

# PROTECTION OF COPPER AND ITS ALLOYS USING CORROSION INHIBITOR-LITERATURE REVIEW

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**Abstract:** A review of the literature dealing with the electrochemical corrosion of copper and its alloys with purpose to find the most suitable inhibitor for its protection has been done. According to their chemical composition of corrosion inhibitors are divided into inorganic and organic inhibitors. Inhibition of alloying metals are possible (such as the addition of arsenic alloy components in brass, preventing its un-zincing). The paper reviews the theoretical basis of application of inhibitors to protect metals from corrosion as well as an overview of current research application of inhibitors to protect copper and copper alloys. Benzotriazole (BTA) is most often used corrosion inhibitor for copper and its alloys in acidic and alkaline solution, because of its high inhibition efficiency. The lowest concentration of inhibitor for protection of copper in various solutions was 0.05%, and for the protection of copper in contact with steel is 0.1%. On the surface of copper and brass BTA forms a protective Cu-BTA film. However, BTA is like many other synthesized organic inhibitors is very toxic and if used in very small concentrations. It turned out that the AETD, AETDA and PTAT good corrosion inhibitors of copper mixed type with the efficiency of inhibition increases with concentration. Due to the adverse effects on the environment, health and other bodies in recent times the focus of research is transferred to the inhibiting action of biological molecules or mixtures of natural compounds called „Green inhibitors“.

**Key words:** corrosion inhibitors, protection of metals, inorganic inhibitors, organic inhibitors, alloys elements, green inhibitors

## Introduction - theoretical basis

Inhibitors are now used for the corrosion protection of metals, production and refining of oil, the heat exchanger, energy facilities, conservation of machinery, missile technology, machinery and other industries. Under inhibitors are substances which include the introduction of the corrosive environment, usually in small quantities, can greatly reduce the speed of electrochemical corrosion of metals and alloys (Mattsson, 1991).

According to their chemical composition of corrosion inhibitors are divided into inorganic and organic inhibitors. According to the mechanism of their effects on the electrochemical corrosion process of corrosion inhibitors, are divided on the anode, cathode and mixed. With his adsorption, corrosion inhibitors slow down the process of anodic or cathode electrochemical corrosion of metals and simultaneously slow down the anodic and cathode corrosion process (Mattsson, 1991). By its nature, corrosion inhibitors are chemical compounds that are adsorbs on the surface of metals.

Requirements that a substance must meet to be inhibitor are as follows ([www.corrosion-project.info](http://www.corrosion-project.info)):

In case of inorganic substances, it must have the possibility of oxidation of metals, creating a passive layer on its surface that protects it from corrosion

Molecules of organic compounds should be structurally high, have  $\pi$  bonds, have the active center or group.

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These properties give the molecules ability to cover large areas of the metal to the firmly-related layer.

In the presence of inhibitors, which slow down only anodic process of corrosion, corrosion rate decreases due to the reduction transition speed of metal ions in solution or reduction of surface anodic metal parts because of formation insoluble protective membranes on them. In the presence of anodic inhibitors, anodic polarization curves of metals are changing (Fig. 1), and increased anode polarization of metals (Mattsson, 1991). Anodic corrosion inhibitors are the in first line oxidant (nitrate, nitrite), inorganic ions of type  $MnO_4^{n-1}$  (Chromate, permanganate, molybdate, phosphate and others), more valent metal cations (copper, ferric and cery ions), and in some cases, oxygen, hydrogen peroxide and other compounds. Certain organic corrosion inhibitors are adsorbs on surface of the anodic metals parts and slow down the anodic reaction corrosion process (Mattsson, 1991; Antonijevic at all, 1998). The action mechanism of anodnic inhibitors corrosion, explains using polarization diagrams in many ways: slowing down the anodic corrosion processes, the influence of equilibrium potential of oxidation agents (inhibitors) at the rate of corrosion of metals, the influence of kinetics of cathodic reactions during corrosion of metals and the influence of density changes in the rate of corrosion of metals .

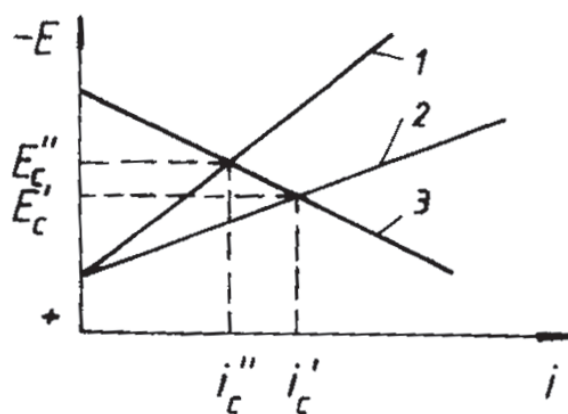


FIGURE 1. POLARIZATION DIAGRAM WHICH SHOWS THE EFFECTS OF ANODNIC INHIBITORS :

1 - WITH THE INHIBITOR, 2 - NO INHIBITOR; 3 - CATHODE BRANCH (MATTSSON, 1991; ANTONIJEVIC AT ALL, 1998)

Anodic corrosion inhibitors, present in the corrosion solution, which slightly affected the course of cathodic polarization curves, and characteristic changes caused by anodic polarization curve, increasing the tendency of metals for passivation (Fig. 2). In the presence of these inhibitors significantly reduce the passive critical current density  $i_p^0$  and metal dissolution current density in the passive state  $i_{pp}^0$ , or the potential of start and end passivation ( $\varphi_p^0$  i  $\varphi_{pp}^0$ ) significantly move in the negative area, while potential of transpassive state  $\varphi_{tp}^0$  becomes more positive. This group of anodic inhibitors belong inhibitors that increase the tendency of metals to passivation by the reduction of active surface anodnic metal parts (phosphate in relation to the iron and steel), by ions adsorbtion of oxidation agent on the surface of metals (chromate in neutral solutions), increasing the speed of chemosorbtion oxygen or chemical oxidation metal surface (poly phosphates, silicates, borate, and others). The principle of action of this group anodic inhibitors is shown by polarization diagram (Fig. 2) (Antonijevic at all, 1998).

