complexes of iron and zinc hydroxide, passivates it much more weakly: $\Delta E=0.10$ or 0.13 V, respectively, and $\tau_{\text{cor}}=3$ days or 6 days.

Better results with two-stage passivation where a HEDPZn solution was used at the first stage were obtained upon subsequent steel treatment in an equimolar solution of SAC and BTA ($\Delta E=0.64$ V, $\tau_{\text{cor}}=33$ days). If, in a similar steel treatment, HEDPZn was replaced by NTPhZn, corrosion tests showed a slightly better result ($\tau_{\text{cor}}=36$ days), although ΔE was noticeably smaller, 0.46 V. Joint pretreatment with HEDPZn + NaNO_2 slightly enhances the subsequent passivation in the same solution ($\Delta E=0.66$ V, $\tau_{\text{cor}}=39$ days), while replacement of HEDPZn with NTPhZn weakens the passivation ($\Delta E=0.54$ V, $\tau_{\text{cor}}=31$ days).

Although an 8 mM SOL solution or its mixture with BTA has a slightly better passivating effect than similar SAC solutions, they are less effective in a two-stage treatment of steel where a zinc phosphonate or its formulation with NaNO_2 serves as the first stage. However, the best result was obtained if a steel surface was modified in a solution of 8 mM NTPhZn+4 mM vinyl trioxymethylsilane (VTMS) with subsequent passivation in 4 mM SOL+4 mM BTA ($\Delta E=0.91$ V, $\tau_{\text{cor}}=69$ days). VTMS, which, as it is known [44–46], undergoes hydrolysis to give vinyl trioxymethylsilanol and enters into condensation. As a result, a siloxane network is formed on the metal, which is not only weakly desorbed by itself, but can also capture inhibitor particles present on the surface, thereby strengthening the protective film. In addition, TAS are well known as adhesion promoters; therefore, they can facilitate the formation of a strong adsorption layer of OIH and BTA.

The stability of the protective film formed by such a treatment is evidenced by the results of even more severe corrosion tests. Before placing passivated steel samples into the heat and moisture chamber, they were immersed for 5 seconds in a 0.1% NaCl solution, then dried in air, which allowed ≈ 20 mg of NaCl per m^2 to be applied to the steel surface. Despite this, the first signs of corrosion on the samples appeared only after 25 days of testing in a humid atmosphere with daily moisture condensation. Thus, it can be expected that further research in this direction would help create new reliable means of temporary protection not only for copper and its alloys but also for low-carbon steels.

The widespread use of BTA in practice is largely due not only to its availability, but also to the capability to be combined with other inhibitors, as already shown above, often causing synergism in protection not only of copper or its alloys, but also of ferrous metals. In this case, an inorganic inhibitor can be the second component. For example, in a 20% aqueous solution of tetra-*n*-butylammonium bromide (TBAB), which is promising for refrigeration conditioning systems due to a higher phase transition temperature, Na_3PO_4 together with BTA can be used to protect steel from corrosion [47]. The highest corrosion inhibition efficiency ($Z=85\%$) was observed with a mixture of 2 g/L Na_3PO_4+2 g/L BTA. Another example is the inhibitory effect of a mixture of sodium molybdate with BTA, first suggested by Japanese researchers for a high-temperature (165°C) coolant (12.45 mol/L LiBr) [48], and later confirmed [49] in a study of carbon steel corrosion in a boiling ($t=146^\circ\text{C}$) solution of 10.24 M LiBr+0.07 M LiOH. Recently, a synergistic effect of BTA and cobalt cations (Co^{2+}) in the protection of low-carbon steel in a 3.5% solution of NaCl was shown [50]. The efficiency of steel corrosion inhibition was determined by electrochemical methods (polarization and EIS measurements). The inhibition mechanism studied using field emission scanning electron microscopy, energy dispersive spectrometry, XPS and EIS was associated with the deposition of a BTA–Co(II) chelate complex. It caused a slowdown of both electrode reactions, *i.e.*, the resulting chelate acted as a mixed type inhibitor.

The use of BTA in various cooling water systems has long been known and a description of a number of examples can be found not only in the patent but also in scientific literature [1, 3, 4, 19]. However, over the past two decades, its use has expanded and is not limited to the protection of copper and its alloys. For example, ionic liquids at room temperature attract attention due to a wide range of their possible applications, in particular, they demonstrate excellent friction reduction for various slip pairs. However, if 1-ethyl-3-hexylimidazolium hexafluorophosphate is used as such an ionic liquid, then the problem of protecting metals from corrosion arises [50]. When choosing inhibitors for corrosion protection (without deterioration of tribological characteristics), BTA was chosen for a steel/Cu–Sn bronze slip pair. It is well miscible with imidazole-based ionic liquids due to the proximity of their molecular structures. Indeed, the tribological characteristics of ionic liquids even improved, mainly due to corrosion reduction. An XPS analysis of the bronze surface showed that complex tribochemical reactions occur on it during friction with steel. However, in the presence of BTA in the ionic liquid, bronze is coated with a film consisting of a $[\text{Cu}(-\text{C}_6\text{H}_5\text{N}_3)]$ complex and Cu_2O . It is able to prevent or slow down the metal contact with the ionic liquid, thus reducing the corrosion caused by surface fluorination.

Not only BTA itself, but also its substituted derivatives and formulations based on them can be used as effective inhibitors for the protection of iron and various steels in neutral environments. Unlike basic studies of BTA derivatives as inhibitors of iron acid corrosion, in neutral solutions only a few inhibitors were studied, and even those did not belong to a common reaction series. This is partly due to the fact that the solubility in water, for example, of 5-alkyl-BTA, decreases rapidly with increasing number of carbon atoms, and as already noted for protection of copper with these compounds, hydrophilic substituents ($R = \text{NO}_2, \text{OH}$

and others) make them less effective than BTA [1]. Of the 5-alkyl-BTA series, tolyltriazole (TTA) corrosion inhibitor is most readily available for industrial use and well known. In some cases, it surpasses BTA in the protection of low-carbon steel in the protection efficiency. For example, a study of 16 different azoles as corrosion inhibitors of C-15 steel in a 3% NaCl solution at $t=25$ and 70°C showed that TTA was the best of them and BTA was somewhat weaker [52].

Of the other substituted BTAs, 5-chloro-BTA has been studied most thoroughly. In this compound, the substituent not only increases the hydrophobicity of the molecule, but also increases its acidity ($\text{p}K_{\text{a}} = 5.46$ compared to 8.38 for BTA), which increases the surface activity of the inhibitor.

The advantages of 5-chloro-BTA over BTA were proven by us convincingly [53]. For example, using the *in situ* ellipsometric method, it was shown that in borate buffer solution with pH 7.4 its adsorption on passive steel at $E=0.2$ V begins at an almost two times smaller C_{in} than with BTA, while the $(-\Delta G_{\text{a}}^0)$ exceeds this value for the unsubstituted compound by more than 10 kJ/mol. It is also important that 5-chloro-BTA does not lose the ability to form formulations with a carboxylate type inhibitors that show synergy of adsorption on low carbon steel and protective action.

Figure 2 shows the plots of $-\delta\Delta$ vs. $\lg C_{\text{in}}$. Their analysis shows that a mixture of 5-chloro-BTA with SFF at the same ratio of components (2:3) has clear advantages over the mixture of BTA with SFF. Anodic polarization curves of steel confirmed that the new formulation at $C_{\text{in}}=3$ mmol/L preserves the passive state of steel up to $E_{\text{pt}}=0.4$ V, although the same concentration of 5-chloro-BTA itself practically does not shift the $E_{\text{pt}}=0.05$ V observed in the borate buffer containing 0.01 mol/L NaCl in the absence of inhibitors. The mixed inhibitor is adsorbed on the oxidized steel surface noticeably better than not only SFF, but also 5-chloro-BTA or a similar mixture of BTA with SFF. However, there is a significant difference between the two triazoles in question.

Figure 2. Dependence of the change in the ellipsometric angle ($-\delta\Delta$) on the concentration of SFF (1), 5-chloro-BTA on the monolayer of SFF (2), BTA+SFF (2:3) (3), 5-chloro-BTA+SFF (4) on the oxidized surface of steel at $E=0.2$ V.

