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# **Triazoles as a class of multifunctional corrosion inhibitors. A review. Part I. 1,2,3-Benzotriazole and its derivatives. Copper, zinc and their alloys**

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## **Abstract**

This article presents an overview of the studies (2003–2018) on the adsorption of 1,2,3-benzotriazole (BTA) and its derivatives on copper, zinc and some of their alloys from aqueous solutions, and their corrosion inhibition capability in neutral and acidic media. It examines the effect of these organic corrosion inhibitors (CIs) on the formation of surface layers, their composition and the effectiveness of their protective action that were investigated by corrosion, electrochemical and other physicochemical methods.

Considerable attention has been given to BTA itself, the wide range of corrosive media in which it can be an effective CI, an analysis of the reasons for its successful application in the practice of anticorrosion protection of copper and its alloys, as well as the new prospects of its usage and increasing its inhibition efficiency. At the same time, the drawbacks of BTA as a CI, including the sharp decrease in protective properties, up to their complete loss, in the presence of even small concentrations of H<sub>2</sub>S and sulfide ions and the relatively low efficiency in acid solutions were noted.

The inhibition of corrosion of zinc and copper–zinc alloys by BTA has been discussed. It has been shown that the protection is based on the formation of sparingly soluble complexes of copper and zinc with BTA. Examples of improving the effectiveness of their protection with mixed CIs are given. The review notes the almost complete absence of studies of BTA derivatives for the protection of Zn, which could also be very useful for improving the corrosion protection not only of zinc but also galvanized steel.

Received: May 28, 2018. Published: July 11, 2018

doi: [10.17675/2305-6894-2018-7-3-1](https://doi.org/10.17675/2305-6894-2018-7-3-1)

**Key words:** *corrosion inhibitors, 1,2,3-benzotriazole, copper, zinc, BTA derivatives, chemisorption, physical adsorption.*

## I. Introduction

The ability of corrosion inhibitors (CIs) to protect a wide range of metals and alloys, and even more so in various corrosive media and under diverse conditions, would certainly be a very valuable property. However, it is hardly easier to imagine such CIs than to believe in the existence of a cure for all diseases and for different people. In other words, their search can be very useful, but the attainment of the goal, at least in a foreseeable future, is apparently impossible. Hence the inaccuracy of the term “universal inhibitor of metal corrosion”, which was more of an advertising nature than reflected the true possibilities of using such an anti-corrosion protection.

The name “multifunctional CIs”, implying that they are able to protect various metals and alloys and to effectively operate under various conditions and in various media, seems more correct. Of course, it is better to refer this term not to individual compounds but to a class of chemical compounds. In it one can find CIs that protect metals in aqueous solutions with various compositions, corrosive atmospheres and natural gas, acid and alkaline media, or hydrocarbons. They can be volatile (VCI) or non-volatile, *i.e.*, of contact type, and slow down not only corrosion but also hydrogenation, as well as stress corrosion cracking of metals and alloys.

The continuous improvement of the methods for application of CIs expands the scope of their usage. Thus, direct injection of CIs into paint and polymer coatings is often impossible due to deterioration of such important properties of the coating as adhesion to the surface to be protected, its curing speed, *etc.* Micro- and nanoencapsulation of CIs eliminates these drawbacks, thereby expanding the CI functionalities previously not implemented in practice.

Incorporation of a VCI into the inner layer of a packaging polymer film, whose outer layer acts as a barrier to penetration of VCI vapors into the external environment and reduces unproductive VCI loss, not only increases the economic efficiency of the protection of metal products but also makes it environmentally safer.

One of the most studied compounds of the triazole class is 1,2,3-benzotriazole (BTA or BTAH<sup>1</sup>), C<sub>6</sub>H<sub>5</sub>N<sub>3</sub>. The protective effect of BTA and its derivatives, as well as compositions based on them, on various metals and alloys have been attracting the attention of researchers for more than half a century [3]. Over the past decade, several interesting reviews have been devoted to them [4–10]. Therefore, the purpose of this article is to consider the new results obtained in recent years and to pay attention to some works that for some reason were not covered by the mentioned reviews.

Probably, BTA and its derivatives are best known as CIs for widely used structural materials. The adsorption behavior of BTA is non-trivial because it can be adsorbed in a

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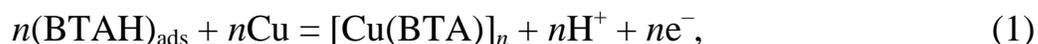
<sup>1</sup> The designation of BTAH, which is very common in the English literature, is convenient to emphasize the presence of acidic properties of this compound ( $pK_a$  8.1–8.2) or hydrogen substitution at the >NH group of the triazole ring with a complexing metal.

variety of forms, depending on the nature of the metal being protected and the corrosive media, in particular on its pH. In acidic media at  $\text{pH} > 1$ , the weak acid BTAH is the predominant adsorbate, replaced by the  $\text{BTAH}_2^+$  cation at  $\text{pH} 0$  and the  $\text{BTA}^-$  anion even in slightly alkaline media [11]. In addition, BTA has the ability to form poorly water-soluble complex compounds with cations of many metals (Ag, Cu, Zn, Ni, Co, Pb) [12], which can form thin protective layers that often inhibit metal corrosion more effectively than adsorption and even chemisorption of the CI itself. Depending on various conditions, it can take one of the possible forms that is capable of providing its inhibiting functions, thus making BTA multifunctional, so it is logical to start the discussion of triazoles from BTA and its substituted derivatives.

## II. Copper

Back in 1963, Cotton and Dugdale [3] explained the inhibition of copper corrosion by BTA additives by its ability to chemisorb and form a Cu(I)–BTA complex on its surface, which takes the form of a  $(\text{Cu(I)–BTA})_n$  polymer that enhances the protection effectiveness. More recent studies have confirmed the important role of the chemisorption film of BTA and the Cu(I)–BTA complex in the protective effect.

The specific features of the mechanism of Cu protection with BTA are discussed in more detail in the review [8]. Its authors discussed the results of about 130 studies performed in the second half of the XX century and the first decade of the XXI century. According to them, the exact composition and structure of the complex on the Cu surface are not clear and do not coincide with those of the specially synthesized complex. They noted a contradiction in the literature data on the orientation of BTA on Cu, which in different works was treated as perpendicular, inclined or parallel with respect to the metal surface. However, in our opinion, this is not surprising since the adsorption of organic molecules depends on the external conditions and on the preparation and state of the Cu surface. The authors of the review questioned the presence of a polymer complex based on the results of using surface-sensitive methods that point to the parallel packing of BTA molecules, which makes the chain structure more likely. At the same time, it was noted that the increase in BTA efficiency with pH increase is in good agreement with the mechanism of Cu protection by this CI developed by Japanese researchers who explained this by shifting the following equilibrium to the right:



*i.e.*, by formation of a polymer complex the existence of which was shown by Aramaki *et al.* [13], as well as by Brusik *et al.* [14] back in the early 1990s. Later, Notoya *et al.* [15], using the time-of-flight secondary ionic mass spectroscopy (ToF SIMS), showed that the BTA state in the protective layers on copper and on six other metals differs, since the degree of polymerization of its compounds with the metal differ markedly. They also determined the effectiveness of BTA as CI of copper in chloride solutions and found that it

is the better, the higher the degree of polymerization of the complex compounds with the metal.

In the reviews mentioned above [4, 5, 8, 10], much attention was paid to the analysis of the adsorption of BTA on copper, its dependence on the solution pH, and the presence of copper oxide on the copper surface. The growth of the protective film BTA basically obeys the logarithmic law. It is believed that BTA is more quickly adsorbed on oxides than on oxide-free copper, and the thickness of a Cu-BTA protective layer is larger on a Cu<sub>2</sub>O substrate than on CuO. However, at high pH, copper oxides are more stable and the action of BTA can be hindered.

The potential of the copper electrode and the BTA concentration ( $C_{\text{BTA}}$ ) play an important role in the formation of the complex. At low  $C_{\text{BTA}}$  and more negative potentials, the adsorption of molecules is more important for copper protection than the formation of complexes. At low BTA concentrations the CI slows down the cathodic reaction; as the concentration increases, a Cu-BTA film is formed that suppresses the anodic dissolution of the metal, *i.e.*, passivation of copper occurs [16]. The effectiveness of corrosion inhibition of copper single crystals by addition of 7.5 mM BTA in 0.05 M H<sub>2</sub>SO<sub>4</sub> depends on the crystal plane and decreases in the series: Cu(100) > Cu(110) > Cu(111). Later [17], the adsorption structures of BTA on Cu(110), (100), and (111) single crystals were studied using the *in situ* scanning tunneling microscopy (STM) method in 0.1 M HClO<sub>4</sub> aqueous solution. It was found that BTA molecules were ordered in accordance with clearly shaped single-crystal Cu surfaces and the structure of the adsorption layer depended on the crystallographic orientation of the Cu surface. The adsorbed BTA molecules were arranged parallel to the Cu(110) and (100) surfaces, but on Cu(111) surface they were arranged vertically to form molecular rows. It has been shown that the molecular orientation of BTA affects electrochemical reactions, for example, hydrogen evolution on copper electrodes.

The irreversible adsorption of BTA on Cu(111) and Cu(110) single crystals from 0.10 M H<sub>2</sub>SO<sub>4</sub> was confirmed by Raman spectroscopy (SERS) [18]. However, in the case of polycrystalline copper in the same solution, the adsorption of BTA is reversible, which the authors explain by the large number of grain boundaries that prevent the formation of Cu-BTA oligomeric chains that are more strongly bound to the surface than a similar monomer. They assume that this is due to the dissolution of the film in the defects at the grain boundaries.

As we noted in [4], an important role in understanding the mechanism of BTA adsorption belongs to studies that employ methods with atomic resolution, primarily STM. In this review, we already briefly discussed the studies on the adsorption of BTA itself on copper single crystals. Here we'll only clarify that in [19], BTA was adsorbed at room temperature ( $t$ ) from the vapor phase in a vacuum chamber ( $\sim 10^{-10}$  mmHg). Measurements *in situ* have shown that on a clean Cu(110) surface, BTA is adsorbed on active centers (steps, grain boundaries), its molecules have a horizontal orientation and form well-ordered structures. A disordered structure with a thickness of several monolayers is formed on the same copper surface pre-oxidized with oxygen at 100°C.

Considering the effect of  $O_2$  on the interaction of BTA with the copper surface, we should note the paper [20] where it was studied in a nitrogen-filled box with controlled  $O_2$  content in the atmosphere when the copper sample was immersed in  $Na_2SO_4$  solution. It was shown that even at  $C_{O_2} < 90 \mu g \cdot l^{-1}$ , a protective film of a [Cu(I)–BTA] complex was gradually formed. Its thickness reached 5 nm in 4 hours, whereas it reached 30 nm in a normal air atmosphere. Thus, such low oxygen concentrations can contribute to the formation of a passive film of the copper complex, even if the primary  $Cu_2O$  oxide on the metal is absent.