Anodic curve  $\varphi_A^0 - A$  refers to a system that difficult subject passivates. Adding inhibitors which slow down the process of anodic polarization curve of anodic metal taking shape  $\varphi_B^0 - B$  with lower density  $i_p$  i  $i_{pp}$  and a larger area of the passive state  $\varphi_p - \varphi_{tp}$  but in the absence of inhibitors. In this case, regardless of which do not affect the cathode process, inhibitors of this type of translation from the active sheet metal with the corrosion current density  $I_c^0$  in a state which the metal dissolves to a slight density  $I_c$  the potential  $\varphi_c$ .

Inhibiting oxidation of characters that directly or significantly affect the kinetics of the process anode and cathodes reduce the polarization process, the corrosive potential of moving metal in the passive state. The mechanism of action of these inhibitors is explained polarization diagram in Fig. 3 (Mladenović at all, 1985).

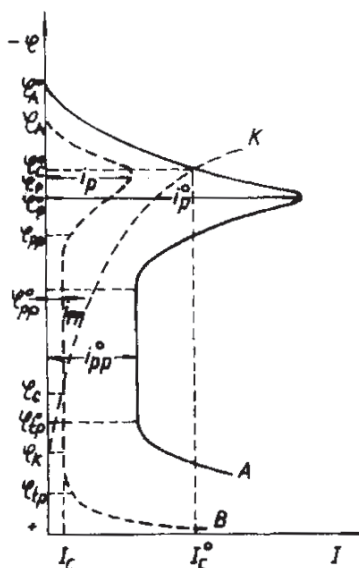


FIGURE 2. POLARIZATION DIAGRAM THAT EXPLAINS THE ACTIVE MECHANISM OF ANODIC INHIBITORS WHICH SLOW DOWN THE ONLY ANODIC PROCESS OF CORROSION:

$I_c^0$  - CURRENTS IN THE ABSENCE OF METAL CORROSION INHIBITOR;

$I_c$  - CURRENTS IN THE PRESENCE OF CORROSION INHIBITORS (ANTONIJEVIĆ AT ALL, 1998)

Anodic polarization curve of metal  $\varphi_A^0 - A$  (Fig. 3) remains unchanged by adding the inhibitor. Cathodic polarization curve of the reduction agent  $\varphi_K^0 - K^0$  after adding the inhibitor goes to curve  $\varphi_K^0 - K$ ; in this case the electrode potential corrosion agent  $\varphi_K$  is positive, and overstrain the reduction agent korozije smaller. By adding this kind of translation inhibitors to metal in the passive condition was stable compared to the initial state. If these inhibitors are added at a reduced rate, cathodic polarization curve of a stream  $\varphi_K - K'$ , corrosion of metals is becoming more intense and runs with power density  $I_c$ . More valent cation ions, in acidic media: ions oxidation character (nitrites, nitrates), reducing process polarization of cathodes in metal corrosion. When inhibitors of characters that slow oxidation process of anodic depolarization process cathodes, intensity effects of inhibitors on the process passivate of metal is determined by the size of the equilibrium potential oxidation agents cathodic reaction kinetics and density changes in the rate of corrosion inhibitors of metals.

The first necessary condition, for reducing the metal corrosion speed, by introduction of inhibitor in the solution, is that the equilibrium potential oxidation agents be more the positive potential of full metal appssivation  $\varphi_{pp}$  (Fig. 2) but more negative than the potential occurrence of metals at the beginning of his transpassive condition. Since the value of oxidation current density changes depends on resources and their ability to passivate metals or slow down the process of corrosion. Greater density changes indicate the low value overstrain of electrode reactions and vice versa.

Oxidant whose density changes little  $j_1$  (Fig. 4) translates into unstable metal active-passive condition. However, the oxidant with a higher current density changes  $j_2$  i  $j_3$  translations of metal in the passive state. In this case establishes the stationary corrosion potential is more negative than the equilibrium potential of oxidation

means  $\varphi_{ox}$ . If the current density changes oxidation agents  $j_4$  greater than passivation current density  $j_3$  establish the corrosion potential  $\varphi_4$  corresponding to the equilibrium potential of oxidation agents.

Partial cathodic polarization curve of anodic inhibitors should be of such a flow curve that cuts metal anodic polarization in its passive state.

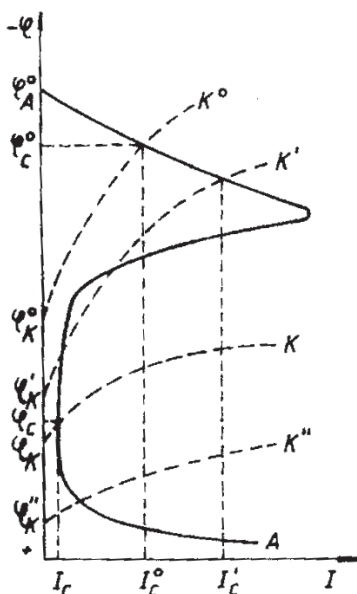


FIGURE 3. POLARIZATION DIAGRAM THAT EXPLAINS THE EFFECTS OF ANODIC INHIBITORS THAT REDUCE THE POLARIZATION OF CATHODES IN THE PROCESS OF CORROSION:

$I_c^o$  - CURRENTS IN THE ABSENCE OF METAL CORROSION INHIBITOR;

$I_c$  -CURRENT CORROSION OF METALS IN THE PRESENCE OF HIGHER CONCENTRATIONS OF INHIBITORS (MLADENVIĆ AT ALL, 1985)

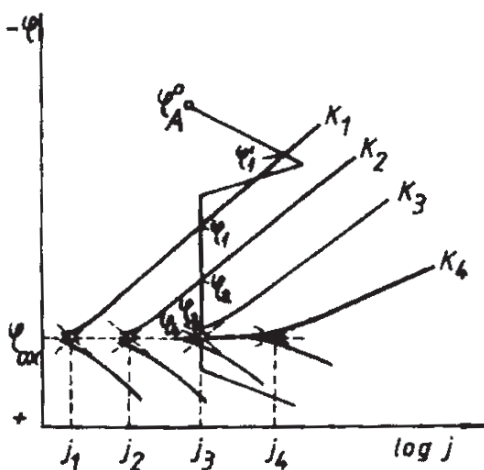


FIGURE 4. POLARIZATION DIAGRAM THAT EXPLAINS THE IMPACT OF CURRENT DENSITY CHANGES ( $j_1 < j_2 < j_3 < j_4$ ) ON THE SPEED OF METALS CORROSION (MLADENVIĆ AT ALL, 1985)

Composition of the corrosive environment also affects the efficiency of protective effect of anodic inhibitors.