In fact, BTA is not adsorbed on the SFF monolayer [36], but its substituted derivatives adsorbed on it even more readily than on the oxidized steel surface. The adsorption isotherm obtained is described by Equation 2 with $a=0.95\pm0.23$ and $-\Delta G_a^0=39.16\pm1.96$ kJ/mol. The attraction constants characterizing the strength of the interaction between 5-chloro-BTA molecules for adsorption on the oxide and on its surface modified by an adsorption monolayer of SFF are very close ($a=1.18\pm0.14$ for 5-chloro-BTA on St3 at $E=0.2$ V).

Valuable information on the structure of the adsorption layers of these inhibitors was obtained by XPS studies [53, 54]. Although, unlike in ellipsometry, the procedure of recording XPS spectra does not allow one to control the metal potential and is an *ex-situ* method, the high strength of adsorption bonds allowed us to hope for their small deformation upon removal of the electrode from the solution and the ability to correctly evaluate the compositions and structures of the adsorption films. An important factor was that the molecules of both compounds contained heteroatoms (N, Cl and F) that served as valuable marks in XPS spectra.

To determine the distribution of elements by the thickness of adsorption layers, the ratio of intensities of the peak element was measured at two angles of electron emission θ_1 and θ_2 , since the peak intensity I_0 , determined by atoms located at a depth d is weakened to intensity I in accordance with the formula:

$$I = I_0 \exp(-d/l \cos \theta) \quad (4)$$

Here l is the average mean free path of a knocked-out electron in an absorbing layer of thickness d . For different angles (for example, $\theta_1=45^\circ$ and $\theta_2=10^\circ$) we obtain:

$$I_1/I_2 = \exp(-d/l \cos \theta_1) / \exp(-d/l \cos \theta_2) \quad (5a)$$

and further conversion leads to:

$$-\ln(I_1/I_2) = d \left[(1/l \cos \theta_1) - (1/l \cos \theta_2) \right] \quad (5b)$$

where $(1/l \cos \theta_1) - (1/l \cos \theta_2)$ is a constant value. Then the logarithm of the intensity ratio gives a relative value of d . Since the absolute value of the thickness depends on λ , which is determined by many parameters such as the kinetic energy of electrons, density of matter, *etc.*, this can affect the value of d . In addition, if the atoms of the same element are located at different depths, then the position of the point on the relative depth graph will be averaged, for example, for carbon.

The results of these measurements are presented in Figure 3a. They indicate that the F atoms are located above the Cl and especially N atoms. The iron cations are located below all of them and form a substrate for the overlying mixed layer. Based on the depth distribution of elements, a model was suggested for the arrangement of 5-chloro-BTA molecules and flufenamic acid (FFA) anions on a FeOOH surface (orientation 100). According to this model, the studied inhibitor molecules are located almost vertically with respect to the surface (Figure 3b).

Figure 3. The relative arrangement of atoms by depth (a) and the possible arrangement of the FFA and 5-chloro-BTA anions on the St3 surface (b) after the samples were kept in a borate solution at pH 7.40 (the arrows indicate the direction of electron emission at two angles relative to the normal to the surface).

Upon layer-by-layer deposition of 5-chloro-BTA on a monolayer of FFA, we obtain a two-layer nanoscale film. In its XPS analysis, the angular dependence of the spectra indicates that the Cl and Na atoms are arranged higher than the F atoms. This indicates that the 5-chloro-BTA molecules are located above the FFA layer. Calculations using the MultiQuant program give $d = 0.8\text{--}1.0$ nm for the FFA anion layer and $\leq 0.1\text{--}0.2$ nm for 5-chloro-BTA. The thicknesses of the adsorption monolayers of the inhibitors were calculated from the ellipsometry data using the McKrakin program. All of them are given in Table 5.

Table 5. The thicknesses of monolayers of inhibitors on the surface of St3 in a neutral solution obtained by different methods.

Inhibitor	Method for calculating thickness, nm	
	XPS	Ellipsometry
SFF	0.9 ± 0.1	1.1 ± 0.1
5-chloro-BTA	0.4 ± 0.1	0.75 ± 0.1
5-chloro-BTA+SFF	0.7 ± 0.3	0.8 ± 0.1
5-chloro BTA on a SFF monolayer	0.2 ± 0.1	0.25 ± 0.1

It should be noted that in all cases there is a good agreement between the calculations by different methods and an understandable fact of the greater thickness of the layers obtained from ellipsometric measurements, since they are carried out *in situ*, *i.e.*, directly in solution. XPS studies involve the removal of a sample from a solution, washing it with a stream of water and treatment in an ultrasonic bath. The greatest discrepancies are observed not in the analysis of the adsorption of a mixture of inhibitors or their layer-by-layer adsorption, but in the case of adsorption of SFF or 5-chloro-BTA themselves. It is possible

that a second layer of an inhibitor is formed in the solution but is easily removed by washing the electrode including ultrasonic treatment.

One of the important directions of the use of corrosion inhibitors for metals and alloys is their addition not to a corrosive environment or passivating solutions, but to organic paint coatings (OPC), more precisely into varnishes and primers, *i.e.*, a thin layer closest to the metal surface being protected. This reduces the consumption of the inhibitor and, together with the barrier properties of the paint, can reliably protect the metal from corrosion in very corrosive environments. However, it has long been known that the direct addition of an inhibitor into a coating can have an adverse effect because of its ability to enter into chemical reactions with a binder and other additives, which worsens the properties of the inhibitor and other OPC components. In order to avoid undesirable phenomena, extensive research is currently underway to search for nano- or microcontainers of a neutral material, which are filled with an appropriate corrosion inhibitor and only then introduced into an OPC. Of course, a number of stringent requirements are imposed on such inhibitors. Among them, an important role belongs to the versatility and high efficiency of the inhibitor toward several metals and alloys, environmental safety, chemical and thermal stability, as well as the ability to diffuse from the containers to reach the metal surface and relatively quickly form a protective layer on it. Coatings containing such encapsulated inhibitors are often referred to as “smart” and self-healing ones.

The objectives of this review do not include a detailed analysis of inhibited OPC. However, it would be wrong not to mention the possibility of using BTA or its substituted derivatives in them. For example, the possibility of using galloisite nanotubes as materials for filling with corrosion inhibitors with subsequent introduction into a paint was studied [55]. Galloisite is a natural product that does not increase environmental pollution and is well compatible with various water and oil-based coatings. BTA was loaded into galloisite tubes with a diameter of 50 nm and mixed with a paint formulation in an amount of 2–10 wt%, which increased the protective properties of OPC 2–4 fold. BTA was released from galloisite nanotubes in approximately 50 hours at a rate described by a power function. If the release rate of BTA is controlled by the formation of a metal complex with BTA, which can form plugs at the ends of the tubes, this will ensure a high loading efficiency of galloisite and a longer release time of the inhibitor. This provides additional opportunities for optimizing the process. Therefore, it is possible to control the rate of BTA release from halloysite nanotubes to obtain the best protective properties of the coating. This is especially important if there is a flow of surrounding water that causes premature removal of the corrosion inhibitor from the metal surface.

Yu. Feng *et al.* [56] obtained nanocontainers by deposition of a polyelectrolyte on SiO₂ nanoparticles, and BTA was encapsulated in them. To characterize the nanocontainers obtained and confirm the loading of BTA, they used FTIR, thermogravimetric analysis, and AFM. The effect of the solution pH on the self-release of BTA from the nanocontainers was studied using EIS measurements. It has been proven that in chloride solution with a low pH 2 or a high pH 11 BTA is released sufficiently to prevent carbon steel corrosion. At pH 5–9,

the nanocontainers remain closed. The efficiency of metal corrosion inhibition depends on the kinetics of the release of BTA, the molecules of which are released from the nanocontainers upon swelling of the latter.

In [57], to protect steel sheets from corrosion, an epoxy coating was used in which mesoporous silica was dispersed with and without BTA. The protective properties of these two coatings were compared in physiological saline containing chlorides. The results of the EIS study showed that the presence of SiO₂ particles filled with BTA in the coating increases its protective ability in a corrosive environment. The impedance modulus and polarization resistance of a steel electrode coated with mesoporous SiO₂ doped with BTA were approximately an order of magnitude higher than for an electrode with a coating without an inhibitor. The AFM image also confirmed the formation of a BTA layer in a scratched area of the coating, which in addition to its healing effect increased the corrosion resistance of the system. The authors concluded that the studied object can be considered as a “smart” anti-corrosion system, which has higher corrosion resistance than the control sample. This behavior is associated with the release of BTA at the interface between the epoxy coating and steel. In addition, less corrosion products were found on a scratched coating with mesoporous SiO₂ doped with BTA than on a sample with a coating without an inhibitor, which confirms the release of BTA “on demand of corrosion”.