The nature of binding of BTA to the reduced and oxidized surfaces of copper single crystals and the possibility of its simulation have been studied for more than 40 years by quantum-chemical methods, of which the functional density theory (DFT) was used particularly often [21–27]. A detailed analysis of their application is beyond the scope of this review, but we note that over the past decade, they have helped to clarify certain features of BTA bonding to the copper surface.

The interest in the simulation is piqued by the fact that BTA can exist in various forms, such as protonated (in acid solution), neutral or deprotonated, which are capable of forming intermolecular structures on copper surfaces either through hydrogen bonds or through the formation of complex compounds with a metal. It was found that BTA can either be chemisorbed in vertical geometry, or physically adsorbed when the molecule is almost parallel to the surface. According to [23], the DFT calculations show that the BTA–Cu complex is thermodynamically more stable than the autonomous chemisorbed  $BTA_{ads}$ . For vertically oriented chemisorbed particles, the lateral interaction acts far and extends to the nearest neighbor, while for physical adsorption the lateral interactions are much less pronounced and the molecules have a weak attraction. At the same time, the value of the chemisorption energy increases upon transition from densely packed Cu(111) to more open surfaces and not completely coordinated defects on Cu(110) or Cu(100). The BTA chemisorption energies extrapolated to zero degree of coverage of these two planes of a copper single crystal are 0.73 and 0.92 eV. This agrees with the conclusion from the experiment carried out in 0.1 M HCl [28], which showed that the adsorption of BTA often begins on Cu surface defects.

The energy of physical adsorption extrapolated to zero degree of coverage does not depend on the surface plane and does not exceed 0.7 eV [23]. The authors believe that due to the large dipole moment of BTA (4.1 D), dipole–dipole interactions are also important. It is dominant on Cu(111), but its relative contribution decreases on the more open surfaces of copper due to the increased role of chemisorption. The significantly increased chemisorption force at the low-coordinated sites correlates with their increasing energy of the d-band center, which leads to a stronger hybridization between the d-levels of the metal electrons and the molecular orbitals. Although the more densely packed surfaces are less capable of interacting with a molecular  $\pi$ -system, the reactivity of the Cu(110) plane appears to be at the beginning of such an interaction. This leads to a very stable parallel

adsorption structure with an adsorption energy of 1.3 eV, which is attributed to the total effect of chemisorption and physical adsorption of BTA particles [23].

In recent years, many different adsorption mechanisms have been proposed, most of which defend the polymer models. The authors [25] who carried out a study on the adsorption of BTA on a Cu(111) single crystal in a high vacuum chamber, analyzed the results obtained by different methods. They came to the conclusion that BTA can be physically adsorbed flatly on the surface in the form of neutral molecules and form mobile particles. This causes their deprotonation and coordination with free copper atoms at the edges of the steps and surface defects, leading to the formation of vertically chemisorbed particles detected by vibrational spectroscopy. STM image analysis shows that these particles are probably  $\text{Cu}(\text{BTA})_2$  dimers at the step edges, and at surface defects, CuBTA monomers are surrounded by dimers.

However, BTA deprotonation on flat terraces is an activated process. On defective terraces, some vertical particles of  $\text{Cu}(\text{BTA})_2$  can be located in parallel and are chemisorbed weakly, so they diffuse under the influence of the STM probe. Starting with an average degree of coverage, STM images show that another pseudohexagonal pattern is being formed. This structure is also observed when a monolayer is formed, with which surface passivation is associated.

Multilayer films formed by BTA on Cu have various morphologies that depend on the first chemisorption layer, but the subsequent layers appear to be formed only by physical adsorption. A metastable structure, which is believed to contain dimers and planarly arranged polymer particles coexisting with a pseudohexagonal structure, can change upon annealing of multilayer films. Measurements of temperature-programmed desorption show that physical adsorption and chemisorption of BTA accompany each other starting from the lowest degree of coverage of the coating. The weakly adsorbed particles are desorbed at 350–375 K, and desorption of the chemisorbed layer begins at 550 K. Using STM and high-resolution electron energy loss spectroscopy (HREELS) spectroscopy, it has been shown that high ordering of the film occurs at ~420 K, when the physically adsorbed layer is completely desorbed. The complete desorption of the chemisorption layer is only observed upon annealing at >600 K.

The results of DFT calculations of the interaction of BTA with Cu single crystals considered above relate to BTA adsorption on non-oxidized surfaces of this metal. Equally important is the identification of the adsorption behavior of BTA and its oxidized surfaces, which was discussed in [24, 25]. DFT calculations showed that BTA can bind to Cu oxide and oxidized Cu surfaces. The binding of corrosive chloride anions is enhanced upon transition from Cu(111) to defects on Cu(110) and Cu (100) planes, *i.e.*, like the adsorption of BTA on the non-oxidized surface but to a lesser extent. On oxide surfaces, BTA binds much more strongly to the coordination unsaturated areas of the surface. This indicates the ability of BTA to passivate “uncoordinated” areas of the surface, which are likely microscopic centers of corrosion.

Kokal [26] believes that BTA is strongly chemisorbed on Cu only in the deprotonated form. Its binding is even stronger when it is incorporated into the organometallic BTA–Cu<sub>ads</sub> adsorption complexes. The results of DFT calculations agree with the experiment proving that the action of BTA as CI for copper is due to the formation of organometallic complexes. This explains why BTA is more effective at higher pH. At a low pH (and low copper potentials) BTA turns into BTAH<sub>ads</sub>, which, although it binds to the copper surface, can be desorbed more easily. According to DFT calculations, the most likely form of adsorption under such conditions is BTAH, which is physically adsorbed parallel to the surface and connected by hydrogen bonds into a network with other BTAH molecules.

The authors of [27] paid great attention to the interaction of various forms of BTA with copper, mainly with the (111) single crystal plane, and found a large difference in the energies of adsorption on this plane between the anion and the molecule of this CI ~2 eV. They believe that the structures formed by molecules and deprotonated BTA<sup>−</sup> on Cu(111) determine the corrosion protection by these CIs. It was found that hydrogen bonds, van der Waals interaction, and spatial difficulties in adsorption make an appreciable contribution to the formation of the adsorption layer. In this case, flat structures are preferred at low degrees of surface coverage of the adsorbate, and the vertical configuration is preferable at high degrees. The interaction of deprotonated BTA<sup>−</sup> with the copper surface predominates in the form of strong chemisorption of organic anions due to the formation of a bond of azole nitrogen with copper adatoms. Dimer or chain structures are the most stable structures for all coatings. This conclusion agrees well with the results of STM studies. The authors concluded that the van der Waals forces play an important role in the adsorption of BTA, the degree of coverage of the copper surface with it, and the possibility of deprotonation of its molecules, and all these factors actually contribute to its efficiency as a CI.

A combination of quantum chemical calculations with the results of the XPS study undoubtedly makes it possible to better understand the features of the formation of protective layers of heterocyclic CIs. However, recently Kazansky drew attention to the contradiction sometimes arising between them [29]. Many papers using the DFT method show that protonated nitrogen atoms carry a greater negative charge than non-protonated ones, which contradicts the XPS data. In this connection, the value of the transferred electron density from a CI to a metal is calculated, although there is often no experimental justification for implementing such a mechanism of interaction of the heterocycle with the metal. In contrast, XPS data sometimes show that electrons are shifted from the metal to the adsorbed CI molecule, so the values of  $\Delta N$  can only be compared for molecules with similar structures. We can add to this the fact that has been established experimentally a long time ago, and which is especially clearly manifested in the example of twenty two 2-substituted benzimidazoles [4, 12, 30], that the efficiency of copper passivation increases linearly with the induction constant of the substituent  $R$  ( $\sigma_I$ ) in the molecules of heterocyclic CIs, indicating an increase in the electron-acceptor properties of  $R$ . The effectiveness of the same protection of zinc by these CIs under analogous conditions,

however, decreases linearly with increasing  $\sigma_1$ , *i.e.*, it increases with the growth in the electron-donor properties of the heterocycle molecule.

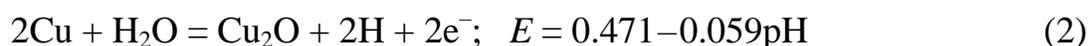
**Neutral media.** Yet another method for studying the interaction of BTA with the Cu surface in these media deserves special attention. Back in 1990, Cohen *et al.* [31] used the *in situ* ellipsometric method to demonstrate its capabilities for revealing the features of BTA adsorption from aqueous solutions on copper. In the paper referred to, they studied the adsorption of BTA from borate buffer (pH 8.2), KOH solution (pH 12) and acidified aqueous solutions (pH 2.0) on a thin Cu film (~2  $\mu\text{m}$ ) sprayed onto a silicon wafer with a thin Ta sublayer. The potential of this electrode was controlled by a potentiostat, creating the possibility to obtain a surface of polycrystalline copper either free of oxide (CuO) or oxidized copper. It turned out that films grown on Cu<sub>2</sub>O–CuO under oxidizing conditions are usually 5–40 Å thick and are best described as Cu(I)–BTA. Adsorption of BTA was observed at negative potentials and on reduced Cu, where it was limited to a monolayer. This was confirmed by the conclusion made earlier in [32] based on studies on the adsorption of BTA from the gas phase by the photoemission method in a deep vacuum ( $7 \cdot 10^{-10}$  Torr) that the presence of Cu<sub>2</sub>O on the copper surface is not a prerequisite for planting this CI on the metal. It is characteristic that the thickness of the BTA layer calculated from XPS data from the ratio of the peak areas in the N1s/Cu3p spectra of electrons was in good agreement with independent ellipsometric measurements on similar samples. However, the ellipsometric method has been underestimated for a long time and has hardly been used to clarify the mechanism of action of triazoles on copper.

Ellipsometry has long been a common method for studying the thickness and kinetics of the formation of films on metals, oxides and other materials. However, over the past decades, in combination with electrochemical methods and XPS, it has become a powerful tool for studying ultrathin adsorption layers, which makes it possible to detect not only their thickness and orientation of adsorbate particles in a film, but also to estimate the standard free energy of adsorption ( $-\Delta G_a^0$ ) of the first organic monolayer of a CI. It was this *in situ* method that proved the possibility of adsorption (“non-oxide”) iron passivation in borate buffer with pH 7.4 by a CI (sodium phenylanthranilate), which was considered in detail in [30, 33]. It also demonstrates the usefulness of combining ellipsometry with XPS (*ex situ*) studies with the example of an even stronger adsorption passivator for iron, sodium oleate. In its solution it was possible to observe the signal from Fe<sup>0</sup> on the X-ray spectrum obtained from the sample. The peak of oxidized iron was attributed not to the oxide, but to iron oleate, which was confirmed by examining the reflection–adsorption IR spectra of the iron surface. Back in the late 1980s, we showed that measurements of the adsorption of organic compounds by the ellipsometric method make it possible to construct their isotherms at various electrode potentials that allow one to give the surface a stable oxidized state or to free it from oxides [34]. Of *in situ* methods, this opportunity is provided by EIS, STM and EQCM methods, each of which has its own assumptions and limitations. It is significant that the results of measurements of the adsorption parameters

of sodium phenylantirilate by these methods are in good agreement with their ellipsometric estimates [30, 35].