Halogenic ions presence, primarily chloride, as well as increased activity of hydrogen ions hinder the translation of passive state of metals. With the increasing aggressiveness of environment increases the current density of passivation, in these conditions, the concentration of anodic inhibitors, it is necessary to passivate metal, is significantly higher, and in some cases it is not possible to translate the metal in the passive condition (Antonijević at all, 1998). Anodic inhibitors may be used only for the protection of metals that can be passivate.

Reducing the speed of corrosion inhibitors using the cathode is based on one of two ways: 1 delayed reaction corrosion cathodic process, 2 reducing the area of cathode metal parts.

Slowing down the process of cathodic corrosion reaction, achieved by increasing overstrain the reduction of corrosion agent (Fig. 5).

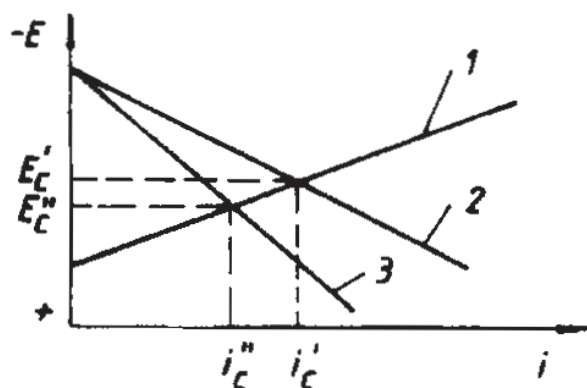


FIGURE 5. POLARIZATION DIAGRAM THAT EXPLAINS THE EFFECTS OF CATHODE INHIBITORS:

1 - ANODE BRANCH; 2 - NO INHIBITOR; 3 - WITH INHIBITOR (MATTSSON, 1991)

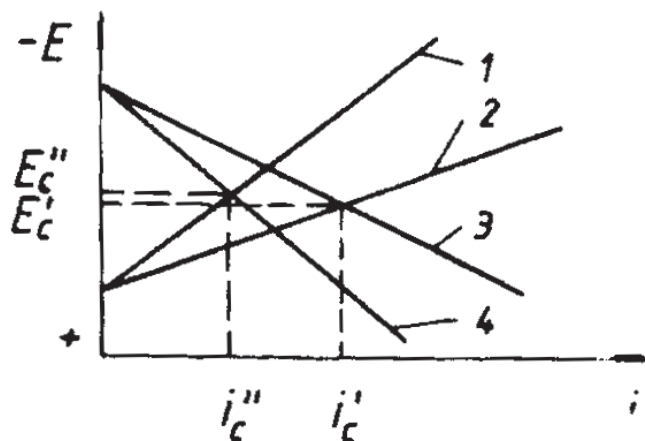


FIGURE 6. POLARIZATION DIAGRAM THAT EXPLAINS THE EFFECTS OF MIXED INHIBITORS:

1,4 - WITH INHIBITOR; 2,3 - NO INHIBITOR (MATTSSON, 1991)

Cathodes in the presence of inhibitor that increases overstrain the reduction agent, metal corrosion potential becomes more negative as the cathodic protection of metals. In the corrosion of metals with

hydrogen cathodes slowing the process is accomplished by adding the solution of some heavy metal salts, such as  $\text{AsCl}_3$  i  $\text{Bi}_2(\text{SO}_4)_3$ ; cations of these salts are reduce on micro catod areas of metals and their separation by increasing overstrain of hydrogen.

Mixed-metal corrosion inhibitors to a greater or lesser degree affect the cathodic and anodic reaction of metal corrosion process (Fig. 6). Many organic inhibitors act as mixed inhibitors. This is an organic compound benzotriazol inhibitor used to protect iron, copper, lead, zinc corrosion in acids; benzotriazol is an effective inhibitor for the protection of copper and its alloys from atmospheric corrosion (Alcibeeva, Levin, 1968).

In his monograph Alcibera and Levin (Antonijevic at all, 1998) gave a short overview of 1545 inhibitors, these views include chemical composition of the inhibitor, its area of application and concentration in which it applies.

Given the very present and extensive atmospheric corrosion of metals, which takes place in the development and use of metal objects and structures, their transport and storage, to protect them from corrosion under such conditions using the inhibitors of atmospheric corrosion (Rozenfeld, Persianceva, 1985).

Atmospheric corrosion inhibitors are divided into contact (unvolatile) and volatile (vapor faze). Contact inhibitors such substance which is made of metal corrosion protection only in their direct contact with the surface metal.

Volatile inhibitors are substances that are relatively easily volatile at normal temperatures, capable for adsorbtion on the surface of metal, particularly in the gap by protecting it from corrosion. Since the surface of metals under conditions of atmospheric corrosion is always moisture under the membrane that runs corrosion, volatile inhibitors should be able to reduce hygroscopic propertis of metal surface or membrane to squeeze out moisture as well as hydrophobic substances.

Inhibitor of the contact number of which is still very big in the industry have found application only nitrites, benzoates, oleate and chromate (Rozenfeld, Persianceva, 1985).

Volatile inhibitors are also numerous, and among them are particularly well-known inhibitors based on amines. Of volatile inhibitors are particularly effective nitrite diciklohexilamine, carbonate and benzoate diciklohexilamine monoetanolamine. The duration of the protective effects of volatile inhibitors depends on the tightness packaging. At the appropriate concentration of inhibitor and total isolation from the outside (cellophane and other impermeable material) objects of ferrous metals are not subject to corrosion for 10 years and more (Šluger at all, 1981). The lack of volatile inhibitors is that, their effects cease after removing their steams from the atmosphere surrounding the metal.

## Literature review of previous studies of copper corrosion inhibitors and its alloys

Copper and its alloys are of great use in modern society because of its high resistance to corrosion, and are often used in refrigeration systems (Muñoz at all, 2004; Sherif, Park , 2006; El-Sayed, Sherif , 2006; Sherif, Park , 2007; El-Sayed at all, 2007). In addition, the copper alloy is widely used in shipbuilding, as well as the development of the petrochemical heat exchangers (Vastag at all, 2001; Zucchi at all, 1996; Mihit a all, 2006; Szócs at all, 2005; Ye at all, 1998).