The use of the layered assembly method for the preparation of nanocontainers loaded with BTA was apparently first described by Schukin *et al.* [58]. Polyelectrolyte shells that modify the surface of silica nanoparticles or galloisite nanotubes were made using various combinations of weak and strong polyelectrolytes. All nanocontainers of this type increased the release rates of BTA release in aqueous acidic or alkaline solutions, and remained almost closed in the neutral pH range. Kamburova and Radeva [59] encapsulated kaolinite nanoparticles with polymers for use as nanocontainers that could release captured BTA under neutral conditions. Nanocontainers were obtained by layered assembly of poly(diallyldimethylammonium chloride) (PDADMAC) and poly(acrylic acid) (PAA) on the surface of kaolinite at various pH values. BTA was captured in a multilayer polyelectrolyte at the assembly stage. In the absence of a salt, stable BTA nanocontainers were preliminarily prepared at pH 8 and 5 for adsorption of the (PDADMAC) and (PAA) layers, respectively. In the presence of 0.01 M NaCl, stable suspensions of nanocontainers could not be prepared at these pH. However, at pH 8 of both polyelectrolyte solutions, a stabilized suspension of nanocontainers is obtained, which was explained by stronger electrostatic interactions between PDADMAC and higher-charged PAA chains. A greater amount of BTA can be introduced into nanocontainers prepared in the presence of a salt. The loading of BTA into nanocontainers prepared in the presence of 10⁻² M NaCl was high enough for their use in protective coatings operating under neutral pH conditions.

The corrosion protection of Q235 carbon steel with an epoxy coating containing polyaniline nanofibers (PANI-PA-NFs) loaded with BTA (PANI-PA-NFs/TA) doped with phytic acid was recently studied [60]. An epoxy coating containing 2.0 wt. % PANI-PA-

NFs/BTA showed better corrosion protection and self-healing, which was explained by the synergistic action of PANI–PA and BTA.

Unfortunately, despite the above examples, the number of which can be expanded, of the positive effect of nanocontainers with BTA on the efficiency of protective coatings containing them, we were not able to find similar studies with its more effective substituted derivatives, for example, 5-chloro-BTA, in the scientific literature.

Weakly alkaline media deserve attention mainly because of the long-known problem of steel corrosion in reinforced concrete structures and attempts to solve it using inhibitors [61]. Although aqueous extracts from cement have an alkaline pH of 11.6–12.4, at which the steel reinforcement would be in a passive state, it can be violated by chlorides. This hazardous phenomenon can be hindered rather efficiently with inorganic nitrite-based corrosion inhibitors [62–64], but even they often cannot satisfy all the process requirements.

In addition, the results of electrochemical methods for assessing the protective ability of inhibitors have shown that sometimes the amount of the inhibitor required to ensure a high inhibitor efficiency, even of nitrite itself, is larger than the amount of chloride [62]. Attempts to use organic corrosion inhibitors in environments simulating concrete pore fluid throughout the half-century history of such attempts cannot be called successful to date. However, successful use of *migrating* inhibitors was predominantly expected from organic compounds or mixtures thereof with inorganic inhibitors [65–69].

In view of regard, the search for effective corrosion inhibitors for reinforced concrete certainly could not bypass such a well-known and affordable inhibitor as BTA, as well as its substituted derivatives. The effect of BTA and its four derivatives on the corrosion resistance of steel in solutions simulating the pore fluid of concrete was studied [70]. To simulate the solution in the concrete pores, a saturated solution of $\text{Ca}(\text{OH})_2$ with pH 12.5 with addition of corrosive NaCl was used. In this case, the Cl^-/OH^- concentration ratio was constant (close to 5), *i.e.*, it exceeded the threshold value of the chloride concentration that should cause pitting corrosion of steel. The studies were carried out by the EIS and potentiodynamic polarization methods, as well as by Fourier transform infrared spectroscopy (FTIR).

It was found that addition of all triazoles to the solution increased the local steel depassivation potential determined by potentiodynamic polarization of the electrode, E_{pt} . 5,6-Dimethyl-1H-BTA was the most effective. The EIS method was used to determine the film resistance R_f and charge transfer resistance R_{ct} , from which the efficiency of the protective action (Z , %) of the inhibitors was calculated by the formula: $Z(\%) = \left[(R_{\text{bg}}^{-1} - R_{\text{in}}^{-1}) / R_{\text{bg}}^{-1} \right] \cdot 100$, where the R values are the sum of the resistances R_f and R_{ct} in the background solution and in the presence of an inhibitor. In this case, the differences in the efficiency of the inhibitors were less noticeable: only BTA, providing 74% protection, was noticeably inferior in efficiency to its derivatives with $Z = 89\text{--}90\%$.

To perform FTIR analysis of surface layers, steel samples were immersed for 3 days in saturated $\text{Ca}(\text{OH})_2$ solutions containing 5 mmol/L BTA or its derivatives. After that, the samples were thoroughly washed with distilled water, dried and rubbed with KBr powder.

The FTIR analysis of BTA derivatives and their iron complexes was performed in the range from 500 to 4000 cm^{-1} . Its results confirmed that complexes of BTA and its derivatives with mono- and bidentate bonds between the nitrogen of the triazole ring and iron cations are formed on the steel surface.

The authors believe that triazoles provide good steel protection in the investigated solutions and can be used to protect steel from corrosion in reinforced concrete structures. However, it is necessary to find out if there is an interaction between such inhibitors and concrete components such as sand, gravel, cement and various chemical additives.

More optimistic are the results obtained in another solution, also simulating pore fluid, but of aged concrete, which is probably why it had a relatively low pH of 9.0 and did not contain calcium [71]. Its composition included (mass %): 2.8 KOH; 0.4 NaOH; 3.5 NaCl and 1.5 BTA or 1.5 nitrite. The high chloride content simulated seawater in contact with a reinforced concrete structure. The studies were performed on reinforcing steel CA-50 containing 98.77% Fe; 0.26% C; 0.91% Mn; 0.03% P and 0.026% S. The effect of BTA on the corrosion resistance of CA-50 steel was studied by the EIS method and potentiodynamic polarization of steel. The authors concluded that the increase in corrosion resistance of steel by this inhibitor is higher than that of nitrites at the same concentration. This is due to the formation of a protective layer with a complex composition $[\text{Fe}_n(\text{Cl})_p(\text{BTA})_m]$ on steel, which acts as a barrier to the access of corrosive environmental particles to the steel substrate. This allowed the authors to suggest that BTA is an “attractive alternative to nitrites” for inhibiting the corrosion of reinforcing steel in concrete.

Later [72], Chinese researchers compared the protective effect of NaNO_2 , $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and BTA toward mild steel in a saturated $\text{Ca}(\text{OH})_2$ solution containing 0.25 M NaCl. Nitrites were chosen due to their widespread popularity as inhibitors of steel corrosion, and $\text{Ca}(\text{NO}_2)_2$ has been used in reinforced concrete for several decades, although the authors note the possibility of loss in concrete strength upon compression if this inhibitor is added to fresh concrete. Moreover, there are limitations to the use of nitrite-based inhibitors due to their toxicity. The ability of sodium phosphate to prevent pitting corrosion of steel in the pore fluid of concrete at its equal concentration with chlorides was noted as far back as [62]. Comparing these two inorganic inhibitors with BTA, the authors used not only electrochemical methods (measuring the corrosion potential of steel over time, its polarization curves and EIS), but also field emission scanning electron microscopy (FESEM) with an energy dispersive X-ray analyzer (EDXA). This allowed them to observe a change in the microstructure and morphology of the steel surface and its corrosion products. It turned out that, compared with nitrites, trisodium phosphate is a weak corrosion inhibitor in a model pore fluid, but BTA is a more effective inhibitor than nitrites under the conditions studied.