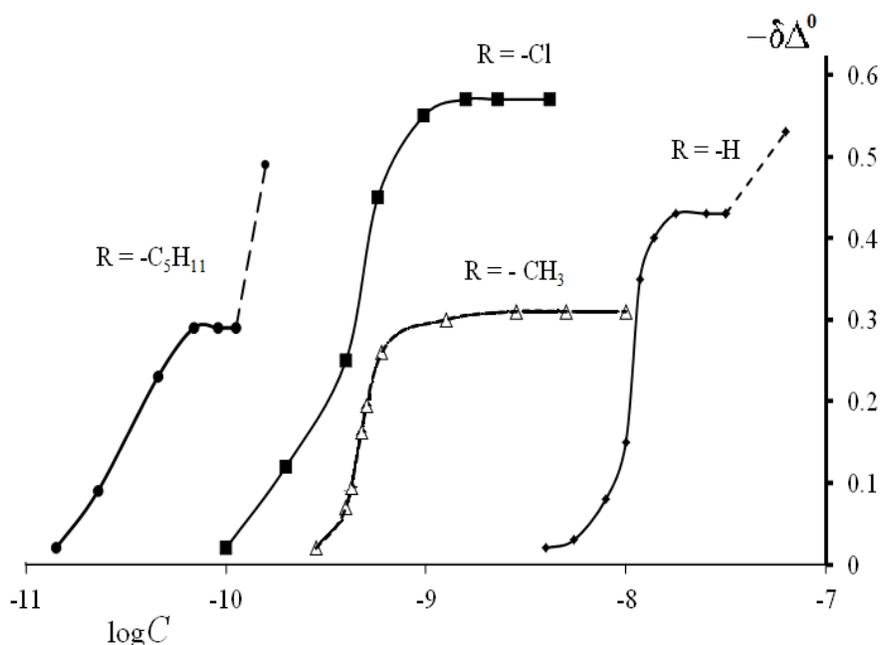
In order to reliably measure the adsorption on copper in borate buffer, it is necessary to select the electrode potential with a stable surface. Only after that, the change in the ellipsometric phase angle  $\delta\Delta = \Delta - \Delta_0$ , where  $\Delta_0$  is the value of this angle for the initial state of the surface and  $\Delta$  is its current value obtained, for example, upon introduction of a CI into the solution, it can be associated with the formation and growth of a film. If  $\delta\Delta$  becomes negative, adsorption occurs on the surface, while a positive value of  $\delta\Delta$  indicates desorption or dissolution of the film.

In many studies on the adsorption of BTA and its substituted derivatives and in measurements of the thickness of the passive film on copper and other metals, borate buffers, most often with pH 7.36, were used as the background solutions. After 30–40 min of electrode reduction at  $E = -0.65$  V, the potential was abruptly shifted to an anodic value, where the surface freed from the air-formed oxide was again oxidized under controlled conditions. The  $\Delta$  angle decreases continuously at any anodic potentials, which indicates the growth of copper oxides on the electrode surface. To measure adsorption, it is necessary to choose a potential at which, before the CI was introduced, the newly oxidized surface was stabilized, *i.e.*, the ellipsometric angles ceased to change. For this reason, the oxidation of Cu was carried out at  $E = 0.0$  V at which, according to the Pourbaix diagram, an equilibrium is established between the Cu and Cu<sub>2</sub>O phases:



After 30 min of electrode exposure, the ellipsometric angles cease to change and we can assume that the Cu<sub>2</sub>O oxide film is stabilized. By adding a BTA concentrate in portions to the electrochemical cell, the dependence of the change in the phase shift angle on  $C_{\text{BTA}}$  was obtained, which under certain assumptions can be considered as the BTA adsorption isotherm [36, 37].

As one can see from Figure 1, the dependences of  $\log C_{\text{in}}$  obtained for oxidized copper at  $E = 0.2$  V in the presence of not only BTA but also its substituted derivatives have the form of logarithmic isotherms. It can be seen from the  $\delta\Delta$  value determined by ellipsometric measurements that the adsorption of BTA on passive copper begins already in a very dilute solution ( $\sim 0.7$  nM), and it reaches saturation with an increase in  $C_{\text{in}}$  within just one order of concentration. It is natural to assume that the adsorbed CI occupies only a small part of the surface area and is localized only in the vicinity of the most active centers, possibly with displacement of some adsorbed oxygen molecules and hydroxyl groups from the copper surface. The formation of such a limiting concentration of adsorbed BTA particles on the surface can be perceived as the formation of its “monolayer” that corresponds to the maximum degree of surface coverage,  $\Theta_{i, \text{max}} = 1$ .



**Figure 1.** Change in the ellipsometric angle ( $\delta\Delta$ ) vs. the concentration of BTA and its substituted derivatives (the R substituent in the 5-R-BTA molecules is shown near the curves) on copper at the anodic potential  $E = 0.0$  V. The dotted lines on the curves show the regions of non-stationary values of the  $\Delta$  angle.

This means that we postulate a linear relationship between the experimentally determined changes in the  $\Delta$  angle and the degree of coverage  $\Theta_i$  of the electrode surface with CI particles of type  $i$  with a change in  $C_i$  expressed in  $\text{mol}\cdot\text{l}^{-1}$  in the solution:

$$\Theta_i(C_i) = \beta |\delta\Delta(\ln C_i)|, \quad (3)$$

where  $\beta$  is a parameter determined from the experimental dependence of (3) on the specifically chosen isotherm of CI adsorption on copper. Taking into account the possibility of chemisorption of BTA on active centers of the copper surface, the authors of [37] concluded that it is most natural to take the logarithmic Temkin isotherm as the adsorption isotherm of the CI in the form:

$$\Theta_i = \frac{1}{f_i} \ln \frac{1 + n^{-1} B_{i,\max}(C_i - C_{i0})}{1 + n^{-1} B_{i,\min}(C_i - C_{i0})} \quad (4)$$

Here  $f_i$  is the surface inhomogeneity factor characterizing the change in enthalpy of adsorption with the surface coverage;  $B_{i,\max}$  and  $B_{i,\min}$  are the adsorption equilibrium constants corresponding to the highest and lowest values of the adsorption energy. In this equation, the  $C_i$  concentration is an independent variable,  $C_{i0}$  is the known value of the minimum concentration, and  $n$  is 55.5. Using the simple mathematical apparatus detailed in [37], the isotherms of the adsorption of substituted BTAs in borate buffer on oxidized copper were determined.

They are presented in Table 1 together with the values of  $pK_a$  constants and the logarithms of distribution coefficients ( $\log P$ ) [38], which were calculated using the ACDLABS program and characterize the acidic and hydrophobic properties of the triazoles studied, respectively.

**Table 1.** Dependence of the acid dissociation constant  $pK_a$ , logarithm of distribution coefficient ( $\log P$ ) and the adsorption parameters  $f$ ,  $(-\Delta G_{a,\min}^0)$  and  $(-\Delta G_{a,\max}^0)$  on the chemical structure of 5-R-BTA corrosion inhibitors.

Inhibitors	$pK_a$	$\log P$	$B_{i,\max}$ $\text{l}\cdot\text{mol}^{-1}$	$B_{i,\min}$ $\text{l}\cdot\text{mol}^{-1}$	$(-\Delta G_{a,\min}^0)$ $\text{kJ}\cdot\text{mol}^{-1}$	$(-\Delta G_{a,\max}^0)$ $\text{kJ}\cdot\text{mol}^{-1}$	$f$
BTA	8.38	1.29	$23.2\cdot 10^8$	$17.27\cdot 10^8$	51.8	52.5	0.30
5-CH <sub>3</sub> -BTA	8.70	1.61	$3.71\cdot 10^{10}$	$2.77\cdot 10^{10}$	58.5	59.2	0.29
5-Cl-BTA	5.46	1.92	$9.55\cdot 10^{10}$	$3.88\cdot 10^{10}$	59.3	61.5	0.90
5-C <sub>5</sub> H <sub>11</sub> -BTA	9.4	3.19	$20.52\cdot 10^{11}$	$7.21\cdot 10^{11}$	66.4	69.1	1.05

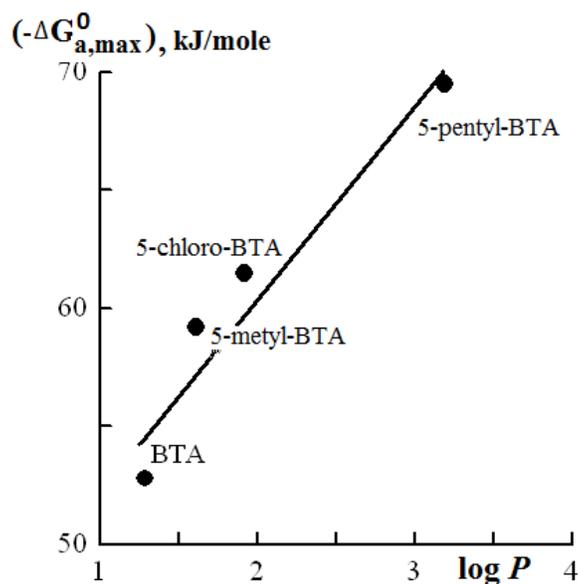
Incorporation of substituents  $R = \text{C}_5\text{H}_{11}$ ,  $\text{CH}_3$  and  $\text{Cl}$  in the structure of BTA can alter the adsorption capability of the CI. As seen from the data in Table 1, the BTA derivatives studied have higher adsorption activity, and 5-pentyl-BTA is the most effective of them. The high  $(-\Delta G_{a,\max}^0)$  values, which are much larger than those of BTA itself, are also in favor of the assumption on the chemisorption of substituted BTAs. It is essential that the chemisorption interaction of BTA and some of its derivatives with copper surface has been proved by various physical and chemical methods of surface investigation, for example, XPS [4]. Studies on the adsorption of 5-R-BTA, *i.e.*, compounds similar in chemical nature, were conducted on electrodes with preformed oxide in order to minimize their effect on the oxide growth. In addition, the CIs studied do not dissolve the oxide, and there are no grounds to believe that 5-R-BTA can stimulate its growth since they have no oxidizing properties. The authors of [39], using the same method to study the adsorption of 5-chloro-BTA on copper surface from borate buffer solution by the XPS method, showed that the thickness of the  $\text{Cu}_2\text{O}$  oxide does not change upon formation of a BTA monolayer and equals  $\sim 1$  nm.

