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Review

Copper Corrosion Inhibitors. A review

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The literature dealing with the electrochemical corrosion of copper and possibility of its prevention using inhibitors is examined. Inorganic compounds are investigated as well, but organic compounds and their derivatives in much greater numbers. Researches are directed to influence of compounds structure, concentration, method of application as well as media that inhibitor is used in on inhibition efficiency. Moreover, action mechanisms are studied. The attempts to find models, which can enable prediction of possibilities of newly synthesized compounds to act as corrosion inhibitors, combining theory and practical investigations of substances with similar structure are also significant.

Keywords: Copper, corrosion, inhibitors

1. INTRODUCTION

Copper is metal that has a wide range of applications due to its good properties. It is used in electronics, for production of wires, sheets, tubes, and also to form alloys. Copper is resistant toward the influence of atmosphere and many chemicals, however, it is known that in aggressive media it is susceptible to corrosion. The use of copper corrosion inhibitors in such conditions is necessary since no protective passive layer can be expected. The possibility of the copper corrosion prevention has attracted many researchers so until now numerous possible inhibitors have been investigated. Amongst them there are inorganic inhibitors [1], but in much greater numbers there are organic compounds and their derivatives such as azoles [2-49], amines [50-56], amino acids [57, 58] and many others. It is noticed that presence of heteroatoms such as nitrogen, sulphur, phosphorous in the organic compound molecule improves its action as copper corrosion inhibitor. This is explained by the presence of vacant d orbitals in copper atom that form coordinative bonds with atoms able to donate electrons. Interaction with rings containing conjugated bonds, π electrons, is also present. Based on these results more and more compounds containing numerous heteroatoms and functional groups are developed synthesized since it is noticed they are responsible for good properties regarding corrosion inhibition because they enable chemisorption. Also molecular weight is larger due to its beneficial effect on physical adsorption.

There are attempts to combine theory and practical experience from investigations of some substances having similar structure in order to find models that would enable prediction of possibilities of newly synthesized compounds to act as corrosion inhibitors.

These are the reasons for espying the need to make up a review that would sum the results published by now and serve as a guidance for the future research.

2. INORGANIC COPPER CORROSION INHIBITORS

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. Three different inorganic inhibitors are investigated: chromate CrO_4^{2-}, molybdate MoO_4^{2-} and tetraborate $B_4O_7^{2-}$ in concentration of 0,033M in solution containing 850g/l LiBr and has pH 6,9. Chromate is generally accapted as efficient corrosion inhibitor that can passivate metals by forming a monoatomic or polyatomic oxide film at the electrode surface, but it is also known that it can promote corrosion acting as a cathodic reactive. Possible process for chromates is the reduction or decomposition of the inhibitor on the metal surface, followed by precipitation. Chromates are reduced to Cr(III)hydroxide or oxyhidrixide on the metal surface that results in corrosion current density decrease. However, the main disadvantage is the toxicity of chromium (VI) oxidation state. This is the reason for search for less toxic alternatives. The logical alternative can be analogue of hexavalent chromium the molybdate species that is an environmentaly friendly inhibitor. Nevertheless, molybdate and tetraborate showed no significant inhibition. The corrosion resistance is not improved because the film formation is not favorised in the electrolyte containing very aggressive anions such as bromides. Inhibion efficiency increases in the following order: molibdate (1.56%)< tetraborate (51.0%)< chromate (78.6%). [1]

3. THE ORGANIC COPPER CORROSION INHIBITORS

3.1. Azoles

Azoles are organic compounds containing nitrogen atoms with free electron pairs that are potential sites for bonding with copper and that enable inhibiting action. Also, there is a possibility of introduction of other heteroatoms and groups in molecules of these compounds so there is a wide range of derivatives that exhibit good inhibition characteristics.