Although, according to BTA itself, there is no consensus among researchers regarding the prospects of its use for corrosion protection of steel in reinforced concrete structures, it can be assumed that there is more chance of finding an effective inhibitor among its substituted derivatives. In view of this, 5-chloro-BTA deserves attention, which, as shown above, better protects steel from corrosion in aqueous solutions than BTA, not only as an

individual compound, but also in binary mixtures with carboxylate inhibitors. In [73], the effect of BTA, 5-nitro-BTA, and 5-chloro-BTA on the corrosion and electrochemical behavior of reinforcing steel containing (in wt. %): 98.50 Fe; 0.32 C; 0.24 Si; 0.89 Mn; 0.024 P 0.019 S in naturally aerated saturated solutions of $\text{Ca}(\text{OH})_2$ with a pH of 12.9 contaminated with chlorides $C_{\text{NaCl}} = 0.1$; 10 and 50 mmol/L was studied. It was found that the efficiency of these inhibitors depends both on their chemical structure, C_{in} and C_{NaCl} , but under all conditions studied it is enhanced in the series 5-nitro-BTA < BTA < 5-chloro-BTA. The efficiency of these inhibitors in terms of the increase in the E_{pt} of steel in a solution containing 10 mmol/L NaCl changes in the same sequence. Later, the initiation and inhibition of pitting corrosion of the same reinforcing steel was studied in more detail and the same order of efficiency of BTA and its substituted derivatives was confirmed in [74]. It can be noted that their protection efficiency increases with the hydrophobicity of inhibitors, which is usually characterized by the logarithm of the distribution coefficient of a compound in the system of two immiscible liquids octanol–water, $\log P$ (Hansch hydrophobicity parameter) [75]. Compounds with $\log P > 0$ are hydrophobic, and those with P less than zero are hydrophilic. In the above series, $\log P$ is 0.87, 1.29, and 1.92, respectively [76]. Of course, the considered sample is statistically insufficient, but it suggests that the surface activity of inhibitors of such a group can positively affect their protective properties. According to [73], they are due to the formation of iron complexes with an inhibitor and/or adsorption of BTA anions on steel surface in accordance with the Langmuir isotherm. Despite the fact that 5-chloro-BTA is noticeably more effective than the unsubstituted compound, it is difficult to say whether this is sufficient to use it as an additive in reinforced concrete. We have to take into consideration its higher cost and lack of information about the effect of such an additive on the technological properties of concrete. It seems more promising to study BTA and its substituted derivatives as a component with the hope of finding a synergy of their protective effect and thereby significantly reduce C_{in} , which will also reduce the risk of deterioration of the physicochemical properties of reinforced concrete.

Acid media, as noted above, significantly more often attracted the attention of researchers studying the protective effect of triazoles and its derivatives in relation to various steels. This topic was covered in several reviews [2–4, 77]. The last one was published relatively recently in 2017, but its authors consider derivatives of 1,2,4-triazole rather than BTA. In another earlier review [3], literature is analyzed up to 2013, and therefore this part of our article will be limited to consideration mainly of articles from 2014 through 2019.

Important features of the inhibition of acid corrosion of steels are the dependences of its efficiency on the composition of the steel itself, the chemical nature of the acid, the concentration and temperature of the solution, as well as C_{in} . Of course, other factors can also influence the efficiency of steel protection, for example, the presence of accumulated Fe(III) cations, corrosive impurities, or products of decomposition or chemical reactions involving an inhibitor in a solution.

It follows from earlier works analyzed in the above reviews that BTA and its substituted derivatives are more effective in protecting steels in hydrochloric acid solutions. It is

reasonable that the largest number of studies of these inhibitors were performed in these solutions. Here, we only mention the work [78], which is important for our review, in which the author compared the efficiency of corrosion protection of steel in 1 M HCl with three triazoles using direct corrosion tests, polarization curves and EIS measurements. It turned out that assessment by these methods in all cases indicates an increase in the degree of protection (with identical C_{in}) in the series BTA < 1,2,4-triazole (TA) < 3-amino-TA (3-ATA).

In addition, studies on the behavior of these molecules on the surface of iron were carried out by molecular dynamics simulation and quantum chemical calculations. This made it possible to evaluate the role of the triazole chemical structure in the inhibition of the acid corrosion of iron. The author simulated the iron/inhibitor/solvent interface, calculated the charges on the inhibitor molecules and their structural parameters taking into account the solvent effect.

Theoretical calculations by quantum chemistry methods allowed the structure and electronic parameters of inhibitors to be obtained. The geometry of inhibitors in the ground state and the energy of their molecular orbitals were estimated. Here, the activity of the inhibitor was judged by the energy values of the highest occupied (E_{HOMO}) and the lowest unoccupied molecular orbitals (E_{LUMO}).

In fact, the adsorption capability (inhibitor efficiency) increases with a decrease in dipole moments, a decrease in molecular size, and an increase in nitrogen charge. E_{HOMO} is often associated with the electron-donating ability of a molecule, and E_{LUMO} with its electron-withdrawing ability. High values of E_{HOMO} suggest that such molecules donate electrons to acceptor molecules with low energy and an empty molecular orbital. E_{HOMO} calculations showed that it is higher for aminotriazole than for triazole and BTA, *i.e.* confirm the assumption of better adsorption of 3-ATA on iron than TA, while BTA is weaker. In this regard, derivatives of 3-ATA and TA in acid media attract much more attention of researchers than substituted BTAs. We note one more advantage of ATA and TA over BTA, which is useful for the use of these inhibitors in neutral media: they have better solubility in aqueous solutions, which is reflected by the hydrophilicity of their molecules: $\log P = -0.87$ and -0.58 , respectively [79].

Substituted BTAs, for example 5-alkyl-BTA, enhance the protective properties of the inhibitor with respect not only to Cu, but also to Fe or steels [80]. The maximum effects are observed at a chain length of six carbon atoms, since with longer chains, limitations on the solubility of the inhibitors begin to appear. In the case of iron, these inhibitors are more effective in HCl solutions where they slow down both electrode reactions, while in sulfate solutions they inhibit only the cathodic reaction, and only in the case of 5-heptyl-BTA. The authors explain the differences in the interaction of cations of organic inhibitors with the metal surface by the fact that the iron surface is negatively charged in HCl solutions where preliminary adsorption of chloride ions occurs. The resulting adsorbed layer enhances the physical adsorption of inhibitor cations. However, upon prolonged contact of the most effective 5-alkyl-BTA with iron in an acid solution, chemisorption may also occur.

However, one should not think that attempts to find effective corrosion inhibitors for carbon steel were limited to this. For example, the effect of 5-chloro-BTA, 1-hydroxy-BTA, and 3-amino-5-mercato-BTA at $C_{in}=0.05\text{--}1.00\text{ g/L}$ on the corrosion behavior of low-carbon steel (composition in wt. %: 99.29 Fe; 0.15 C; 0.09 Si; 0.4 Mn) in 0.5 M H_2SO_4 at $t=25^\circ\text{C}$ was studied [81]. The authors used electrochemical research methods (potentiodynamic polarization and EIS), FTIR, and microscopy. 5-Hydroxy-BTA was the weakest of the inhibitors studied, and 5-chloro-BTA was the most effective: it provided the highest degree of steel protection $Z=98.55\%$ at $C_{in}=0.5\text{ g/L}$. The EIS results confirmed a high Z value in the presence of 5-chloro-BTA in the solution. The authors associated the efficiency of corrosion inhibition by these inhibitors with their adsorption or formation of an insoluble iron complex by the inhibitor.

In yet another study [82], the protective effect of BTA was compared with that of 1-benzyl-1H-BTA in relation to low-carbon steel (99.746% Fe; 0.10% Mn, 0.03% C) in solutions of 1.0, 2.0 and 3.0 M HCl, where C_{in} was varied within 5–25 mM and at $t=(40\text{--}60)^\circ\text{C}$. The efficiency of inhibition depends on C_{in} and the chemical structure of triazoles. Polarization measurements always showed somewhat overestimated Z values compared with the values calculated from the mass losses of the samples. At $C_{in}=25\text{ mM}$, the degree of protection is $80\% < Z \leq 98\%$, and at the lowest $C_{in}=5\text{ mM}$, $65\% < Z \leq 85\%$ of the lowest concentration (5 mM) in 1 M HCl. With increasing t or acid concentration at constant C_{in} , the value of Z decreases. Both triazoles are mixed inhibitors with predominant inhibition of the cathodic reaction, and BTA is always more effective than its substituted derivative.