After the formation of a conditional monolayer, further changes in the ellipsometric angle  $\Delta$  occur in time. This may be due to the fact that copper cations slowly accumulating in the solution form complex compounds with the CI. These compounds begin to adsorb and form the second and subsequent layers, so the formation of the second layer is shown on the isotherms by the dashed line (Figure 1).

The adsorption capability of BTA and its derivatives depends on the chemical structure of the compounds studied, so it is logical to trace how this property is affected by their acid-base properties usually characterized by the value of the acid dissociation

constant  $pK_a$ . The smaller the  $pK_a$  value, the stronger the acid. Obviously, no direct dependence of  $(-\Delta G_{a,\max}^0)$  on  $pK_a$  of the adsorbate is observed: 5-chloro-BTA, the strongest NH-acid is characterized by a larger  $(-\Delta G_{a,\max}^0)$  value than BTA or 5-methyl-BTA, but it is much inferior in this to 5-pentyl-BTA, which has the weakest acid properties (Table 1). Nevertheless, comparison of the criteria for the adsorption capability of organic compounds on copper measured *in situ* with the criteria reflecting the chemical structure of the compounds being studied is very important for understanding the protective effect of corrosion inhibitors. Its optimization can be an important step in the further development of the theory of corrosion inhibition.

Back in 1999 [40], when considering the effect of the length of alkyl R in 5-R-BTA on the protection of copper by these compounds in acid solutions, it was shown that its hydrophobicity plays a significant role in the protection effectiveness. Usually, the logarithm of the distribution coefficient ( $\log P$ ) of a compound in a system of two immiscible liquids, octanol–water (Hansch hydrophobicity parameter) is taken as its criterion [38]. If we compare the values of  $(-\Delta G_{a,\max}^0)$  with the values of  $\log P$  for the four triazoles studied, it can be seen that as the hydrophobicity increases, the value characterizing the adsorption strength of an organic compound of this class increases linearly (Figure 2). Obviously, this regularity will be observed only up to a certain limit above which the adsorbate particles become insoluble in the medium under consideration. The simplest case is when R are alkyls varying in the number of carbon atoms.



**Figure 2.** Correlation of the free adsorption energies  $(-\Delta G_{a,\max}^0)$  of BTA and its derivatives with  $\log P$  [37].

The adsorption of a CI on oxidized copper is a complex process due to the fact that surface oxide atoms can be partially hydrated and hydroxylated. When triazoles are

adsorbed, their donor atoms can replace water or hydroxyls on the surface of copper oxide or, if the molecule has a planar symmetry, it can be parallel to the oxide plane due to  $\pi$ -interactions.

In the case of the chemisorption of weak NH acids, such as 5-R-BTA, realization of the following interaction scheme between a CI and hydroxylated copper oxide is possible:



As a result, a surface complex is formed in which a strong Cu-N bond and a water molecule appear. The linear correlation of the  $(-\Delta G_{a,\max}^0)$  values *versus*  $\log P$  confirms the important role of the surface activity of the CIs in neutral solutions, though it should be admitted that the statistical selection of these compounds is small. In view of this it is interesting to compare the results of adsorption and electrochemical measurements. Although the copper polarization curves were obtained not in pure borate buffer, but in the same buffer with an activating additive of 0.01 M NaCl, they provide valuable information not only about the passivating action of 5-R-BTA but also on their ability to stabilize the passive state of copper under conditions of competitive adsorption of a CI and chloride.

The passivating ability was estimated from the minimum value of a  $C_{\text{in}}$  that is sufficient for spontaneous passivation of copper when the electrode is immersed in the solution and kept there for  $\leq 5$  min. It turned out that the protective effect of 5-methyl- and 5-chloro-BTA is slightly higher than that of BTA, while that of 5-pentyl-BTA is considerably higher. The anodic polarization curves of copper obtained in borate-chloride solutions with  $C_{\text{in}} = 1.5$  mM showed that 5-methyl- and 5-chloro-BTA is noticeably superior to BTA in the ability to stabilize the passive state of copper, whereas 5-pentyl-BTA far exceeds even them in this respect. Based on these studies, the authors of [37] concluded that the values of  $\log C_{\text{in}}$  and  $\Delta E = E_{\text{pt}}^{\text{in}} - E_{\text{pt}}^{\text{backgr}}$  for 5-R-BTA, which characterize their passivating ability and inhibition efficiency in local depassivation of copper, respectively, although not in such an explicit form as  $(-\Delta G_{a,\max}^0)$ , correlate linearly with the value of  $\log P$ .

One can find the results of studies on other BTA derivatives in the literature but, unfortunately, they do not always give a basis (even indirectly) to confirm this conclusion. For example, Aramaki *et al.* [13,41,42], having investigated the adsorption and inhibiting effect on copper of BTA and some of its derivatives in neutral sulfate solutions, showed that 5-nitro-BTA is less effective than BTA, 5-methyl-BTA and especially 5-chloro-BTA. This fact agrees with the above correlation, since the  $\text{NO}_2$  group is hydrophilic and its introduction into the BTA molecule reduces the hydrophobicity of the CI, *i.e.*, the value of  $\log P$ . They also found that 1-hydroxy-BTA is a weak CI for copper and is significantly inferior in efficiency to BTA itself. Later, Finšgar and Milosev [43] confirmed this fact for a 3% solution of NaCl, which can be explained by the less hydrophobic nature of 1-hydroxy-BTA due to the introduction of hydrophilic  $\text{R} = \text{OH}$ . However, strictly speaking, to compare the results of these studies it is not enough to know the value of  $\log P$  of

substituted BTAs, but it is also important to retain the position of R in the molecule. In the reaction series investigated in our work [37], introduction of 5-R in BTA does not deprive the CI molecule of acidic properties, although it is capable of weakening them, as in the case of alkyls  $R = -CH_3$  or  $-C_5H_{11}$  (Table 1). This allows us to preserve the above described mechanism of interaction of CI with copper, that was confirmed by quantum-chemical calculations as well. When R is introduced into position 1, deprotonation of the heterocycle group does not occur and the formation of a strong Cu–N bond is no longer so obvious.

According to [40, 44–46], increasing the alkyl length in 5-R-BTA results in an increase in the protection efficiency of copper in various neutral solutions (3.5% NaCl, 0.1 M NaCl, 0.1 M  $Na_2SO_4$ ). 5-Butyl- and 5-hexyl-BTA studied by Italian researchers, which inhibit copper dissolution significantly better than BTA, are therefore more likely to increase the number of CIs in the correlation shown in Figure 2.

Among substituted BTAs, 5-chloro-BTA is one of the most studied CIs for copper. It is a stronger NH-acid (Table 1), so it is easier to deprotonate in aqueous solution and at the same time has a higher hydrophobicity than BTA. It has one more advantage, because it contains a Cl atom which easily distinguishable when analyzing the surface of metals, including copper.

As shown by Angle resolved XPS and Auger spectroscopy methods [39], 5-chloro-BTA anions form a monomolecular layer whose thickness is comparable to the size of the molecule taken along the virtual axis between Cl– and 1–NH< of the heterocycle. The anions form a self-assembled layer in which the molecular planes can be connected to each other in parallel or at an angle to each other, and adsorption occurs by forming coordination bonds between the metal cations and the N atoms. Naturally, for the surface of oxidized polycrystalline samples of different metals (Cu, Zn, Fe) the packing density can be different, however, the use of the layer specific density showed that the thickness of the layer is comparable with the molecule length. It allowed the conclusion to be made about the vertical orientation of 5-chloro-BTA on the surface of copper.

On copper, the film growth is not limited to a monomolecular layer, and the thickness of such a layer can reach several hundred nm. This is due to the formation of a poorly soluble polymeric complex with the following ratio:  $Cu(I) : 5\text{-chloro-BTA} = 1 : 1$ . To form a second layer, the N atoms free of interaction with copper surface atoms could coordinate the Cu cations released from the surface. According to [47], the thickness of the BTA film formed depends linearly on the logarithm of time. It is natural to assume that a complex is formed on the first chemisorbed layer through which the copper cations diffuse, having either a polymeric character or possessing rather poor solubility. Unfortunately, XPS analysis does not allow the deviation of the molecule plane from the vertical direction to be determined, but it can be assumed that if the planes of densely packed molecules are inclined, the density of the layer increases slightly. It is assumed that such a dense packaging due to the interaction between benzene rings should stabilize the monomolecular chemisorption layer.

Although introduction of hydrophobic R into BTA molecules makes it possible to enhance the protection of copper in neutral media by these compounds, it is limited by a decrease in the solubility of CIs in water. Of course, there are other ways to achieve the same goal, among which the method of using BTA in combination with a CI that enhances the protective effect has long been known and is often very effective. There are cases where synergists for the protection of copper from corrosion in aqueous solutions are chemical compounds that themselves are not CIs for this metal. The mixture of  $\text{Na}_3\text{PO}_4$  with BTA in a 17% aqueous tetra-*n*-butylammonium bromide (TBAB) solution, a well-known coolant carrier, is indicative [48]. The addition of trisodium phosphate, which slows down the corrosion of steel, only accelerates it for copper, but its formulation with BTA protects this metal more efficiently than the triazole itself.

Published reviews contain many examples of such mixtures [4, 5, 8, 10, 12]. In the past decade, work in this area continued. For example, in [49–51] the synergism in copper protection against corrosion was shown in the joint application of BTA with salts of carboxylic acids (phenylundecanoic, sorbic, *etc.*). The ability of dimegin, *i.e.*, disodium salt of protoporphyrin IX [2,4-di(1-methoxyethyl)-deuteroporphyrin IX] containing two carboxy groups, to enhance the adsorption of BTA on copper, which was shown for the first time in [51], is worthy of note.

It follows from consideration of the results of ellipsometric measurements on passive Cu in borate buffer with pH 7.4 at  $E = 0.2$  V (Table 2) that the preliminary adsorption of dimegin adequately described by the Temkin equation, even at a small degree of surface coverage,  $\theta_{\text{Dmg}} = 0.10$ , can stimulate the adsorption of BTA. Its adsorption begins at such a  $C_{\text{in}}$  where it was not observed without the modification. As a result, the  $(-\Delta G_{\text{a}}^0)$  value increases to  $63 \text{ kJ}\cdot\text{mol}^{-1}$  (instead of  $58 \text{ kJ}\cdot\text{mol}^{-1}$ ). The inhomogeneity factor of BTA adsorption,  $f$  in the Temkin equation, also increases, which indicates an uneven distribution of both CIs on the electrode surface.

**Table 2.** Characteristics of BTA adsorption (Temkin isotherm) on Cu surface without ( $\theta = 0$ ) and with pre-modification by dimegin.