Because of great importance in industry and large commercial use, the corrosion behavior of copper and brass is the most studied. In particular, we were studying the dissolution of zinc as an integral component alloys (Marconato at all, 1998), then followed by the stress corrosion (Subramanian, Lakshminarayanan , 2002; Ramesh, Rajeswari, 2005; El-Sayed at all, 2007), and lately it attaches great importance to study pitting corrosion as one of the most devastating forms of corrosion (El-Sayed at all, 2007; Lalitha at all,

2005; Naggar, 2000). It is precisely due to the use of brass in aggressive environments was studied a large number of compounds that inhibit the corrosion processes on the surface of brass. Inhibiting corrosion of copper and its alloys are now a significant industrial and scientific research topic (Abdullah, 2006).

Organic compounds are often used as corrosion inhibitors for many metals and alloys (Sherif, Park, 2006; Hao at all 1999; Zhou at all 1997; Zhang at all 2004; Mamas at all, 2005; Yu at all, 2003). Examined the organic compounds from groups: azoles (Guilminot at all, 2000; Zhang at all, 2003; Villamil at all, 2002; Bartley at all, 2003; Pavlović at all, 2004; Faltermeier, 1998; Frignani at all, 1999; Zerbino, 1999), terdenta (Loo at all, 1998), peptides (Bastidas at all, 2003). Also examined are alloy elements: arsenic (Polo at all, 2003; Arancibia at all, 2005; Tromans, Sun, 1991; Tromans, 1998; Matos at all, 2001; Otieno-Alego at all, 1999; Huynh at all, 2002; Zhang at all, 2004), aluminum (Elmorsi, Hassanein, 1999), tin (Elmorsi, Hassanein, 1999), phosphorus (Wu at all, 1993), lead (Jin Lee, 2003), antimony (Tromans, 1998), boron (Stupnišek-Lisac at all, 2002).

In recent years, interest in the combined inhibitors is increased because of their many characteristics that give them certain advantages compared to the cathodic or anodic inhibitors (Larabi at all, 2006; Otmačić, Stupnišek-Lisac, 2003).

Inhibiting action was followed in different solutions. The most commonly used chloride solution (Marconato at all 1998; Guilminot at all, 2000; Zhang at all, 2003; Bartley at all, 2003; Pavlović at all, 2004; Faltermeier, 1998; Zerbino, 1999; Loo at all, 1998; Lee, 2003; Stupnišek-Lisac at all, 1999; Zhao at all, 2006; Quartarone, 2003), since the early observed that chloride ions have a strong influence on the mechanism of corrosion of copper. Of course, there are a large number of papers in which examined the effect of inhibiting compounds in other solvents such as sulfuric acid (Faltermeier, 1998; Sherif, Park, 2006; Sherif, Park, 2005; Hutt, Liu, 2005), solution of nitric acid (Bastidas at all, 2003; Stupnišek-Lisac at all, 2000), sodium nitrite (Ma at all, 2002) the resulting solution in synthetic sea water (Villamil at all, 2002; Ehteshamzadeh at all, 2006).

In their work the researchers used different methods to better and more effectively investigate the structure of the award-winning safety film, stability and solubility of protective film, the efficiency of inhibitors, electrochemical properties of the film formed on the surface of brass.

Benzene three azoles (BTA), tiourea, hydrazine sulfate, DS-3 and EDTA, used to be very effective inhibitors in acid solutions (Mansfeld, Smith, 1973; Weisstuh, Lange, 1971; Kabasakaloglu at all, 2002; Miller, 1969; Abrantes at all, 1984). Inhibitor DS-3 is the inhibitor corrosion of iron and steel in solutions chloro-H-acid, the degree of inhibition of 93%, while HS was a good inhibitor corrosion inhibitor of steel and copper in nitric acid and alkaline solutions, where the degree of inhibition achieved value of 73% to 100% (Abrantes at all, 1984). As a good corrosion inhibitor ferrous metals and copper in acid (HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>) tiourea used, with the degree of inhibition of 65% to 98%, depending on the concentration of inhibitor (Abrantes at all, 1984; Moreton, 1985). Research interest is focused on determining the impact these corrosion inhibitors on corrosion behavior of cold-deformed samples of brass in an acid solution of sodium sulphate, with the addition of chloride ions.

## **Inorganic corrosion inhibitors of copper and its alloys**

The use of inorganic inhibitors as an alternative to organic compounds is based on the possibility of degradation of organic compounds with time and temperature. Studied three different inorganic inhibitors: chromate CrO<sub>4</sub><sup>2-</sup>, molybdate MoO<sub>4</sub><sup>2-</sup> and tetraborate B<sub>4</sub>O<sub>7</sub><sup>2-</sup> whose concentration amounted to 0.033 M in a solution containing 850g/dm<sup>3</sup> LiBr and has pH 6.9. Generally is agreed that effective chromate corrosion

inhibitor that can passivate metal forming monoatomic or poliatomic oxide film on the surface of electrodes, but it is also known to be and promote corrosion effect as cathode reagent. The possible mode of action of chromate reduction or decomposition of the inhibitor on the surface followed by precipitation of metals. Chromate is reduced to Cr(III) hydroxide or oxihydroxide metal surface which leads to a reduction in corrosion current density. But the main drawback is the toxicity of chromium (VI) oxidation states. This gave rise to the search for less toxic alternatives. The logical alternative is a kind of analog six valence chromium molybdate inhibitor that is environmentally friendly. However, molybdate and tetraborate did not show remarkable inhibition. Resistance to corrosion is improved because the film formation is not favored in the electrolyte that contains ions bromidne very aggressive. Inhibition efficiency increases in the following order: molybdate (1.56%)-tetraborate (51.0%)-chromate (78.6%) (Muñoz at all, 2004).

## Organic inhibitors of copper and its alloys

Azoles are a group of organic compounds containing nitrogen atoms, with free e-pairs that are potential sites for bonding with copper, which allows inhibiting effect. Also, there is the possibility of introducing other heteroatoms and groups in the molecules of these compounds and a wide range of products that have proven to be good corrosion inhibitors of copper.