Attempts were also made to use BTA and benzothiazole (BT) to inhibit corrosion of stainless steel containing (wt. %): 0.04 C, 0.08 P, 0.75 Si, 8 Ni, 18 Cr, 2 Mn, 0.1 N, 0.8 S, remainder Fe, in 1 M HCl [83]. For this purpose, we used electrochemical methods and SEM surface analysis. Analysis of the polarization curves of steel showed that BTA, even at small $C_{in}=50$ and 100 mg/L, significantly slows down the corrosion of steel (5.6- and 8.0-fold, respectively). BT, which is apparently inferior in efficiency to BTA at $C_{in} \leq 200\text{ mg/L}$, exceeds it at large $C_{in}=300\text{ mg/L}$ where Z reaches 90% for BTA and 93% for BT. The addition of both inhibitors almost does not affect the rate of the cathodic reaction but significantly slows down the anodic dissolution of steel. The advantage of BT over BTA at $C_{in}=300\text{ mg/L}$ is confirmed by Nyquist diagrams in the analysis of ESI and the results of electrochemical noise studies in the same solution.

Despite the fact that BTA in solutions, at least of hydrochloric acid, is able to protect various steels quite well from corrosion, it should be noted that it was little studied in mixed inhibitors. Meanwhile, over the past decades, many synergistic formulations have been found that not only dramatically increase their protective effect in acidic solutions, but also to significantly reduce the inhibitor cost [84–86].

An example of such rare studies where the mixture contains not only BTA but also another organic compound that has a good protective effect with respect to steel in a hydrochloric acid solution was reported [87]. In that study, a mixed corrosion inhibitor containing combinations of BTA with one of three 2-alkylbenzimidazoles was studied for

protection of carbon steel in 1.0 M HCl. Methyl, ethyl and propyl alkyl substituents were used, *i.e.* the corrosion inhibitors studied were 2-MBI, 2-EBI, and 2-PBI, respectively. The protective effects of the binary inhibitor mixtures at $C_{in}=200$ mg/L, where the ratio of the components was $n=1:3$; $1:1$ and $3:1$, were estimated by electrochemical and gravimetric methods and compared with the effects of BTA and 2-alkyl-BIs at the same C_{in} . The measurements were carried out by immersing the samples in the acid solution for 24, 48, and 72 hours. The corrosion rates were determined by mass loss, potentiodynamic polarization, and EIS methods and by quantum-chemical DFT calculations. The DFT method was used to calculate the electronic properties of molecules and determine the inhibitory effect, molecular structures, and synergistic interaction of inhibitors. The efficiency of corrosion inhibition by organic compounds is associated with the total energy, energy of the E_{HOMO} and E_{LUMO} orbitals, and the difference between them (ΔE). BTA interacts with alkylbenzimidazoles to a bond length of ~ 1.99 Å. This interaction represents the formation of a hydrogen bond between these molecules and provides increased corrosion inhibition efficiency for low carbon steel in hydrochloric acid solution. A higher efficiency of steel corrosion inhibition was observed in the combination of 150 mg/L 2-PBI and 50 mg/L BTA in the longest tests. The protection efficiency of steel increases upon transition to BTA mixtures with 2-alkyl-BIs with longer alkyls, but decreases with an increase in temperature. The studied mixtures are mixed-type inhibitors, *i.e.*, they reduce the rates of both electrode reactions. The authors explained the synergy of the protective effect by inhibition of corrosion by a mixture of inhibitors by the mechanism of joint adsorption. Synergism is more pronounced at elevated temperatures, but as the temperature decreases, competing adsorption between molecules of different inhibitors becomes more noticeable.

References

1. Yu.I. Kuznetsov, Triazoles as a class of multifunctional corrosion inhibitors. A review. Part I. 1,2,3-Benzotriazole and its derivatives. Copper, zinc and their alloys, *Int. J. Corros. Scale Inhib.*, 2018, **7**, no. 3, 271–307. doi: [10.17675/2305-6894-2018-7-3-1](https://doi.org/10.17675/2305-6894-2018-7-3-1)
2. Yu.I. Kuznetsov and L.P. Kazansky, Physicochemical aspects of metal protection by azoles, *Russ. Chem. Rev.*, 2008, **77**, no. 3, 219–232. doi: [10.1070/RC2008v077n03ABEH003753](https://doi.org/10.1070/RC2008v077n03ABEH003753)
3. A.A. Khadom, Protection of steel corrosion reaction by benzotriazoles: a historical background, *J. Fail. Anal. Prev.*, 2015, **15**, no. 6, 794–802. doi: [10.1007/s11668-015-0043-4](https://doi.org/10.1007/s11668-015-0043-4)
4. N. Phadke Swathi, Vijaya D.P. Alva and Seranthimata Samshuddin, A review on 1,2,4-triazole derivatives as corrosion inhibitors, *J. Bio Tribo Corros.*, 2017, **3**, no. 42. doi: [10.1007/s40735-017-0102-3](https://doi.org/10.1007/s40735-017-0102-3)
5. T.G. Neznamova, V.P. Dobrovolskaya and V.P. Barannik, *Ukrainskii khimicheskii zhurnal (Ukrainian chemical journal)*, 1965, no. 12, 1337–1342 (in Russian).

6. S.A. Balezin, E.G. Zak, F.B. Glikina and I.Ya. Simonovskaya, Issledovaniye vzaimnogo vliyaniya benzotriazola i nekotorykh aminov na zashchitu stali ot korrozii v vode (Investigation of the mutual influence of benzotriazole and certain amines on the protection of steel against corrosion in water), *In the book: Ingibitory korrozii metallov (Metal corrosion inhibitors)*, 1969, Moscow: MGPI, no. 3, 202–210 (in Russian).
7. R.J. Chin and K. Nobe, Electrochemical characteristics of iron in H_2SO_4 containing benzotriazole, *J. Electrochem. Soc.*, 1971, **118**, 545–548.
8. R.J. Chin, D. Altura and K. Nobe, Corrosion inhibition of iron and copper in chloride solutions by benzotriazole, *Corrosion*, 1973, **29**, 185–187.
9. D. Altura and K. Nobe, Hydrogen evolution and corrosion behavior of Fe-Ni Alloys in H_2SO_4 – effect of temperature, Cl^- and benzotriazole, *Corrosion*, 1976, **32**, 41–47.
10. N. Eldakar and K. Nobe, Electrochemical and corrosion behavior of iron in presence of substituted benzotriazoles, *Corrosion*, 1977, **33**, 128–130.
11. C. Fiaud, Theory and practice of vapour phase inhibitors, *In the book: Corrosion Inhibitors*, 1994, London: The Institute of Materials, 1–11.
12. A.A. Mikhailov, Yu.M. Panchenko and Yu.I. Kuznetsov, *Atmosfernaya korroziya i zashchita metallov (Atmospheric corrosion and metal protection)*, Tambov: Publishing House R.V. Pershina, 555 (in Russian).
13. A.Yu. Luchkin, O.A. Goncharova, N.N. Andreev, Yu.I. Kuznetsov and N.P. Andreeva, Zashchita medi obrabotkoy parami maloletuchikh ingibitorov korrozii pri povyshennoi temperature (Copper protection by treatment with vapors of low-volatility corrosion inhibitors at elevated temperatures), *Korroz.: Mater., Zashch. (Corrosion: materials, protection)*, 2017, no. 11, 25–31 (in Russian).
14. O.A. Goncharova, A.Yu. Luchkin, Yu.I. Kuznetsov, N.N. Andreev, N.P. Andreeva and S.S. Vesely, Octadecylamine, 1,2,3-benzotriazole and a mixture thereof as chamber inhibitors of steel corrosion, *Int. J. Corros. Scale Inhib.*, 2018, **7**, no. 2, 203–212. doi: [10.17675/2305-6894-2018-7-2-7](https://doi.org/10.17675/2305-6894-2018-7-2-7)
15. J.L. Yao, B. Ren, Z.F. Huang, P.G. Cao, R.A. Gu and Z.Q. Tian, Extending surface Raman spectroscopy to transition metals for practical applications IV. A study on corrosion inhibition of benzotriazole on bare Fe electrodes, *Electrochim. Acta*, 2003, **48**, 1263–1271. doi: [10.1016/S0013-4686\(02\)00834-4](https://doi.org/10.1016/S0013-4686(02)00834-4)
16. P.G. Cao, J.L. Yao, J.W. Zheng, R.A. Gu and Z.Q. Tian, Comparative study of inhibition effects of benzotriazole for metals in neutral solutions as observed with surface-enhanced raman spectroscopy, *Langmuir*, 2002, **18**, 100–104. doi: [10.1021/la010575p](https://doi.org/10.1021/la010575p)
17. Yu.I. Kuznetsov, L.P. Kazanskii and A.A. Solomatin, Passivatsiya zheleza v neytral'nykh vodnykh rastvorakh geterotsiklicheskimi soedineniyami (Passivation of iron in neutral aqueous solutions with heterocyclic compounds), *Korroz.: Mater., Zashch. (Corrosion: materials, protection)*, 2007, no. 10, 20–25 (in Russian).
18. L.P. Kazanskii and I.A. Selyaninov, XPS of 1,2,3-benzotriazole nanolayers formed on iron surface, *Prot. Met. Phys. Chem. Surf.*, 2010, **46**, no. 7, 797–804. doi: [10.1134/S2070205110070117](https://doi.org/10.1134/S2070205110070117)