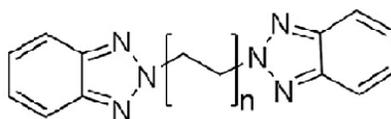
Coverage degree, $\theta_{\text{Dmg}}$	Standard free energy, $(-\Delta G_{\text{a}}^0)$ $\text{kJ}\cdot\text{mol}^{-1}$	Surface energetic heterogeneity factor, $f$
0	$58 \pm 2.8$	2.4
0.10		5.4
0.30		3.1
0.47	$63 \pm 3.1$	3.4
1.00		3.2

Corrosion tests confirmed the improvement of the protective properties of BTA after preliminary adsorption of dimegin on copper. A plate treated with a dilute BTA solution (1 mM) and then placed in a chamber with periodic condensation of moisture remains completely protected for several days: the first signs of copper corrosion were observed after 9 days. If the plate was preliminarily treated in a solution of dimegin with the  $C_{in}$ , which provided  $\theta_{Dmg} = 0.47$ , and then with the same BTA solution, the induction period of corrosion in the moist chamber increased twofold.

Another interesting way to increase the effectiveness of BTA in the protection of copper was proposed in [52]. It consists of accelerating the formation of a protective film by this CI from an “intelligent” self-healing coating, for example, an epoxy one. To do so, nanostructured  $\alpha\text{-Mn}_2\text{O}_3$  was added to the coating where it served as a catalyst for the reaction between BTA and copper. In the epoxy coating, the rate of formation of the protective film on copper increased by a factor of 3 with the addition of  $\alpha\text{-Mn}_2\text{O}_3$ . In the opinion of the authors, this was due to the catalysis of the  $\text{O}_2$  reduction reaction. They came to the conclusion that the addition of such catalysts to the coating matrix could be a new strategy for developing fast, effective and durable active coatings with feedback.

According to [53], the protection of copper with BTA and its slightly more effective derivatives, 1-(2-thienyl carbonyl)-BTA (TCBT) or 1-(2-pyrrole carbonyl)-BTA (PCBT), can be improved by adding a nonionic surfactant - Triton X-100, which is an oxyalkylated *p*-alkylphenol, to corrosive groundwater. EIS measurements showed that the efficiency of copper protection increased in the series  $\text{BTA} \approx \text{TCVT} < \approx (\text{BTA} + \text{TX-100}) < \text{TCBT} + \text{TX-100} < \text{PCBT} + \text{TX-100}$ . A study of the composition of protective layers on copper by means of Fourier reflection transmission IR spectroscopy (FT-IR) and X-ray diffraction analysis (XRD) allowed the authors to associate the inhibition of its corrosion with the formation of an insoluble film formed by the adsorption of CI molecules. The molecules of TX-100 are adsorbed on this film and create an additional barrier for the penetration of corrosive solution components to the metal.

An interesting idea of increasing the protection of copper by BTA derivatives in a 3.5% NaCl solution was implemented in [54]. The authors synthesized dibenzotriazoles in which BTA molecules were linked together by a polymethylene bridge (linker). These di-BTA, with the general formula:



The compounds with  $n = 1$  ( $C_1$ ); 2 ( $C_2$ ); and 3 ( $C_3$ ) were studied as CIs of copper in comparison with N-alkyl-BTA, *i.e.*, 2-ethyl-BTA ( $n = 1$ ;  $C_4$ ); 2-butyl-BTA ( $n = 2$ ;  $C_5$ ) and 2-hexyl-BTA ( $n = 3$ ;  $C_6$ ). The efficiency of the CIs was determined from the polarization curves, the EIS results, and direct corrosion tests performed for 15 days. It is shown that the efficiency determined by electrochemical methods decreased in the series:  $C_3 > C_2 > C_1 > C_6 > C_5 > C_4$ , *i.e.*, even di-BTA with a shorter and less hydrophobic linker surpassed 2-

hexyl-BTA in copper protection. The best CIs from both groups ( $C_3$  and  $C_6$ ) were tried in corrosion tests that confirmed at the optimum  $C_{in} = 15$  mM that the di-BTA ( $Z = 98.1\%$ ) provided better copper protection than the alkyl-BTA ( $Z = 88.4\%$ ).

The analysis of the CIs ( $C_3$  and  $C_6$ ) and their adsorption films on copper electrodes was carried out by FT-IR spectra. The results showed that their molecules were adsorbed on copper through N atoms. XPS analysis confirmed the conclusions drawn from the FT-IR analysis, since the CIs adsorbed on copper are bound to its surface mainly through the formation of chemical bonds.

BTA has long been known not only as a contact inhibitor, but also a volatile corrosion inhibitor (VCI) of copper and its alloys [55–58]. Though BTA possesses a relatively low saturated vapor pressure ( $p_s = 8 \cdot 10^{-6}$  Torr [56]), it is adsorbed from the vapor-gas phase due to its high reactivity and forms on the surface of oxidized Cu an ultrathin film that can protect the metal or its alloys for a fairly long period in a humid atmosphere [59, 60]. In this application, BTA and its derivatives, if they are sufficiently volatile, are adsorbed on an oxidized surface and, as already noted above, form not only a chemisorption layer but also complex compounds with Cu cations. It is not surprising that such films are also stable under conditions of moisture condensation on the copper surface, including the harsh tropical atmosphere conditions. According to [32], BTA can be chemisorbed from the vapor-gas phase not only on oxidized but also on oxide-free polycrystalline copper.

Note that while this situation is possible, it is very rare in the practice of VCI application. At the same time, Chen and Häkkinen [61] used DFT calculations to study several possible configurations of interaction from the gas phase of BTA with the surface of a Cu(111) single crystal. They came to the conclusion that the formation of a negatively charged complex  $[BTACu(I)BTA]^-$  is optimal. Moreover, all nitrogen atoms in BTA can be bind with Cu atoms, while Cu–N bonds have the smallest average distance when a Cu adatom in the complex is on one of the peaks of the Cu surface. The Cu–N interaction dominates over the adsorption mechanism, and  $[BTACu(I)BTA]$  is energetically preferable than the  $[BTACu]_n$  polymer on Cu(111) that was previously suggested in the references described above. The authors believe that, since the adsorption mechanism does not depend on the density of  $[BTACu(1)BTA]^-$  single complexes on the Cu(111) plane and BTA can be arranged on it at an angle, such layers can be densely packed on the surface. Hence, it is concluded that the protection of copper by these complexes can be effective, and the atomistic mechanism of copper protection by BTA becomes clearer.

A similar point of view was expressed by Grillo *et al.* [62] who also investigated the initial stages of BTA adsorption on a Cu(111) single crystal in ultra-high vacuum. They identified two key factors affecting the structure of adsorption at low surface coverages. Firstly, because of the strong Cu–N interaction, the BTA molecule is deprotonated with the formation of  $Cu(BTA)_2$  and  $CuBTA$  species. Interactions of  $Cu(BTA)_2$  dimers induce their attraction laterally to each other, which leads to the formation of chains. The latter consist of a series of discrete units, the length of which is 3–5 dimers, rather than a continuous organometallic polymer, which, as was suggested earlier, is in some cases

stabilized by the formation of hydrogen bonds. Secondly, the authors believe that the expanded ( $2\times 1$ ) surface reconstruction, which was observed for the initial period, plays a role in the further stabilization of adsorbed particles. In confirmation of this adsorption mechanism, the images obtained by STM are shown, where chain aggregates are visible. The latter are formed from initially adsorbed BTA molecules on edge defects or terrace defects. These results can contribute to a further understanding of the interaction between BTA and copper and, in turn, the mechanism for protecting copper and copper alloys from corrosion.

However, the relatively weak protection of carbon steels by BTA vapours caused the need to apply it not independently, but as part of a mixed VCIs, which is usually patented, and the mechanism of joint action is not disclosed. Mixed VCIs are often used in the form of solutions, powders, inhibited papers, polymer films or other packaging materials. Convenient in practice are silica gels, zeolites and other porous supports pre-impregnated with a VCI or its solution. The use of porous carriers, especially silica gels, is a compromise and a widely used option. Advantages of this method consist not only in the convenience of use and simplicity of production, but also the possibility, if necessary, of a certain “drying” of the space being protected. These methods of VCI application are most convenient for the preservation of large items and containers, packing of which in inhibited papers is hardly advisable [60].

A wide application of BTA for the protection of copper in aqueous and aqueous-organic solutions, or in humid vapor-gas corrosive media in wide range of temperature and pH is associated with the formation of a complex compound  $[\text{Cu}(\text{I})\text{BTA}]$  on its surface. The presence of even a thin layer of  $\text{Cu}_2\text{O}$  on copper can facilitate the formation of such a complex, so the authors of [63] studied the ability of BTA to prevent the oxidation of copper in a low-temperature humid air plasma. To do this, they used a plasma device in which a sliding electric arc is ignited between two electrodes and blown by a gas flow along the axis of the electrodes. This gas is an air-water mixture, and the resulting plasma is of interest because it is a source of strong oxidants ( $\text{OH}\cdot$ ,  $\text{H}_2\text{O}_2$  and  $\text{O}_3$ ). Samples of copper foil carefully polished, washed in ethanol and dried for 4 hours were immersed in 0.1 M BTA solution to form a protective film and then subjected to humid air plasma. It turned out that such a treatment in BTA solution prevented the oxidation of copper by gaseous reagents under such severe conditions for at least 40 minutes. With a longer exposure, the film formed by BTA on the copper surface begins to degrade to  $\text{CO}_2$  and other volatile compounds. The authors suggested to use such tests as a tool for studying the effectiveness of organic inhibitors that form protective films on metals.

In addition to strong oxidizing effects, yet another obstacle is also dangerous to the multifunctional use of BTA for the protection of copper and its alloys, namely, the presence of  $\text{H}_2\text{S}$  or its ions in the corrosive environment. It is known [64] that the presence of even a small amount of sulfides in seawater negatively affects the stability of copper–nickel alloys. In such media,  $\text{HS}^-$  ions successfully compete with BTA in the formation of complexes with  $\text{Cu}(\text{I})$  ions, which leads to the destruction of the protective film of

[Cu(I)BTA]<sub>n</sub> and the appearance of corrosion on exposed areas [65]. It is sufficient to add as little as 0.1 mM HS<sup>-</sup> to a 3.5% NaCl solution containing 10 mM BTA in order to increase the dissolution rate of copper by almost two orders of magnitude. The situation is almost not improved by preliminary copper passivation in a BTA solution. A similar attempt to use BTA to protect α-brass (71.7% Cu, 28% Zn, 0.006% Pb, 0.01% Fe) from corrosion in 0.58 M NaCl by addition of 10 mM BTA failed. The inhibition efficiency Z = 98% deteriorated sharply in the presence of only 0.12 mM S<sup>2-</sup> [66].