TABLE 1. RESULTS OF THE EFFICIENCY OF COPPER CORROSION INHIBITION USING AETD, AETDA AND PTAT (SHERIF, PARK , 2006; SAYED, SHERIF, 2006; SHERIF, PARK , 2006; SAYED AT ALL, 2007

Solution	Concentration AETD	EI (%)	
0,5M HCl • after 12h exposure	1,0mM	40,00	
	5,0mM	59,00	
	10,0mM	77,00	
3% NaCl	1,0mM	83,00	
	5,0mm	94,00	
Method, solution 3% NaCl	Concentration AETDA	EI (%)	
		Immediately	After 10 day
Weight loss	1•10 <sup>-3</sup> M	60,00	60,00-62,00
	5•10 <sup>-3</sup> M	97,00	97,00-100,00
Potency dynamic polarization; 5•10 <sup>-3</sup> M AETDA	Non aerated	Aerated	Oxygenated solution
	41,00	71,40	87,40
Concentration PTAT 1500ppm; 3,5% NaCl	Covered area		
	After immersion		After 100h
Peaceful solution	0,87	0,97	
Mixed solution	0,71	1,00	

El-Sayed M. Sherif (Sherif, Park , 2006; Sayed, Sherif, 2006; Sherif, Park , 2006; Sayed at all, 2007) examined the influence of 2-amino-5-ethyltio-1 ,3,4-tiadiazoles (AETD) on the corrosion of copper in aerated solution HCl (Sherif, Park, 2006) as and influence of 2-amino-5-ethyltio-1 ,3,4-tiadiazoles (AETD) (Sherif, Park, 2006), 2-amino-5-ethyl-1,3,4-tiadiazoles (AETDA) (Sherif, Park, 2006) i 5-(phenyl)-4H-1,2,4-threeazole-



3-thiole (PTAT) (Sayed at all, 2007) in NaCl solution. It is expected that these compounds show high efficiency of inhibition as heterocyclic compounds containing more donor atoms, in addition to the non-toxic and cheap. It turned out that the AETD, AETDA and PTAT good corrosion inhibitors of copper mixed type with the efficiency of inhibition increases with concentration (Sayed, Sherif, 2006; Sherif, Park, 2006; Sayed at all, 2007; Vastag at all, 2001; Zucchi at all, 1996), time of exposure (Sherif, Park, 2006; Sherif, Park, 2006; Sayed at all, 2007) and the oxygen content (Sayed, Sherif, 2006; Sherif, Park, 2006). AETD molecules, and PTAT AETDA are very adsorbed on copper while forming complexes with copper ions and prevent the formation of the Cu chloride and oxychloride complex. Inhibition efficiency values obtained are shown in Table 1.

F. Zucchi et al. (Zucchi at all, 1996) studied the inhibiting effect of tetrazoles derivatives in 0.1 M NaCl solution. Examined the following compounds: tetrazole (T), 5-mercapto-1-methyl-tetrazol (5Mc-1Me-T), 5-mercapto(Na so)-1-methyl-tetrazol (5NaMc-1Me-T), 5-mercapto-1-acetate acid (Na solt)-tetrazol (5-Mc-1Ac-T), 5-mercapto-1-phenyl-tetrazole (5Mc-1Ph-T), 5-phenyl-tetrazole (5Ph-T) i 5-amino-tetrazole (5NH<sub>2</sub>-T) in range pH from 4 to 8 and in temperature 40 and 80°C. The collected data are shown in Table 2.

TABLE 2. THE EFFICIENCY OF INHIBITION OF TETRAZOLES DERIVATIVES (TEMPERATURE 40°C, pH OF THE SOLUTION WITHOUT INHIBITOR SETTINGS) (ZUCCHI AT ALL, 1996)

Inhibitor	Concentracion	EI%
T	10 <sup>-3</sup> M in solution	53,50
	Exposure to 10 <sup>-3</sup> M solution during 1h and measured after 1h in NaCl	36,80
5Ph-T	10 <sup>-3</sup> M in solution	99,40
	Exposure to 10 <sup>-3</sup> M solution during 1h and measured after 1h in NaCl	1,30
5Mc-1Ph-T	10 <sup>-3</sup> M in solution	98,40
	Exposure to 10 <sup>-3</sup> Msolution during 1h and measured after 1h in NaCl	93,00
5Mc-1Me-T	10 <sup>-3</sup> M in solution	93,40
	Exposure to 10 <sup>-3</sup> Msolution during 1h and measured after 1h in NaCl	25,90
5NH <sub>2</sub> -T	10 <sup>-3</sup> M in solution	85,30
	Exposure to 10 <sup>-3</sup> Msolution during 1h and measured after 1h in NaCl	-4,10
5NaMc-1Me-T	10 <sup>-3</sup> M in solution	66,20
	Exposure to 10 <sup>-3</sup> M solution during 1h and measured after 1h in NaCl	28,00
5-Mc-1Ac-T	10 <sup>-3</sup> M in solution	-110,00
	Exposure to 10 <sup>-3</sup> M solution during 1h and measured after 1h in NaCl	-25,70

All inhibitors except 5Mc-1Ac-T that stimulates showed corrosion inhibition efficiency from 50 to 99%. EI increases with increasing pH and concentration, while temperature has no effect on the effect of different derivatives of some of them has a positive effect, while in other cases decreasing EI. Best protective properties showed 5Mc-1pH-T and 5pH-T. Order by lowering the EI is as follows: 5pH-T>5Mc-1pH-T>5Mc-1Me-T>5NH<sub>2</sub>-T>5NaMc-1Me-T>T. Previous exposure to solution of inhibitor is effective only if 5Mc-1pH-T, while for a long time exposure only in the presence of middle-T 5Ph corrosion attack is observed. Effect of inhibitors is explained by adsorption on the surface of copper and building complex with copper.

Studied the impact of adding 1-phenyl-5-mercapto-1,2,3,4-tetrazoles (PMT) on the corrosion resistance of Cu 0,1M HNO<sub>3</sub>. The effect of PMT is compared with the effect of other organic compounds of the same type, such as 1,2,3,4-tetrazol (TTZ), 5-amino-1,2,3,4-tetrazol (AT) and 1-phenyl-1 2,3,4-tetrazol (PT). The results are shown in Table 3 Behave as mixed inhibitors. The mechanism of action is chemisorption

copper on the surface of the model Lengmirove isotherms. Inhibition efficiency follows the following order: TTZ<AT<PT<PMT.