-
19. Yu.I. Kuznetsov, *Organic inhibitors of corrosion of metals*, 1996, New York: Plenum Press, 283.
 20. Yu.I. Kuznetsov and N.P. Andreeva, Joint adsorption of organic anions on passive iron, *Russ. J. Electrochem.*, 2001, **37**, no. 5, 462–466. doi: [10.1023/a:1016615802304](https://doi.org/10.1023/a:1016615802304)
 21. Yu.I. Kuznetsov, N.P. Andreeva, N.P. Sokolova and R.A. Bulgakova, Joint adsorption of oleic and phenylantranilic acids at passive iron, *Prot. Met.*, 2003, **39**, no. 3, 462–466.
 22. Ya.G. Bober, Yu.I. Kuznetsov and N.P. Andreeva, Adsorption at iron and passivation effect of anions of substituted phenylantranilic acids, *Prot. Met.*, 2008, **44**, no. 1, 84–90. doi: [10.1134/S0033173208010116](https://doi.org/10.1134/S0033173208010116)
 23. Yu.I. Kuznetsov, L.B. Maksaeva, M.A. Petrunin, and N.P. Andreeva, Adsorption of sodium phenylantranilate on gold electrode from aqueous solution, *Russ. J. Electrochem.*, 2009, **45**, no. 11, 1240–1244. doi: [10.1134/S1023193509110044](https://doi.org/10.1134/S1023193509110044)
 24. Yu.I. Kuznetsov and N.P. Andreeva, The designing of nanometer sized passive films at metal surfaces using organic inhibitors, *Russ. J. Electrochem.*, 2012, **48**, no. 4, 438–445. doi: [10.1134/S102319351204009X](https://doi.org/10.1134/S102319351204009X)
 25. N.P. Andreeva, Yu.V. Ushakova, Yu.I. Kuznetsov, M.O. Agafonkina, L.P. Kazanskii and Yu.Ya. Andreev, Adsorption of sodium flufenamate on zinc from aqueous solutions, *Prot. Met. Phys. Chem. Surf.*, 2014, **50**, no. 7, 860–865. doi: [10.1134/S2070205114070041](https://doi.org/10.1134/S2070205114070041)
 26. Yu.I. Kuznetsov, I.A. Kuznetsov and N.P. Andreeva, Adsorption of sodium tridecanoate on copper from aqueous solutions and copper protection from atmospheric corrosion, *Int. J. Corros. Scale Inhib.*, 2018, **7**, no. 4, 648–656. doi: [10.17675/2305-6894-2018-7-4-11](https://doi.org/10.17675/2305-6894-2018-7-4-11)
 27. V.A. Ogorodnikova, Yu.I. Kuznetsov, N.P. Andreeva and A.A. Chirkunov, Adsorbtsiya oleata natriya iz shchelochnykh rastvorov na okislennom magnii (Adsorption of sodium oleate from alkaline solutions on oxidized magnesium) *Korrozi.: Mater., Zashch. (Corrosion: materials, protection)*, 2018, no. 5, 27–31 (in Russian).
 28. N.P. Andreeva, Yu.I. Kuznetsov and M.O. Diyanova, Adsorbziya 1,2,3-benzotriazola na zheleze iz vodnogo rastvora (adsorption 1,2,3-benzotriazole on iron from an aqueous solution), *Korrozi.: Mater., Zashch. (Corrosion: materials, protection)*, 2008, no. 3, 21–25 (in Russian).
 29. M.O. Agafonkina, Yu.I. Kuznetsov and N.P. Andreeva, Novyy effektivnyy ingibitor korrozii metallov v neytral'nykh sredakh (New effective metal corrosion inhibitor in neutral environments) *Korrozi.: Mater., Zashch. (Corrosion: materials, protection)*, 2009, no. 9, 17–22 (in Russian).
 30. Yu.I. Kuznetsov, N.P. Andreeva and M.O. Agafonkina, On co-adsorption on passive iron from aqueous 1,2,3-benzotriazole and sodium phenylundecanoate, *Russ. J. Electrochem.*, 2010, **46**, no. 5, 560–564. doi: [10.1134/S1023193510050101](https://doi.org/10.1134/S1023193510050101)
 31. U. Rammelt, S. Koehler and G. Reinhard, Synergistic effect of benzoate and benzotriazole on passivation of mild steel, *Corros. Sci.*, 2008, **50**, 1659–1663. doi: [10.1016/j.corsci.2008.02.016](https://doi.org/10.1016/j.corsci.2008.02.016)

-
32. B.B. Damaskin, A.N. Frumkin and N.A. Borovaya, Effect of a constant concentration of a surfactant on the form of the adsorption isotherm of another substance, *Russ. J. Electrochem.*, 1972, **8**, no. 6, 807.
33. Yu.I. Kuznetsov, M.O. Agafonkina, N.P. Andreeva and A.B. Solov'eva, Modification of iron surface by dimegin and adsorption of 1,2,3-Benzotriazole, *Prot. Met. Phys. Chem. Surf.*, 2010, **46**, no. 7, 743–747. doi: [10.1134/S2070205110070014](https://doi.org/10.1134/S2070205110070014)
34. T.M. Zhientaev, N.S. Melik-Nubarov, E.A. Litmanovich, N.A. Aksenova, N.N. Glagolev and A.B. Solov'eva, The effect of pluronics on the photocatalytic activity of water-soluble porphyrins, *Polym. Sci.: Ser. A*, 2009, **51**, no. 5, 502–511. doi: [10.1134/S0965545X09050034](https://doi.org/10.1134/S0965545X09050034)
35. Yu.I. Kuznetsov, Progress in inhibition of metal corrosion and modification of safety nanolayers on metals, *Prot. Met. Phys. Chem. Surf.*, 2011, **47**, no. 7, 821–829. doi: [10.1134/S2070205110070014](https://doi.org/10.1134/S2070205110070014)
36. Yu.I. Kuznetsov, M.O. Agafonkina and N.P. Andreeva, Ingibirovaniye korrozii nizkouglerodistoy stali sovmestnoy adsorbtsiyey flyufenaminata natriya i 1,2,3-benzotriazola (Corrosion inhibition of mild steel by the joint adsorption of sodium flufenamate and 1,2,3-benzotriazole), *Korrozi.: Mater., Zashch. (Corrosion: materials, protection)*, 2013, no. 2, 25–30 (in Russian).
37. R.C. Pemberton, A.D. Mercer, E.J. Wright and J.G.N Thomas, Sodium sebacate-benzotriazole mixtures as inhibitors in neutral solutions, *In Proceedings of the 6th European Symposium on "Corrosion inhibitors"*, Ferrara, Italy, 1985, **2**, 1241–1247.
38. D. Lahem, M. Poelman, F. Atmani, and M.-G. Olivier, Synergistic improvement of inhibitive activity of dicarboxylates in preventing mild steel corrosion in neutral aqueous solution, *Corros. Eng., Sci. Technol.*, 2012, **47**, no. 6, 463–471. doi: [10.1179/1743278212Y.0000000030](https://doi.org/10.1179/1743278212Y.0000000030)
39. Yu.I. Kuznetsov, I.A. Filippov and A.A. Chirkunov, Vliyaniye sul'fata medi na passivatsiyu nizkouglerodistoy stali organicheskimi ingibitorami (The effect of copper sulfate on the passivation of low-carbon steel by organic inhibitors), *Korrozi.: Mater., Zashch. (Corrosion: materials, protection)*, 2012, no. 12, 23–27 (in Russian).
40. A.A. Chirkunov, I.A. Filippov and Yu.I. Kuznetsov, Vliyaniye oksietilidendifosfonata medi na passivatsiyu nizkouglerodistoy stali organicheskimi ingibitoramiyu (The effect of copper oxyethylidenediphosphonate on the passivation of low carbon steel by organic inhibitors), *Korrozi.: Mater., Zashch. (Corrosion: materials, protection)*, 2013, no. 7, 29–34 (in Russian).
41. D.O. Chugunov, A.A. Chirkunov and Yu.I. Kuznetsov, Zashchita nizkouglerodistoy stali ot atmosfery korrozii dvukhstadiynoy passivatsiyey rastvorami ingibitorov (Protection of mild steel from atmospheric corrosion by two-stage passivation with inhibitor solutions), *Korrozi.: Mater., Zashch. (Corrosion: materials, protection)*, 2018, no. 9, 17–21 (in Russian).