In this context, a new method of copper protection in HS<sup>-</sup>-containing media deserves attention [67]. It consists in conducting vacuum pyrolysis of a CI in the presence of copper samples. BTA, *N*-[benzotriazol-1-yl(phenyl)-methylene]-*N*-phenylhydrazine (Azole-2) and *N*-[benzotriazol-1-yl-(4-methoxy-phenyl)-methylene]-*N*-phenylhydrazine (Azole-3) were studied as the CIs. A glass tube inside which Cu samples (99.9%) were placed along with 0.3 g of a CI of interest were sealed and placed in a pyrolyzer, which was brought to *t* = 200°C. After 30 minutes of vacuum pyrolysis, the glass tube was opened and the samples were taken from it. In most cases, both sides of the copper samples were covered with a film formed by a CI. One side was again cleaned to ensure electrical contact, and the other side served as the working surface of the electrode when the polarization curves were recorded in salt water contaminated with sulfides (3.5% NaCl). The test results were compared. It was found that the samples treated in the presence of Azole-2 and Azole-3 had excellent corrosion resistance, since they resisted the “poisoning” effect of HS<sup>-</sup>. BTA demonstrated some stability at low C<sub>HS<sup>-</sup></sub> = 1 mM, but did not withstand higher C<sub>HS<sup>-</sup></sub>, for example, 10 mM.

Microphotographs of the cross-sectional area of copper samples taken with SEM after pyrolysis of CIs showed that the thickness of the compact CI layer in the case of Azole-2 reached 128 μm at maximum, while that of Azole-3 was 59 μm. Unfortunately, the authors limited themselves to evaluating the protective effect by polarization curves, which does not allow us to judge on the longevity of the coatings obtained. At the same time, these experiments showed that if BTA itself is not effective enough, the use of its substituted derivatives can significantly increase the protection of copper.

**Acid media.** Earlier in the review [4] we have already considered studies performed in acidic solutions at the turn of the 20<sup>th</sup> and 21<sup>st</sup> centuries and devoted to certain features of the protection of single crystals and polycrystalline copper with BTA. They mostly studied the protective films formed by CI on copper surface. Even Mansfeld and Smith [68], noting the complete agreement with the results of corrosion inhibition of copper by BTA in a neutral 5% NaCl solution [3, 55], found a significant difference in the thickness of the films formed in a chloride solution with pH 3.0. They assumed that the chemisorption of BTA, which occurs in a neutral solution, does not occur in acid solutions due to the absence of an oxide on the copper surface. Later the authors of [14, 31] noticed that the film formed by BTA on copper in an acid solution is very porous and brittle, and the degree of its polymerization is low.

Unlike neutral media, direct measurement of the adsorption of BTA from a solution in an acid is practically impossible, but an indirect method for its estimation used in [69] deserves attention. In that study, Bastidas made the assumption that the adsorption isotherm can be built using the equation  $\theta = Z/100$ , where  $Z$  is the degree of protection of copper by BTA expressed in percent. In his opinion, this is true under the following conditions: the adsorption centers on copper are distributed uniformly; the adsorption of CI is limited by the formation of a monolayer, and corrosion proceeds uniformly, *i.e.*, there is no local dissolution of the metal. Apparently, the author forgot to mention one more important condition: the CI action is manifested only in blocking of the surface. The necessity of this condition was already explained in [70]. Having obtained the dependence of copper corrosion rate on temperature (25–55)°C in 0.001–0.5 M HCl solutions, he studied the protective effect of BTA in a wide range of its concentrations,  $C_{\text{BTA}} = 0.01$ –100 mM. Analysis of the isotherms obtained with the help of an objective function that takes into account the parameters of the attraction interaction between the adsorbate particles and their configuration made it possible to conclude that out of 12 equations (Langmuir, Temkin, Frumkin, Volmer, Hill-deBour, Parsons, Flory–Huggins, Bockris–Svinkels, *etc.*), the Frumkin isotherm is the most suitable for describing adsorption:

$$BC = [\theta/(1-\theta)] \cdot \exp(-2 \cdot a \cdot \theta), \quad (6)$$

where  $B = 1/55.5 \exp(-\Delta G_A^0 / RT)$  is the adsorption constant, which allows the value of  $(-\Delta G_A^0)$  to be found. It was found that  $(-\Delta G_A^0)$  is slightly dependent on temperature, its largest averaged value is observed in 1.0 mM HCl (28.2 kJ/mol) and the lowest value, in 10 mM HCl (22.0 kJ/mol). From these values it can be concluded that the adsorption of BTA from acid solutions is relatively weak and is most likely physical by nature. Note that the isotherm of BTA adsorption from a borate buffer with pH 7.4 obtained in [71] on oxidized copper is also adequately described by Eq. (6), indicates its chemisorption with  $(-\Delta G_A^0) = 50.5$  kJ/mol.

The value of  $a$  turned out to be more sensitive to temperature and usually decreased with an increase of the latter: for 1 mM and 0.5 M HCl, from 3.60 (25°) to 0.18 (55°) and from 1.51 (25°) to 0.09 (55°), respectively. This indicates a decrease in the attractive interaction between BTA particles in the adsorption layer, even with a slight temperature increase. The effect of  $C_{\text{HCl}}$  is not so unambiguous, but the tendency of  $a$  to decrease with its growth is evident.

To determine the optimal orientation of BTA during adsorption on copper, its landing area was calculated using molecular models. The area occupied by a vertically oriented adsorbed BTA particle, *i.e.*, the area of the rectangle surrounding the molecule projected onto the copper surface is  $\sim 20 \text{ \AA}^2$ , whereas it is  $\sim 38 \text{ \AA}^2$  in the case of horizontal orientation of BTA. The area occupied by a vertically adsorbed water molecule is in the range of 8–12  $\text{ \AA}^2$ , therefore these results were interpreted in favor of the vertical orientation of BTA on Cu, where each BTA molecule replaces several water molecules on the metal surface.

The obvious contradiction of the substitution of more than one water molecule when Frumkin's equation is used was explained by the fact that one adsorption site on the copper surface is occupied by a group of bound water molecules.

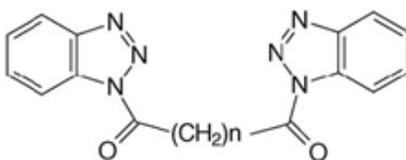
Tommeseani *et al.* [45] who studied the protective effect of films on copper formed by BTA and its 5-alkyl substituted derivatives in 3.5% NaCl with pH 7.0 and 2.5 by means of polarization measurements, showed that the protection effectiveness in an acidic solution is much lower. However, as the alkyl length increases, the effect of the solution pH decreases, but only 5-hexyl-BTA strongly reduces the anodic dissolution of copper. Therefore, with increased hydrophobicity of BTA derivatives, the pH range of corrosive media in which they provide effective anti-corrosion protection of copper broadens, although the mechanism of action of such CIs can vary significantly. Indeed, according to [72], BTA and its 5-derivatives with  $R = \text{Cl}, \text{CH}_3$  inhibit the corrosion of copper in 0.1 M HCl with efficiency increasing along with  $C_{\text{in}}$ . The protective effect of CI increases in the series  $\text{BTA} < 5\text{-methyl-BTA} < 5\text{-chloro-BTA}$ , *i.e.*, in the same series as their hydrophobicity.

A good example of the correctness of this conclusion is brought by the results of a study of the inhibitory effect of a mixture of octyl esters of 4- and 5-carboxybenzotriazole, OE4(5)K-BTA with respect to copper in aerated 0.5 M sulfate solutions with pH 0–8 [73]. Corrosion tests showed that at pH 0, the protection efficiency of the mixture was  $Z \sim 98\%$  at  $1 \cdot 10^{-4}$  M. This is significantly higher than for BTA under similar conditions ( $Z \sim 50\%$ ). At pH 8, the efficiency of protection is still significant (75%), which indicates the possibility of using the mixture to inhibit copper corrosion in a relatively wide pH range, unlike BTA. In this region, the hydrolysis of esters was not observed. Surface investigation by the SERS method allowed the authors to conclude that, at low pH, esters, like BTA, inhibit copper corrosion due to the adsorption of protonated particles  $[\text{OE4(5)K-BTAH}_2]^+$  through the nitrogen of the azole ring. They explained the enhanced inhibition at low pH by van der Waals attraction forces between the neighboring octyls oriented away from the copper surface. They also believe that with a higher  $C_{\text{in}}$ , chemisorption changes to precipitation of a polymer complex which, unlike the BTA complex, is not as effective in copper protection as adsorbed  $(\text{OE4(5)K-BTAH}_2)^+$ . Polarization curves of copper also confirmed the fact of the change in the protection mechanism with increasing pH.

The same authors [74] showed that coatings obtained by copper immersion in solutions of mixture of isomers of 4- and 5-carboxy-BTA esters, in which  $\text{Alk} = \text{CH}_3; \text{C}_4\text{H}_9; \text{C}_6\text{H}_{13}; \text{C}_8\text{H}_{17}$ , and then dried, have a protective ability in strongly acidic (pH 0) and close to neutral (pH 8.0) solutions of sulfates. Their effectiveness depends on the solvent from which the coatings were formed, the solution temperature, and the duration of copper immersion in this solution. Preliminary treatment of copper by immersing its samples for 2–3 hours in a hot (70°C) aqueous solution with  $C_{\text{in}} = 0.1$  mM gives the best protection. At a higher temperature and immersion duration of copper, the use of ethanol or acetone as a solvent reduces the protection effectiveness.

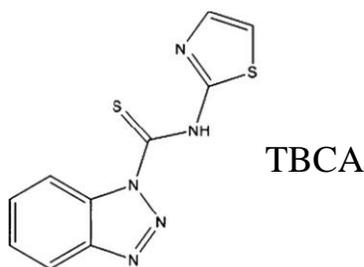
In both acidic and neutral sulfate solutions, the efficiency of corrosion inhibition by the protective film increased with increasing chain length of the ester alkyl in the following order: methyl < butyl < hexyl < octyl. It was established by the EIS method that the protective film formed by the octyl ether maintains stability for 3 days in the acid medium and for 10 days in a neutral medium. Protective films also prevent the tarnishing of copper during short-term (1 min) immersion of dried samples into a solution containing 100 mg/l of Na<sub>2</sub>S, followed by quick rinsing of the electrode with water and then cathodic reduction in 0.1 M CH<sub>3</sub>COONa. In this case, the inhibition efficiency increases with the length of the alkyl chain. In all studies, only the methyl ether was slightly inferior to the effectiveness of copper protection by BTA itself, while 5-carboxy-BTA octyl ester the was best CI.