Inhibition efficiency increases with increasing concentration and decreases with increasing temperature from 25 to 50 ° C. It also depends on the time of exposure. It increases with time and achieves a maximum value after 48 hours, and then decreases (Mihit at all, 2006).

In the paper Gy. Vastag (Vastag at all, 2001) examined the derivatives tiazol: 5-benziliden-2,4-dioxotetrahydro-1,3-tiazol (BDT); 5-(4-izopropylbenziliden)-2,4-dioxotetrahydro-1,3-tiazol (IPBDT); 5-(3-teniliden)-2,4-dioxotetrahydro-1,3-tiazol (TDT) i 5-(3,4-dimetoxibenziliden)-2,4-dioxotetrahydro-1,3-tiazol (MBDT) as corrosion inhibitors of copper in 0.1 M sodium sulfate solution, pH=2,94. The results are shown in Table 4. The best protection is to IPBDT as expected after the analysis of the structure, i. e. the presence of isopropyl groups. Proved to be investigated tiazol derivatives (especially IPBDT) have the potential to replace toxic inhibitors (such as threazolo) used in closed systems (Table 4).

TABLE 3. THE EFFECTIVENESS OF INHIBITION IN THE PRESENCE OF 10<sup>-3</sup>M TETRAZOL (MIHIT AT ALL, 2006)

Inhibitor	Method	EI%
TTZ	Losing weight after submersion in 0,1M HNO <sub>3</sub> during 72h	31,50
	polarization	29,80
AT	Losing weight after submersion in 0,1M HNO <sub>3</sub> during 72h	56,40
	polarization	59,60
PT	Losing weight after submersion in 0,1M HNO <sub>3</sub> during 72h	94,50
	polarization	93,70
PMT	Losing weight after submersion in 0,1M HNO <sub>3</sub> during 72h	97,50
	polarization	95,40

TABLE 4. THE VALUES OF THE EFFICIENCY OF INHIBITION IN THE PRESENCE OF DERIVATIVES TIAZOLE (VASTAG AT ALL, 2001)

	Method	Inhibitor			
		IPBDT	BDT	TDT	MBDT
EI (%)	Weight loss	89,00	86,00	65,00	73,00
	EIS	93,00	86,00	80,00	71,00

There are a number of organic compounds that have proven to be good inhibitors of corrosion of brass. Organic compounds that show inhibiting properties belonging to different groups, although the compounds from the group of azoles Viewed Most Talked investigated (Ravichandran, Rajendran, 2005; Ravichandran at all, 2004; Ravichandran, Rajendran, 2005; Mamaş at all, 2005; Mountassir, Srhiri, 2007; Otieno-Alego at all, 1996; Antonijevic at all, 2005; Mihit at all, 2005; Notoya, Poling, 1976; Ying at all, 1995; Wu at all, 1993; Dafali at all, 2000).

Investigated compound showed good inhibiting properties in the tested conditions. Good inhibiting properties are a consequence of two polar atoms in the molecule inhibitors: N and S. Atom S provides a high density of electrons, which contributes to increase efficiency (Ravichandran, Rajendran, 2005; Abed at all, 2004). Atom N is the reaction center, which leads to the formation of film on a metal surface (Abed at all, 2004). With increasing concentrations of inhibitor leads to decrease density. Peptides predominantly controlled by cathodic reaction, ie. acting as a cathode inhibitors. Appendix peptide does not modify the mechanism of electrode process.

Y. Abed et al. (Abed at all, 2004) monitored the effect of Boc-Phe-Met-OCH<sub>3</sub> on the electrochemical behavior of brass in 0.5 M HNO<sub>3</sub> solution. They came to the conclusion that the efficiency of inhibitor depends on its nature. Stability of helate alloy forms on the surface affects the efficiency of organic inhibitors (Dus, Smialowska, 1972). In general, a strong coordination relationship causes highly efficient inhibitor (Aggal at all, 1994; Kertit, Hammouti, 1996; Bouayed at all, 1999; Cheng at all, 1999; Raicheva at all, 1993).

TABLE 5. DEPENDENCE OF CURRENT DENSITY AND EFFICIENCY OF CARE BRASS CONCENTRATIONS OF INHIBITORS IN DIFFERENT ENVIRONMENTS (ABED AT ALL, 2004; ASAN AT ALL, 2005; OSMAN, 2001).

Solution	Inhibitor	C <sub>inh</sub>	I <sub>corr</sub> [μA/cm <sup>2</sup> ]	IE[%]
0,5M HNO <sub>3</sub>	Boc-Phe-Met-OCH <sub>3</sub>	10 <sup>-5</sup> M	30.1	40
		10 <sup>-4</sup> M	10.5	79
		10 <sup>-3</sup> M	1.3	97
0.1M NaCl	L <sub>1</sub>	20ppm	3,11	66
		50ppm	2,42	73
		100ppm	1,46	84
		200ppm	1,13	88
		Modified	3,11	97
	L <sub>2</sub>	20ppm	3,53	61
		50ppm	2,65	71
		100ppm	1,75	80
		200ppm	1,30	86
		Modified	0.47	95
3.5% NaCl	SDBS	200ppm	60.30	/
		600ppm	26.15	/
		1000ppm	13.6	/
Sea water	SDBS	200ppm	115.33	/
		600ppm	62.57	/
		1000ppm	31.51	/
3.5% NaCl	DPh(EO) <sub>9</sub>	200ppm	93.75	/
		600ppm	40.50	/
		1000ppm	28.60	/
Sea water	DPh(EO) <sub>9</sub>	200ppm	200.00	/
		600ppm	85.40	/
		1000ppm	73.00	/
3.5% NaCl	LAPACI	200ppm	75.12	/
		600ppm	30.25	/
		1000ppm	22.63	/
Sea water	LAPACI	200ppm	140.50	/
		600ppm	70.90	/
		1000ppm	59.11	/

A. Asan and others (Asan at all, 2005) on the basis of their research and results presented in Table 5 came to the conclusion that with increasing concentration of inhibitor leads to fear the fall curent density. Examined the inhibiting effect of the following compounds: 1,1 - (Lauryl Amido) propyl ammonium chloride (LAPACI),

sodium benzene sulfonate dodecil (SDBS), phenol dodecil etoxilateda (DPH (EO)<sub>9</sub>), and found that the inhibiting effect of changing the following order: DPh(EO)<sub>9</sub><LAPACI<SDBS(Osman, 2001).