-
42. A.A. Chirkunov, D.O. Chugunov, G.V. Red'rina and Yu.I. Kuznetsov, The influence of steel surface modifying with zinc complexes of phosphonic acids on the efficiency of its passivation by organic inhibitors, *Russ. J. Electrochem.*, 2019, **55**, no. 2, 115–121. doi: [10.1134/S1023193519010026](https://doi.org/10.1134/S1023193519010026)
43. A.A. Chirkunov, D.O. Chugunov and Yu.I. Kuznetsov, Vliyaniye viniltrimetoksisilana na effektivnost' passiviruyushchikh plenok na modifitsirovannoy fosfonatami poverkhnosti stali (The effect of vinyltrimethoxysilane on the efficiency of passivating films on a phosphonate-modified steel surface), *Korroziy.: Mater., Zashch. (Corrosion: materials, protection)*, 2019, no. 9, 14–18 (in Russian). doi: [10.31044/1813-7016-2019-0-9-14-18](https://doi.org/10.31044/1813-7016-2019-0-9-14-18)
44. E.R. Pohl, A. Chaves, C.T. Danehey *et al.*, *Silanes and Other Coupling Agents*, **2**, Ed. K.L. Mittal, 2000, VSP 15
45. M. Stratmann, W. Furberh, G. Grundmeier, R. Losch and C.R. Reinartz, *Corrosion Mechanisms in Theory and Practice*, Ed. By P. Marcus, J. Oudar, New York, Marcel Dekker, Inc. 1995, 373–420.
46. A.A. Chirkunov, A.M. Semiletov, Yu.I. Kuznetsov and N.P. Andreeva, Passivation of steel by aqueous solutions of trialkoxysilanes, *Prot. Met. Phys. Chem. Surf.*, 2013, no. 11, 27–34. doi: [10.1134/S2070205115070059](https://doi.org/10.1134/S2070205115070059)
47. S. Liu, N. Xu, J. Duan, Z. Zeng, Z. Feng and R. Xiao, Corrosion inhibition of carbon steel in tetra-N-butylammonium bromide aqueous solution by benzotriazole and Na₃PO₄, *Corros. Sci.*, 2009, **51**, 6, 1356–1363. doi: [10.1016/j.corsci.2009.03.021](https://doi.org/10.1016/j.corsci.2009.03.021)
48. I. Masahiko, A. Michihiko and T. Kazuo, *Boshoku Gijutsu*, 1987, 36, 142, (*Chemical Abstract*, 1987, 107, 11194)
49. N.-B. Huang and C.-H. Liang, Corrosion behavior of carbon steel in lithium bromide solution, *J. Chin. Chem. Soc.*, 2003, **50**, 5, 979–984. doi: [10.1002/jccs.200300138](https://doi.org/10.1002/jccs.200300138)
50. H. Akhavan, M. Izadi, I. Mohammadi, T. Shahrabi and B. Ramezanzadeh, The synergistic effect of BTA-Co system on the corrosion inhibition of mild steel in 3.5 wt. % NaCl solution, *J. Electrochem. Soc.*, 2018, **165**, no. 10, 670–680. doi: [10.1149/2.1111810jes](https://doi.org/10.1149/2.1111810jes)
51. X. Liu, F. Zhou, Y. Liang and W. Liu, Benzotriazole as the additive for ionic liquid lubricant: one pathway towards actual application of ionic liquids, *Tribol. Lett.*, 2006, **23**, 191–196. doi: [10.1007/s11249-006-9050-7](https://doi.org/10.1007/s11249-006-9050-7)
52. M. Finšgar, B. Petovar, K. Khanari and U. Maver, The corrosion inhibition of certain azoles on steel in chloride media: Electrochemistry and surface analysis, *Corros. Sci.*, 2016, **111**, 370–381. doi: [10.1016/j.corsci.2016.05.028](https://doi.org/10.1016/j.corsci.2016.05.028)
53. M.O. Agafonkina, Y.I. Kuznetsov, N.P. Andreeva, Yu.E. Pronin and L.P. Kazanskii, Formation of protective layers by 5-chlorobenzotriazole and its mixture with sodium fluphenamate on low-carbon steel from aqueous solutions, *Prot. Met. Phys. Chem. Surf.*, 2012, **48**, no. 7, 773–779. doi: [10.1134/S2070205112070027](https://doi.org/10.1134/S2070205112070027)

-
54. L.P. Kazansky, I.A. Selyanov and Yu.I. Kuznetsov, Angle resolved XPS of monomolecular layer of 5-chlorobenzotriazole on oxidized metallic surface, *Appl. Surf. Sci.*, 2012, **259**, 385–392. doi: [10.1016/j.apsusc.2012.07.056](https://doi.org/10.1016/j.apsusc.2012.07.056)
55. E. Abdullayev, R. Price, D. Shchukin and Yu. Lvov, Halloysite tubes as nanocontainers for anticorrosion coating with benzotriazole, *ACS Appl. Mater. Interfaces*, 2009, 1437–1445. doi: [10.1021/am9002028](https://doi.org/10.1021/am9002028)
56. Y. Feng, S. Chen and Y. Frank Cheng, Fabrication of SiO₂ nanoparticle-polyelectrolyte nanocontainers with preloaded benzotriazole inhibitors and their self-releasing mechanism and kinetics, *J. Mater. Sci.*, 2017, **52**, 8576–8590. doi: [10.1007/s10853-017-1074-x](https://doi.org/10.1007/s10853-017-1074-x)
57. M. Yeganeh, M. Omid, A. Etemed, M. Reza Rostami and M. Esmaeil Shafiei, Application of mesoporous silica containing benzotriazole in epoxy coating applied to plain carbon steel and study of its corrosion behavior, *Adv. Mater. Process.*, 2018, **6**, no. 3, 89–97.
58. D.G. Shchukin, M.L. Zheludkevich, K.A. Yasakau, S.V. Lamaka and M.G.S. Ferreira, Layer-by-layer assembled nanocontainers for self-healing corrosion protection, *Adv. Mater.*, 2006, **18**, 1672–1678. doi: [10.1002/adma.200502053](https://doi.org/10.1002/adma.200502053)
59. K. Kamburova and Ts. Radeva, Polyelectrolyte-modified kaolinite nanocontainers for entrapment of corrosion inhibitor benzotriazole, *Colloid Polym. Sci.*, 2018, **296**, 1157–1164. doi: [10.1007/s00396-018-4336-5](https://doi.org/10.1007/s00396-018-4336-5)
60. Y. Hao, Y. Zhao, X. Yang, B. Hu, S. Ye, L. Song and R. Li, Self-healing epoxy coating loaded with phytic acid doped polyaniline nanofibers impregnated with benzotriazole for Q235 carbon steel, *Corros. Sci.*, 2019, **151**, 175–189. doi: [10.1016/j.corsci.2019.02.023](https://doi.org/10.1016/j.corsci.2019.02.023)
61. S.N. Alekseev, V.B. Ratinov, N.K. Rosenthal and N.M. Kashurnikov, *Ingibitory korrozii stali v zhelezobetonnykh konstruktsiyakh (Steel corrosion inhibitors in reinforced concrete structures)*, 1985, M.: Stroyizdat, 272.
62. L. Dhouibi, E. Triki, A. Raharinaivo, G. Trabanelli and F. Zucchi, Electrochemical methods for evaluating inhibitors of steel corrosion in concrete, *Br. Corros. J.*, 2000, **35**, no. 2, 145–149. doi: [10.1179/000705900101501182C](https://doi.org/10.1179/000705900101501182C)
63. L. Page, V.T. Ngala and M.M. Page, Corrosion inhibitors in concrete repair system, *Mag. Concr. Res.*, 2000, **52**, 25–37.
64. E.V. Starovoitova, I.A. Gedvillo, A.S. Zhmakina and N.N. Andreev, Nitrite-benzoate inhibitors for protection against corrosion of steel reinforcement in concrete, *Prot. Met. Phys. Chem. Surf.*, 2010, **46**, no. 7, 793–796. doi: [10.1134/S2070205110070105](https://doi.org/10.1134/S2070205110070105)
65. B. Miksic, L. Gelner, B. Bjegovic and L. Sipos, Migrating corrosion inhibitor for reinforced concrete, *In Proceedings of 8th Europ. Symp. on Corros. and Scale Inhib.*, University of Ferrara, Italy; 18–22 September 1995, 569–588.
66. B. Elsener, M. Büchler, F. Stalder and H. Böhni, A migrating corrosion inhibitor blend for reinforced concrete – Part 2: inhibitor as repair strategy, *Corrosion*, 2000, **56**, no. 7, 727–732. doi: [10.5006/1.3280576](https://doi.org/10.5006/1.3280576)