Zhang *et al.* [75] investigated the effect of a novel CI, bis-(1-benzotriazolyl-methylene)-(2,5-thiadiazolyl) disulfide (BBTD) on the corrosion of copper in 3% NaCl and 0.5 M HCl. The results show that BBTD is a more effective CI in 3% NaCl than in a 0.5 M HCl solution. Being a mixed-type CI, it slows down the anodic dissolution of copper more strongly than the cathodic reaction rate, therefore it increases the  $E_{\text{cor}}$  in both solutions. FT-IR spectroscopy showed that BBTD prevents corrosion of copper due to adsorption on its surface and formation of a protective complex with Cu(I). Later, the same authors synthesized and then studied the protective properties of three new CIs for copper protection in 0.5 M H<sub>2</sub>SO<sub>4</sub>. These inhibitors had the general formula [76]:



The best efficiency was shown by bis-(1,1'-benzotriazolyl)- $\alpha,\omega$ -succinyl diamide (BSU),  $n = 2$ . The CIs with  $n = 4$  and 6 are less effective than BSU and even BTA, for which the degree of copper protection is  $Z = 78\%$  at  $C_{\text{in}} = 1.0$  mM. Addition of 0.5 mM BSU to the same solution gives  $Z = 85\%$ , and with an increase in pH to 5.0 it improves to 95%. The authors explained the high effectiveness of BSU by the conformation that is convenient for the formation of a protective layer (in its molecule, two benzotriazolyl units are oriented parallel to each other).

Khaled [77] studied the effectiveness of *N*-(2-thiazolyl)-1*H*-benzotriazole-1-carbothioamide (TBCA) as a non-toxic CI for copper in 0.5 M HCl by gravimetric and electrochemical methods. He showed that the TBCA is a mixed type CI. According to molecular simulations and quantum chemical calculations, the protection mechanism is associated with the adsorption of TBCA that is accompanied by the formation of hydrogen bonds of the CI with the Cu surface, which is apparently partially hydroxylated.



EIS measurements showed a wide peak, presumably because of more than one time constant in the presence of TBCA. In addition, it was found that with increasing  $C_{in}$ , the values of CPE (constant phase element) tend to decrease, while the inhibition efficiency increases. Direct corrosion tests confirmed this:  $Z$  increased from 51.4% to 72.4 and 96.4% with a growth in  $C_{in}$  from 0.01 to 0.5 and 50 mM, respectively.

Later, several BTA derivatives were synthesized and studied as CIs for copper in 1.0 M  $HNO_3$  (benzotriazole-1-carboxamide (BCA), 1*H*-benzotriazole-1-acetonitrile (BAN), benzotriazole-1-carbonyl chloride (BCCh) [78]; and *N*-(2-thiazolyl)-1*H*-benzotriazole-1-carbothioamide (TBCA), *N*-(furan-2-ylmethyl)-1*H*-benzotriazole-1-carbothioamide (FBCA) and *N*-benzyl-1*H*-benzotriazole-1-carbothioamide (BBCA) [79]. In the first CI group, BCA was the most effective and BCCh was the weakest, but they, according to the authors, are superior to BTA in protective capacity. For example, 5 mM BCA provides a high level of copper protection:  $Z = 93.5\%$ , but at this  $C_{in}$ , even for BCCh,  $Z = 85.0\%$ . In the second group, at  $C_{in} = 5$  mM, the best CI, *i.e.*, TBCA, provides  $Z = 97.4\%$ , and the least effective BBCA provides  $Z = 89.7\%$ . Khaled *et al.* believe that the best BTA derivatives are able to be chemisorbed on copper from a solution of such a strong acid, but in our opinion, additional studies are needed to obtain proof of this assumption.

In conclusion of this part of the review, it can be noted that BTA itself is not an effective CI for copper in acid media, and it is no coincidence that it is not only unused in relatively concentrated mineral acids, but is even almost not studied. However, BTA exhibits inhibitory properties in dilute acids and high efficiency in neutral media, including that in the atmosphere, which allows its wide application independently or in combinations with various additives that enhance the protection of copper.

A method for producing an electrically conductive coating of polypyrrole (PP) on copper in 0.1 M oxalic acid solution suggested in [80] is an interesting example. In this method, to improve copper protection against corrosion by a PP film and to reduce its corrosion during the film synthesis, BTA was added to an aqueous acid solution containing the pyrrole monomer. BTA added to the solution prior to the initiation of anodic polymerization covered the electrode with a layer of a BTA–Cu complex that prevented copper dissolution. The polymerization deposition of PP on a copper surface, which started when anodic current was turned on, was no longer so aggressive, and the resulting film was uniform in thickness and had excellent adhesion to the electrode. Since it contained

BTA, it protected copper from corrosion in 3.5% NaCl as well: for 400 hours of electrode exposure to a corrosive neutral solution, copper dissolution was inhibited by 80%.

Significantly more efficient CIs were found among BTA derivatives, at least in 0.5–1.0 M HCl, H<sub>2</sub>SO<sub>4</sub> or HNO<sub>3</sub> solutions. It is interesting that, unlike in neutral media, in acid media, for example, in distilled water adjusted to pH 3.0 with 0.1 M HCl, the initial presence of an oxide film on the bronze surface, which approximates the experimental conditions to real preservative treatment, does not contribute to its protection against BTA corrosion, and conversely, it slows down its chemisorption on the bronze surface [81]. This is important and should be taken into account in activities for preservation of the cultural heritage such as products made of copper alloys, since treatment with BTA solutions does not remove copper chloride from the artifact. It is more likely that it forms a barrier between copper chloride and a humid atmosphere. BTA forms an insoluble complex compound with copper ions, which is a barrier against any moisture. As a result, there is no activation of copper chloride, which can cause the destruction of bronze.

### III. Zinc

The use of BTA and its substituted derivatives for zinc protection is of course less common for a number of reasons. One of them is that it has excellent resistance under natural conditions. According to [82], that is why nearly half of the world's zinc consumption falls on coatings for the protection of steel products in atmosphere and water. Another reason is that zinc and galvanized steels are often passivated by additional treatment with converters to increase their corrosion resistance. In the 20<sup>th</sup> century they were treated with toxic Cr(VI) compounds, which for several decades are being replaced by less environmentally hazardous P- or Si-containing organic passivators, as well as inorganic reagents [83]. In addition, Leroy [84], while considering the chelating CIs for zinc, mentioned BTA among them, but noted that in this case there is “significant but not exceptional protection to zinc” and it is inferior in effectiveness to 2,5-dimercapto-1,3,4-thiadiazole and thioglycolic acid esters.

It should be added that zinc, unlike copper, is not used as a conductor for various electronic devices where only ultra-thin protective coatings are often allowed. However, the authors of [85] suggested that the formation of Zn<sup>2+</sup>(BTA<sup>-</sup>)<sub>2</sub> complex on zinc surface can improve the resistance of this metal to corrosion and oxidation in the atmosphere, making zinc treatment with a BTA solution an alternative to traditional technologies in electromechanical engineering, and possibly for future applications in electronics. They found by XPS that BTA reacts with ZnO to form a Zn<sup>2+</sup>(BTA<sup>-</sup>)<sub>2</sub> complex, which has the same structure as Cu<sup>2+</sup>(BTA<sup>-</sup>)<sub>2</sub>. XPS studies in combination with ellipsometry have shown that a layer of ZnO and Zn<sup>2+</sup>(BTA<sup>-</sup>)<sub>2</sub> with a thickness of about 2 nm is formed on zinc surface treated with an alcohol solution of BTA (10 g/100 ml of C<sub>2</sub>H<sub>5</sub>OH). The authors believe that such a layer is sufficient to ensure good protection of zinc due to the stability of this complex. They found a good agreement between the thickness of the surface layers

calculated from the intensity of the XPS peak and ellipsometry, which respectively amounted to 0.4 nm  $\text{Zn}^{2+}(\text{BTA}^-)_2$  layer on 0.6 nm ZnO and 0.5 nm  $\text{Zn}^{2+}(\text{BTA}^-)_2$  on a layer thicker than 0.5 nm ZnO.

However, such an analogy between BTA complexes with copper and zinc cations should be drawn carefully, since in the first case the protection is due to the formation of a Cu(I) polymeric complex rather than a Cu(II) complex. Notoya *et al.* [15] studied by ToF SIMS the surface composition of Cu, Ag, Zn, Ni, and Fe pretreated with BTA. It is no coincidence that they discussed the results of the study in terms of the relationship between the degree of polymerization of the BTA–metal compounds formed and the corrosion inhibition efficiency determined by measurements of the polarization resistance for metals in a solution containing 0.01 M BTA and 0.1 M NaCl. It turned out that the inhibition efficiency decreased in the series  $\text{Cu} \gg \text{Ag} \gg \text{Zn} > \text{Ni, Fe}$ , which corresponded to the order of decrease in the degree of polymerization: the higher the degree of polymerization, the higher the inhibition efficiency.

Aramaki [86] found that in an aerated 0.5 M NaCl solution, BTA forms on Zn a film of a presumably polymeric  $[\text{Zn}(\text{BTA})_2]_n$  complex. He used XPS to analyze zinc surface after immersing it for 3 hours in a solution containing 1.0 mM BTA. A difference in the binding energies  $E_b$  of electrons of the Zn  $2p_{3/2}$  peak in the spectrum of the complexes formed on zinc upon BTA adsorption ( $E_b = 1022.4$  eV) and the complexes synthesized in a solution containing BTA and  $\text{Zn}^{2+}$  cations ( $E_b = 1021.7$  eV) was observed. It was shown that BTA exhibits high protective properties at  $C_{\text{in}} > 0.1$  mM that exceed those of 8-hydroxyquinoline or sodium benzoate, however it is inferior to sodium *S*-octyl-3-thiopropionate.

Fenelon and Breslin [87] compared the behavior of copper and zinc in acidic and neutral solutions of chlorides upon BTA addition. They paid special attention to the analysis of the results obtained by the EIS method and found evidence of the formation of a polymeric layer of a complex on zinc, although they noticed that it occurs more slowly than on copper.

Pickering *et al.* [88] used the quartz crystal electrochemical microbalance method (EQCM) to study the inhibition of the corrosion of galvanic zinc coatings by BTA in acid  $\text{Na}_2\text{SO}_4$  solutions. They found that BTA preferentially slows down the anodic dissolution of zinc. In a stagnant solution, the limiting stage of corrosion is the diffusion of dissolved oxygen to the electrode surface, so BTA slightly reduces the rate of corrosion. If air is bubbled through the solution, the corrosion rate increases significantly. In the solution deaerated by bubbling with nitrogen, the corrosion rate is controlled by the charge transfer process, and the inhibitory effect of BTA increases significantly.

Milošev *et al.* [89, 90] used EIS and XPS to study the surface layers formed on copper, zinc and Cu–10Zn, Cu–40Zn alloys in 0.5 M NaCl solution containing BTA. They confirmed the effectiveness of BTA in protecting not only copper and zinc, but also the above alloys, attributing this effect to the formation of a mixed polymeric structure of

Cu(I)BTA and Zn(II)BTA complexes. In addition, it included the Cu<sub>2</sub>O and ZnO oxides, as confirmed by a study of the in-depth profile of the layers formed.