TABLE 5. DEPENDENCE OF CURRENT DENSITY AND EFFICIENCY OF CARE BRASS CONCENTRATIONS OF INHIBITORS IN DIFFERENT ENVIRONMENTS (ABED AT ALL, 2004; ASAN AT ALL, 2005; OSMAN, 2001).

Solution	Inhibitor	C <sub>inh</sub>	I <sub>corr</sub> [μA/cm <sup>2</sup> ]	IE[%]
0,5M HNO <sub>3</sub>	Boc-Phe-Met-OCH <sub>3</sub>	10 <sup>-5</sup> M	30.1	40
		10 <sup>-4</sup> M	10.5	79
		10 <sup>-3</sup> M	1.3	97
0.1M NaCl	L <sub>1</sub>	20ppm	3,11	66
		50ppm	2,42	73
		100ppm	1,46	84
		200ppm	1,13	88
		Modified	3,11	97
	L <sub>2</sub>	20ppm	3,53	61
		50ppm	2,65	71
		100ppm	1,75	80
		200ppm	1,30	86
		Modified	0.47	95
3.5% NaCl	SDBS	200ppm	60.30	/
		600ppm	26.15	/
		1000ppm	13.6	/
Sea water	SDBS	200ppm	115.33	/
		600ppm	62.57	/
		1000ppm	31.51	/
3.5% NaCl	DPh(EO) <sub>9</sub>	200ppm	93.75	/
		600ppm	40.50	/
		1000ppm	28.60	/
Sea water	DPh(EO) <sub>9</sub>	200ppm	200.00	/
		600ppm	85.40	/
		1000ppm	73.00	/
3.5% NaCl	LAPACI	200ppm	75.12	/
		600ppm	30.25	/
		1000ppm	22.63	/
Sea water	LAPACI	200ppm	140.50	/
		600ppm	70.90	/
		1000ppm	59.11	/

Found that investigated inhibitors form a thin and robust chemisorbed film on the surface of brass. Adsorption inhibitors on the surface of alloys is one of the most important steps in the mechanism of inhibition. Protective film on the surface of brass is further modified benzotthreazole, where the resistance of the film significantly improved and the coverage area of alloys. Presence –C=N– links in the molecule inhibitors contributes to its better adsorption on the surface of alloys and better efficiency. Investigated ligands are very suitable for the formation of coordinative complexes with Zn<sup>2+</sup> i Cu<sup>2+</sup> ions (Hökelek at all,

2000; Srinivasan, 2003). To what extent are investigated compounds had effects on the electrochemical parameters of alloys can be seen from Table 5.

## Influence of alloy elements on corrosion of brass

One of the best ways for corrosion inhibition of brass in neutral and weak acid solutions to remove dissolved oxygen (Tabela 6). It is best to simultaneously inhibit the anodic dissolution of copper alloy components and prevent oxidation of copper, which can be accomplished by adding a third alloy components (Marshakov, 2005). As is known to prevent unzinanization brass. Arsenic addition (Zou at all, 1997; Bowers at all, 1978; Ogilvie, 1982; Bengough, R. May, 1924; Langenegger, Robinson, 1969; Bowers, 1982; Luceu, 1966; Newman at all, 1988), antimony (1997), boron (Toivanen at all, 1985), phosphorus (Fiaud at all, 1987), tin (Fiaud at all, 1987) and aluminum (Fiaud at all, 1987) in small amounts prevents unzinanization. As alloy element is best to add As, because As supplement increases the corrosion resistance of brass in a sour environment, inhibits the corrosion of brass and prevents unzinanization (Langenegger, Robinson, 1970; Luo, Yu, 1996). Unzinanization prevent small amounts of arsenic of all at 0.04% (Marshakov, 2005), however, arsenic has two shortcomings. First, it is limited to  $\alpha$ -brass. Second, very small amounts of iron and manganese can form a complex with arsenic which results in significantly reducing the efficiency of arsenic inhibitors (Bowers at all, 1978; Ogilvie, 1982; Bowers, 1982).

In particular, the performance followed by arsenic and arsenic's anions:  $AsO_2^-$  i  $HAsO_4^{2-}$  as inhibitors of corrosion of brass in a solution of sodium nitrite (Luo, Yu, 1996). M.J. Pryor and others (Pryor, Giam, 1982) concluded that arsenic in brass inhibit corrosion in chloride solution oxidate to the  $AsO_2^-$  i in the solution, and to come to the surface of brass produced chemisorption oxide. Lucey et al. (Luceu, 1966) considered that arsenic has a impact on the process redeposition copper. It is considered that there is a reduction  $Cu^{2+}$  in  $Cu^+$  ions and alloy composition on corrosion rate significantly affect the composition of the environment as can be seen from Table 6. From the Table it can be concluded that the unzinanization intensified in acid solutions. Difficult to reduce the liquid compounds of copper and unzinanization and speed of corrosion.

TABLE 6. CORROSION SPEED FACTOR UNZINANIZATION BRASS IN 0.5 M SOLUTION ON 20°C (MARSHAKOV, 2005)

Solutions	Cu	$\alpha$ -B70		$(\alpha+\beta)$ -B62		$(\alpha+\beta)$ -B58	
	K*10 <sup>3</sup> [g/dm <sup>2</sup> day]	K*10 <sup>3</sup> [g/dm <sup>2</sup> day]	z	K*10 <sup>3</sup> [g/dm <sup>2</sup> day]	z	K*10 <sup>3</sup> [g/dm <sup>2</sup> day]	z
NaCl	4,3	4,3	1,8	1,1	66,8	1,2	$\infty$
KBr	3,0	2,2	1,0	1,3	58,2	1,7	$\infty$
KI	0,8	0,7	1,1	1,0	1,3	1,3	66,2
HCl	530	500	1,8	22,0	$\infty$	40	$\infty$
H <sub>2</sub> SO <sub>4</sub>	37,6	42,5	1,9	38,2	28,2	42,6	$\infty$
Na <sub>2</sub> SO <sub>4</sub>	2,8	3,6	5,1	1,1	14,6	1,2	13,0
Na <sub>2</sub> CO <sub>3</sub>	5,1	3,1	1,1	1,2	1,3	1,4	1,9
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	46,5	40,8	1,9	54,2	3,3	54,0	3,1

It was observed that small quantities of aluminum and tin, only 1 to 2% in brass alloys to improve corrosion resistance in seawater (Rabab M at all, 2004). I like this small amount of influence on the microstructure, the number of defects and features award-winning safety film on the surface of brass. Alloying of Al and Sn prevents unzinanization (Seungman, Kang, 2002). However, tin is showing better results with nickel,

while nickel have not been significantly changed the investigated corrosion resistance of brass Cu40Zn (Seungman, Kang, 2002). It was also noted that antimony and phosphorus to prevent unzinization, and lead to improved properties of brass (Rabab M at all, 2004).