El-Sayed M.Sherif [2-5] investigated the influence of 2-amino-5-ethylthio-1,3,4-thiadiazole (AETD) on copper corrosion in aerated HCl solution [2] as well as the influence of 2-amino-5-ethylthio-1,3,4-thiadiazole (AETD) [3], 2-amino-5-ethyl-1,3,4-thiadiazole (AETDA) [4] and 5-(phenyl)-4H-1,2,4-triazole-3-thiole (PTAT) [5] in NaCl solution. It is expected that these compounds show high inhibition efficiency since they are heterocyclic compounds containing more donor atoms, besides that they are non-toxic and cheap. AETD, AETDA and PTAT proved to be good mixed type copper corrosion inhibitors and the inhibition efficiency increased with concentration [2-5], exposure period [2,4,5] and oxygen content [3,4]. AETD, AETDA and PTAT molecules strongly adsorb on copper forming complexes with copper ions and prevent forming of Cu chloride and oxychloride complexes. The obtained values of inhibition efficiency are presented in Table 1.

Table 1. The results of the study of the efficiency of copper corrosion inhibition by AETD, AETDA and PTAT

solution	AETD concetration		IE (%)	references
0,5M HCl •after 12h exposure	1.0mM		40.00	[2]
	5.0mM		59.00	
	10.0mM		77.00	
3% NaCl	1.0mM		83.00	[3]
	5.0mm		94.00	
Method; 3% NaCl solution	AETDA concentration	IE (%)		[4]
		immediately	after 10 days	
Weight loss	1•10^{-3} M	60.00	60.00-62.00	
	5•10^{-3}M	97.00	97.00-100.00	
Potenciodynamic polarization; 5•10^{-3}M AETDA	deaerated	aerated	oxygenated solution	
	41.00	71.40	87.40	
PTAT concetration of 1500ppm; 3.5% NaCl	surface coverage			[5]
	after immersion		after 100h	
steady solution	0.87		0.97	
stirred solution	0.71		1.00	

In his work Gy.Vastag [6] investigated thiazole derivatives: 5-benzylidene-2,4-dioxotetrahydro-1,3-thiazole (BDT); 5-(4'-isopropylbenzylidene)-2,4-dioxotetrahydro-1,3-thiazole (IPBDT); 5-(3'-thenylidene)-2,4-dioxotetrahydro-1,3-thiazole (TDT) and 5-(3',4'-dimetoxybenzylidene)-2,4-dioxotetrahydro-1,3-thiazole (MBDT) as copper corrosion inhibitors in 0.1M sodium sulphate solution, pH=2.94. Results are shown in table 2. The best protection is achieved by IPBDT as expected based on the structural analyses i.e. the presence of isopropyl group. It is shown that the investigated thiazole derivatives (especially IPBDT) have potential to replace toxic inhibitors (such as triazoles) that are used in closed systems.

Table 2. The efficiency of inhibition in the presence of thiazole derivatives [6]

	method	inhibitor			
		IPBDT	BDT	TDT	MBDT
IE (%)	weight loss	89.00	86.00	65.00	73.00
	EIS	93.00	86.00	80.00	71.00

F.Zucchi et al. [7] studied the inhibiting action of tetrazole derivatives in 0.1M NaCl solution. Following compounds are tested: tetrazole (T), 5-mercapto-1-methyl-tetrazole (5Mc-1Me-T), 5-mercapto(Na salt)-1-methyl-tetrazole (5NaMc-1Me-T), 5-mercapto-1-acetic acid (Na salt)-tetrazole (5Mc-1Ac-T), 5-mercapto-1-phenyl-tetrazole (5Mc-1Ph-T), 5-phenyl-tetrazole (5Ph-T) and 5-amino-tetrazole ($5NH_2$-T) in the range of pH from 4 to 8 and at temperatures of 40 and 80°C. Recorded data are presented in table 3. All the inhibitors except 5Mc-1Ac-T that promotes which stimulates corrosion show an inhibition efficiency (IE) between 50 and 99%. IE increases with increasing pH and concentration while the temperature has a different influence on various derivatives. The best protective characteristics are shown by 5Mc-1Ph-T and 5Ph-T. IE decreases in the following order: 5Ph-T>5Mc-1Ph-T>5Mc-1Me-T>$5NH_2$-T>5NaMc-1Me-T>T. The prefilming treatment is efficient only with 5Mc-1Ph-T, while at longer exposure time only 5Ph-T prevents corrosion attack. The inhibiting action is explained by adsorption of the inhibitor on the copper surface and formation of complex with copper.