When considering the joint use of zinc and BTA, its important role in the progress of the development of self-healing “smart” coatings should be noted. It was shown rather recently [91] that the properties of an active protective coating can be improved using the nanocontainers of ZnO with BTA assembled stepwise. The authors synthesized nanocontainers for the CI by the LbL (layer by layer) method of assembling oppositely charged polyelectrolyte species and BTA proposed previously by Shchukin *et al.* [92], but changed SiO<sub>2</sub> nanoparticles by ZnO in this method. The selection of ZnO as the inorganic core of the assembly was dictated by its notable advantages over other oxides (anticorrosive action on mild steels, semiconductor properties, low cost, environmental safety, *etc.*). Polyaniline and a polyester of polyacrylic acid were used in the assembly of the container, and BTA was encapsulated in the prepared nanocontainer assembly into which it was trapped in a shell between the layers. The performance of nanocontainers was studied in a corrosive environment after they were introduced into an alkyd resin. If the alkyd coating on mild steel was damaged, its anticorrosive properties remained effective due to BTA exit from the nanocontainers.

In the protection of zinc or galvanized steel, like in the case of corrosion inhibition of other metals, BTA can be used in combination with other CIs, but there are few scientific publications on this subject. It seems that this information can be found in patent literature. Of the greatest interest are mixtures based on BTA that have a high protective ability with respect to several metals. Such an example is given by a combination with Na<sub>3</sub>PO<sub>4</sub> studied by Liu *et al.* [48, 91, 92] for the corrosion inhibition of copper, carbon steel and zinc. The mixture of the nearest BTA analogue, 3-methyl-BTA (TTA), with sodium heptanoate CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>COONa shows a synergism in zinc protection, which according to [93] is due to co-precipitation of water-insoluble Zn<sup>2+</sup> compounds with CI components. It was found that heptanoate anions preferably slow down the anodic dissolution of zinc, forming a hydrophobic layer of the zinc salt, while TTA slows down the cathodic reduction of O<sub>2</sub>. Measurements of the polarization resistance, polarization curves, and changes in electrode mass by the EQCM method showed a sharp decrease in the corrosion rate and stabilization of the passive state of zinc, which persists even at  $E > 1.0$  V, upon addition of 0.25 g/l TTA to a 0.05 M CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>COONa solution. Practically deposited on the Zn surface, the layer suppresses the formation of “white rust” and creates an effective barrier against O<sub>2</sub> penetration into the metal and reduces its reduction rate. The authors believe that TTA molecules are incorporated into the zinc heptanoate layer, probably in the form of Zn(TTA)<sub>2</sub>, which explains the high efficiency of this formulation.

It should be noted that the BTA derivatives have been little studied on zinc, in contrast to copper protection discussed above. Meanwhile, some of them may be more effective CIs for zinc since, like BTA, they can form thin protective films on it. This is indicated by the results of XPS studies on the composition of the surface layers formed in borate buffer with pH 7.4 containing 5-chloro-BTA [39].

It was found that 5-chloro-BTA forms a monomolecular layer on oxidized copper and zinc surfaces that is not washed away even in 15 minutes of ultrasonic washing in water. The anions form a self-assembled layer where the molecular planes can be arranged in parallel or at some angle to each other, and adsorption occurs due to the formation of coordination bonds between the metal cations and the unshared pairs of electrons on the N atoms. Naturally, the packing density on the surface of oxidized polycrystalline samples can vary, nevertheless, if the specific density of the layer is assumed to be the same as in a BTA crystal (with allowance for the contribution of chlorine), the thickness of the layer is comparable to the molecule length. Calculation of the spectra (using the MultiQuant program) made it possible to estimate the thickness (with elimination of  $\sim 1.5$  nm for the contamination layer) as  $0.6 \pm 0.3$  nm for 5-chloro-BTA and  $2.7 \pm 0.5$  nm for  $\text{Zn}(\text{OH})_2$ .

The formation of a 5-chloro-BTA film on oxidized zinc, like on copper, does not end with the formation of only a monomolecular layer. It can be assumed that on the first chemisorbed layer of Cl, through which  $\text{Zn}^{2+}$  diffuses, a complex appears that has either polymeric nature or is poorly soluble. Unfortunately, XPS analysis does not allow one to determine the deviation of the molecule plane from the vertical orientation. However, the authors assumed that the layer density increases a little if the molecular planes are slightly inclined. Such a dense package assumes a  $\pi$ - $\pi$  interaction between the benzene rings, which should contribute to the stabilization of the monomolecular layer.

#### IV. Alloys of copper and zinc

We have already mentioned the protective properties of BTA and its derivatives with respect to certain Cu–Zn alloys. The effectiveness of protection of Cu alloys by these CIs depends significantly on their composition. For example, the possibility of weak protection of Cu–Zn brass from dezincification in chloride solutions by BTA was reported repeatedly [96, 97]. However, in 3% NaCl it is effectively inhibited by BTA derivatives (1-hydroxymethyl-BTA or *N*-[1-(benzotriazol-1-yl)-methyl]-aniline) [97], but in 0.5  $\text{H}_2\text{SO}_4$  both BTA and 1-[*N,N*-bis-(hydroxyethyl)aminomethyl]benzotriazole, which exceeds the former in protective properties, did not prevent the dezincification of 60/40 brass [98].

As a rule, BTA and its substituted derivatives better protect bronze than Cu–Zn alloys. For example, it was known for a long time [99] that  $\alpha$ -Al-bronzes have good strength properties and excellent resistance to erosion, cavitation and impingement attack. However, a single-phase  $\alpha$ -Al-bronze (Cu–7% Al) in saline water (3.4% NaCl) undergoes severe corrosion, although it is less susceptible to dealumination than similar two-phase bronzes containing more than 9% Al [99]. Ashour *et al.* [100] found that in this environment, BTA is able to completely suppress the corrosion of single-phase  $\alpha$ -Al-bronze at  $C_{\text{in}} = 20$  mM, and even 10 mM BTA reduces its rate 37.5-fold in 45-day tests. Unfortunately, as mentioned above, in the presence of even small amounts of sulfide ions in chloride solutions, BTA can dramatically reduce the protection of copper alloys [66].

In this context, it is interesting to recall the results of studies on the corrosion resistance of ancient Etruscan bronzes carried out almost half a century ago by Trabanelli *et al.* [101]. They tested bronze plates and fragments of a Gallic cup covered with natural patina. Before placing into a chamber with 100% relative humidity containing 1% H<sub>2</sub>S, some of them were treated with a BTA solution in benzene. After 72 hours of testing the fragments that were not treated with BTA blackened and their corrosion was so severe that patina changed completely. In contrast, the fragments treated with the CI retained the natural patina color, and the areas without the patina retained their metallic luster. The action of the CI on the bronze plates was not quite distinct, though the conclusion was reached that the additive had some degree of efficiency even in the presence of such a high C<sub>H<sub>2</sub>S</sub> that is never found in practice. It should be noted that, apparently, the presence of H<sub>2</sub>S in low concentrations in a humid atmosphere is less dangerous than in an aqueous solution.

Substituted BTAs can be much more effective than BTA itself in protecting of not only copper but also various bronzes. Brunoro *et al.* [102] studied the protective effectiveness of BTA derivatives, predominantly 5-alkyl-BTA, on 4 bronzes (5.4–10.6% Sn, 0.0–5.1% Zn), by films formed in 0.10 mM aqueous hot solutions (60°C) of these compounds under an acid rain (pH 3.1). These alloys are close in composition to the bronzes used in antiquity for making coins, furniture and statues. The best results were obtained with 5-octyl-BTA, whose long alkyl provided a high protective effect. The authors attributed it to the high hydrophobicity of the film, rather than to the film thickness as such.

However, as it was established later [103], it is more effective to use acrylic varnishes containing small amounts of BTA for protection of bronzes against corrosion in an open atmosphere. To prolong the action of the coating, it is further treated with a wax that gives it hydrophobic properties. According to the authors, an increase in the protection of sculptural monuments from tin bronzes by treatment with an emulsion of microcrystalline wax in an organic solvent can be achieved by addition of 5 mM BTA and 1 mM 5-hexyl-BTA to it.

It was concluded in the review [8] that BTA and its derivatives are the most widely used CIs for conservation of the world's cultural heritage since they are very effective in protecting copper from atmospheric corrosion. However, it was noted in [102] that BTA proved to be much less effective in protecting bronzes than copper due to the presence of Sn and Pb in them, for which BTA is a weak CI. In addition, BTA and some of its derivatives do not always comply with the increased environmental requirements [104–106]. In view of this, a search for more environmentally friendly CIs, at least not inferior to BTA in the effectiveness of bronze protection, was performed in recent years. According to [107], 3-mercaptopropyltrimethoxysilane can be regarded as such an inhibitor.

Copper alloys with Ni, Fe and Co constitute another type of copper alloys widely used in heat exchange equipment. In our laboratory, the adsorption of BTA and 5-chloro-BTA

in borate buffer with pH 7.4 on the MNZh 5-1 alloy (90.6–93.7% Cu, 5.0–6.5% Ni + Co, 1.0–1.4% Fe) was studied by ellipsometry [108, 109]. It was shown that the adsorption of 5-chloro-BTA on MNZh 5-1 surface is of polymolecular nature with a ( $-\Delta G_{a,\max}^0$ ) value of 80.6 kJ/mol for the first monolayer, which exceeds by 18 kJ/mol the same value for BTA and by 19 kJ/mol for this BTA derivative on copper. It is not surprising that 5-chloro-BTA stabilizes the passive state of MNZh 5-1 alloy in borate buffer with pH 7.4 containing 10 mM NaCl even at  $C_{in} = 0.12$  mM. In 3% NaCl, even 5 mM of BTA reduces the corrosion rate of the alloy only 2.1-fold, while 5-chloro-BTA slows it down 12.5-fold at  $C_{in} = 2.0$  mM and practically suppresses corrosion of the alloy at  $C_{in} = 3.0$  mM.

When considering the protective properties of BTA and its substituted derivatives for multicomponent alloys, it should be noted that they depend on the duration of experiments, especially in electrochemical measurements. In this context, the dynamic electrochemical impedance spectroscopy method (DEIS) successfully developed by Darovitsky [110, 111], including its application for the corrosion protection of brass by BTA [112, 113], deserves attention. It is based on an estimation of the electrical parameters of the equivalent circuit in time and allows tracking the dynamics of the alloy corrosion and its inhibition. Spectra of instantaneous impedance automatically recorded for 10 hours prove that exposures for 2–3 h are insufficient for the determination of the protection effectiveness. For example, a study of the behavior of MM55 brass using DEIS in artificial seawater in the presence of various BTA concentrations has shown how the charge transfer resistance ( $R_{ct}$ ) changes with time. The usefulness of investigating nonstationary phenomena is that allow one to obtain evidence not only of inhibition of brass corrosion with BTA, but also of the increase in the protection efficiency with increasing  $C_{in}$  [113].

## Acknowledgements

This review was financially supported by the Russian Science Foundation (RSF), grant no. 17-13-01413 “Fundamental aspects of formation of ultrathin passivating films from organic compounds in protection from atmospheric corrosion”.

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