-
67. M. Forsyth, A. Phanasgaonkar and B.W. Cherry, Migratory corrosion inhibitor for corrosion control in reinforced concrete, *In Proceedings of 9th European Symp. on Corros. and Scale Inhib.*, University of Ferrara, Italy; 2000, **1**, 335–346.
68. F. Bolzoni, S. Goidanich, M. Ormellese, E.A. Perez and C. Pistolesi, Effect of organic substances on critical chloride threshold for chlorides induced corrosion in reinforced concrete, *In Proceedings of 10th European Symp. on Corros. and Scale Inhib.*, University of Ferrara, Italy; 2005, **2**, 683–698.
69. N.N. Andreev, E.V. Starovoitova, I.A. Gedvillo and A.S. Zhmakina, Physicochemical principles for the creation of migrating corrosion inhibitors, In” *Book of Abstracts, EUROCORR 2010*, Moscow, September 13–17, 2010, 303.
70. M. Sheban, M. Abu-Dalo, A. Ababneh and S. Andreescu, Effect of benzotriazole derivatives on the corrosion of steel in simulated concrete pore solutions, *Anti-Corros. Methods Mater.*, 2007, **54**, no. 3, 135–147. doi: [10.1108/00035590710748605](https://doi.org/10.1108/00035590710748605)
71. M.M. Mennucci, E.P. Banczek, P.R.P. Rodrigues and I. Costa, Evaluation of benzotriazole as corrosion inhibitor for carbon steel in simulated pore solution, *Cem. Concr. Compos.*, 2009, **31**, 418–424. doi: [10.1016/j.cemconcomp.2009.04.005](https://doi.org/10.1016/j.cemconcomp.2009.04.005)
72. J.-J. Shi and W. Sun, Electrochemical and analytical characterization of three corrosion inhibitors of steel in simulated concrete pore solutions, *Int. J. Miner., Metall. Mater.*, 2012, **19**, 38–47. doi: [10.1007/s12613-012-0512-7](https://doi.org/10.1007/s12613-012-0512-7)
73. S.M. Abd El Haleem, S. Abd El Wanees and A. Bahgat, Environmental factors affecting the corrosion behaviour of reinforcing steel VI. Benzotriazole and its derivatives as corrosion inhibitors of steel, *Corros. Sci.*, 2014, **87**, 321–333. doi: [10.1016/j.corsci.2014.06.043](https://doi.org/10.1016/j.corsci.2014.06.043)
74. S. Abd El Wanees, A. Bahgat Radwan, M.A. Alsharif and S.M. Abd El Haleem, Initiation and inhibition of pitting corrosion on reinforcing steel under natural corrosion conditions, *Mater. Chem. Phys.*, 2017, **190**, 79–95. [10.1016/j.matchemphys.2016.12.048](https://doi.org/10.1016/j.matchemphys.2016.12.048)
75. C. Hanch and A. Leo, *Substituent constants for correlation analysis in chemistry and biology*, Wiley-Interscience, New York, 1979, p. 339.
76. M.O. Agafonkina, N.P. Andreeva, Y.I. Kuznetsov and S.F. Timashev, Substituted benzotriazoles as inhibitors of copper corrosion in borate buffer solutions, *Russ. J. Phys. Chem. A*, 2015, **89**, no. 6, 1414–1421. doi: [10.1134/S0036024417080027](https://doi.org/10.1134/S0036024417080027)
77. M.R. Vinutha and T.V. Venkatesha, Review on mechanistic action of inhibitors on steel corrosion in acidic media, *Port. Electrochim. Acta*, 2016, **34**, no. 3, 157–184. doi: [10.4152/pea.201603157](https://doi.org/10.4152/pea.201603157)
78. K.F. Khaled, Molecular simulation, quantum chemical calculations and electrochemical studies for inhibition of mild steel by triazoles, *Electrochim. Acta*, 2008, **53**, 3484–3492. doi: [10.1016/j.electacta.2007.12.030](https://doi.org/10.1016/j.electacta.2007.12.030)

-
79. Yu.I. Kuznetsov, M.O. Agafonkina, Kh.S. Shikhaliev, N.P. Andreeva, A.Yu. Potapov, Kh.S. Shikhaliev and A.Yu. Potapov, Adsorbtsiya i passivatsiya medi triazolami v neitral'nom vodnom rastvore (Adsorption and passivation of copper by triazoles in neutral aqueous solution), *Korroziya: Mater., Zashch. (Corrosion: materials, protection)*, 2014, no. 7, 33–39 (in Russian).
80. G. TrabANELLI, A. Frignani, C. Monticelli and F. Zucchi, Alkylbenzotriazole derivatives as inhibitors of iron and copper corrosion, *Int. J. Corros. Scale Inhib.*, 2015, 4, no. 1, 96–107. doi: [10.17675/2305-6894-2015-4-1-096-107](https://doi.org/10.17675/2305-6894-2015-4-1-096-107)
81. F. Branzoi and V. Branzoi, Corrosion inhibition of carbon steel by using some benzotriazole derivatives in 0.5 M H₂SO₄ medium, *Rev. Roum. Chim.*, 2015, 60, no. 1, 85–96.
82. P.S. Desai and N.S. Indorwala, Triazoles used as a corrosion inhibitor for mild steel in hydrochloric acid, *Int. J. Curr. Microbiol. Appl. Sci.*, 2015, 4, no. 2, 928–938.
83. B.P. Markhali, R. Naderi, M. Mahdavian, M. Sayebani and S.Y. Arman, Electrochemical impedance spectroscopy and electrochemical noise measurements as tools to evaluate corrosion inhibition of azole compounds on stainless steel in acidic media, *Corros. Sci.*, 2013, 75, 321–333. doi: [10.1016/j.corsci.2013.06.010](https://doi.org/10.1016/j.corsci.2013.06.010)
84. Ya.G. Avdeev, P.A. Belinskii, Yu.I. Kuznetsov and O.O. Zel'b, A new inhibitor of steel corrosion in sulfuric acid, *Prot. Met.*, 2007, 43, no. 6, 587–590. doi: [10.1134/S0033173207060112](https://doi.org/10.1134/S0033173207060112)
85. Ya.G. Avdeev, Yu.I. Kuznetsov and A.K. Buryak, Inhibition of steel corrosion by unsaturated aldehydes in solutions of mineral acids, *Corros. Sci.*, 2013, 69, 50–60. doi: [10.1016/j.corsci.2012.11.016](https://doi.org/10.1016/j.corsci.2012.11.016)
86. Ya.G. Avdeev, E.N. Yurasova, K.L. Anfilov and T.A. Vagramyan, Protection of low-carbon steel in solutions of mineral acids by nitrogen-containing pharmaceutical agents of triphenylmethane series, *Int. J. Corros. Scale Inhib.*, 2018, 7, no. 1, 87–101. doi: [10.17675/2305-6894-2018-7-1-8](https://doi.org/10.17675/2305-6894-2018-7-1-8)
87. K. Ramya, R. Mohan, A. Joseph, Interaction of benzimidazoles and benzotriazole: its corrosion protection properties on mild steel in hydrochloric acid, *J. Materio Eng. Perform.*, 2014, 23, no. 11, 4089–4101. doi: [10.1007/s11665-014-1183-5](https://doi.org/10.1007/s11665-014-1183-5)