Rabab M. El-Sheriff and his associates (Rabab M at all, 2004) concluded that with the addition of Pb in the range of 1.0 to 3.4% leads to decrease current density. The fall of current density can be attributed to precipitation of  $PbCl_2$  in the working solution containing chloride ions (Badawy at all, 1995). It was observed that with increasing Pb content in the alloy leads to increase resistance to pitting corrosion of alloys (Rabab M at all, 2004).

## Future inhibitors

Especially important properties that must be met in the future inhibitors that its toxicity does not harm the environment and do not endanger the lives of people and other organisms. In Table 7 provides an overview of required properties through during their use, and development (2).

TABLE 7. SEARCH PROPERTIES INHIBITORS OVER TIME THEIR USE AND DEVELOPMENT (WWW.CORROSION-PROJECT.INFO)

Time period	Required property	Type of inhibitor
Up to 1960	effectiveness	chromate, phosphate, nitrite, borate, silicate, inhibitors with zinc
1960-1980	economy	poly phosphate, gluconate, molybdate, carboxylate
from 1980	environmental acceptability	tannin, the natural polymers, vitamins

Environmental acceptability inhibitors has long been required capacity, but there is still no completely ecologically acceptability inhibitors („green inhibitors“). Future researches in this area will be focused on obtaining completely environmentally sound inhibitors („green inhibitors“), which will have the greater effectiveness and efficiency. „Green inhibitors“ are:

- a set of compounds that meet the above characteristics
- vegetable or animal origin
- biodegradable and contain no heavy metals, which makes them environmentally acceptable
- extract the research plant recently, the area of great interest in terms of corrosion inhibitors
- extracts usually make a mixture of compounds that contain oxygen, sulfur and nitrogen, which are natural antioxidants, cheap and does not harm environment
- inhibiting effect of extract of some plants is achieved thanks to the presence of tannin in their capacity.

## Conclusions

Compounds that can be used as corrosion inhibitors of copper and its alloys are very numerous and the possibility of their application depends on many factors. First of all, the presence of aggressive ions and pH value of solution of the most important parameter. Depending on the nature of the inhibitors are different mechanisms of action.

Compounds influence over the formation of oxide films. Organic compounds mainly act by adsorption on the surface of metal and the formation of the complex. Therefore, the adverse impact of elevated temperature on the efficiency of organic compounds.

The structure of molecule inhibitor has the greatest impact on his performance. The presence of hetero atoms (S, N, O) with free e-pairs, the aromatic ring with delocalized  $\pi$  electrons, alkyl chains of high molecular weight, generally supstituentskih group leads to improved efficiency of inhibition.

Noted the greater efficiency of inhibition using organic compounds to the inorganic. It is particularly beneficial effect of electron donor groups. Tiazoles, benzothreeazole, triazolo provide good protection except in very acidic media, where the tetrazoles and imidazoles proved to be good. However, the introduction of supstituentskih group that may change. Amines showed good inhibition efficiency of corrosion in chloride and acid environments, but with a high concentration so that this application is not economical. Opinion threephnylmethane derivatives, tannins, amino acids have shown that it is possible to use compounds that are accessible, harmless and effective. Just ordered layers efficiency inhibitors show great inhibition while inhibitors of low consumption, which is a big advantage of such treatment (Antonijević, Petrović, 2007).

The efficiency of organic compounds as inhibitors depends on the nature of the compounds, and strong coordination links a crucial role in the effectiveness of inhibitors. In acidic environments as good inhibitors are peptide compounds and polypropyl with the degree of efficiency of 97% and 88%. The efficiency of inhibitor is generally affected by free electron pair in the molecule compounds, and the chain orientation during the formation of protective layer on the surface of alloys. Environment significantly affects the efficiency of action of inhibitors. Compounds from the group of azoles are the most important corrosion inhibitors. Because of its importance, these compounds have been thoroughly investigated. Good results are given in chloride solutions, in acid solutions, in neutral and alkaline environments, as well as in solutions with the addition of sulphide ions. Extremely good performance from the group of azoles compounds are manifested in solutions of synthetic sea water. Inhibition of corrozion process is achieved by forming azocomplex ions and their adsorption on the surface of brass (Antonijević, Radovanović, 2008).

Alloy elements as brass corrosion inhibitors proved to be very successful. The most frequently observed alloy elements are: As, B, P, Sn, Al, Pb. The best results showed As, and is therefore the most studied as a corrosion inhibitor brass. As is well given but at a concentration at 0.02%, while the optimal concentration of 0.04 at% to 0.05 at%. Gave good results and lead to the solution with chloride ions. Pb, Al, Sn and As, and successfully inhibit unzincanization, while As difficult as the appearance of voltage corrosion. As one of the drawbacks is that at higher potentials leads to dissolution of arsenic in the alloy. Also, small amounts of Fe and Mn decreased efficiency As such inhibitors. Arsenic anions also showed good inhibiting properties in chloride solutions. Efficiency of alloy elements generally increases with the content in the alloy and the solution. Anions of arsenic are chemisorbed on the surface of the brass. In general, the efficiency depends on the stability and solubility of protective film, as well as its sensitivity to the corrosion action (Antonijević, Radovanović, 2008).

Most inhibitors were used that are organic or inorganic substances, as well as alloy elements (heavy metals) are usually environmentally unacceptable. And if used in very small concentrations, given the volume of world production are significant „burden“ the environment. Even now, the damage caused by corrosion very large in the world, and one of the ways that they can reduce the corrosion inhibitors are just. However, it is necessary to reconcile ecology and profit is only possible by investing in new research. The invention of new effective inhibitors and study their mechanisms of action, and the development of „green inhibitors“ a combination of molecular modeling and experimental electrochemistry will be the subject of many scientific research.

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