Table 3. Tetrazole derivatives inhibition efficiency (temperature of 40°C, pH of the inhibitor solution without adjustments) [7]

inhibitor	concentration	IE%
T	10^{-3}M in solution	53.50
	exposure in 10^{-3}M solution for 1h and measured after 1h in NaCl	36.80
5Ph-T	10^{-3}M in solution	99.40
	exposure in 10^{-3}M solution for 1h and measured after 1h in NaCl	1.30
5Mc-1Ph-T	10^{-3}M in solution	98.40
	exposure in 10^{-3}M solution for 1h and measured after 1h in NaCl	93.00
5Mc-1Me-T	10^{-3}M in solution	93.40
	exposure in 10^{-3}M solution for 1h and measured after 1h in NaCl	25.90
$5NH_2$-T	10^{-3}M in solution	85.30
	exposure in 10^{-3}M solution for 1h and measured after 1h in NaCl	-4.10
5NaMc-1Me-T	10^{-3}M in solution	66.20
	exposure in 10^{-3}M solution for 1h and measured after 1h in NaCl	28.00
5-Mc-1Ac-T	10^{-3}M in solution	-110.00
	exposure in 10^{-3}M solution for 1h and measured after 1h in NaCl	-25.70

The influence of 1-phenyl-5-mercapto-1,2,3,4-tetrazole (PMT) on the corrosion resistance of Cu in 0.1M HNO_3 is also studied. The action effect of PMT is compared with the influence action of other organic compounds of this type the same family such as 1,2,3,4-tetrazole (TTZ), 5-amino-1,2,3,4-tetrazole (AT) and 1-phenyl-1,2,3,4-tetrazole (PT). The results are shown in table 4. They behave as mixed type inhibitors. The mechanism of action is chemisorption on the copper surface that follows Langmuir isotherm. Inhibition efficiency increases in the following order: TTZ<ZT<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 immersion. The inhibition efficiency increases with time and reaches a maximum value after 48h, and afterwards decreases. [8]

E.Szőcs [9] in his research investigated the inhibitor 5-mercapto-1phenyl-tetrazole (5-MPhTT) in 1mM H_2SO_4 solution. The results show reveal that the anodic current density and mass loss are two times twice less lower in the presence of 5-MPhTT. The investigated concentration is 0.5mM. Measuremens are conducted in three intervals where the first is in blank solution, the second in the solution containing inhibitor while the third is again in the blank solution. The mass change is observed in the first interval while in the 2. and the 3. mass didn’t change. The inhibition efficiencies for the second and the third interval are 99.93% and 99.8% respectively. It is concluded that inhibitor forms a protective film chemisorbed on the surface. The structure of the protective film is further investigated by X.R.Ye [10] and the following conclusion is reached. The film contains a layer of inert, insoluble and long-lasting polymeric Cu(I) complex. These films are probably built over Cu_2O layer through surface reaction of PMT and Cu(I) ions. The copper surface treated with PMTA can be described as composite structure Cu-PMTA/Cu_2O/Cu. Each molecule of PMTA bridges two or more Cu(I) ions via N and S atoms. The hydrophobic backbone on PMTA ligand in Cu-PMTA prevents contact between hydrated corrosive ions and the metal surface and thus inhibit substrate corrosion. The optimum conditions for PMTA treatment are: 0.005mol/l PMTA solution, pH=3, temperature 20-50°C and 30min of treatment time. It is noticed that the films of coordination compounds formed by reaction of PMTA with copper surface are more efficient in corrrosion inhibition (under the influence of atmosphere, sulphide and chloride media) than those formed with TTA (tetrazole), BTA (benzotriazole), HBTA (hydroxybenzotriazole), MBT (2-mercaptobenzothiazole), MBI (2-mercaptobenzoimidazole), 2-AP (2-aminopyrimidine), IBM (imidazole) and chromates.

Table 4. The efficiency of inhibition in the presence of 10^{-3}M tetrazole [8]

inhibitor	method	IE%
TTZ	weight loss after 72h exposure to 0.1M HNO_3	31.50
	polarization	29.80
AT	weight loss after 72h exposure to 0.1M HNO_3	56.40
	polarization	59.60
PT	weight loss after 72h exposure to 0.1M HNO_3	94.50
	polarization	93.70
PMT	weight loss after 72h exposure to 0.1M HNO_3	97.50
	polarization	95.40

J.C.Marconato [11] investigated the effect of 2-mercaptobenzothiazole in the ethanol solution. The solution contains 10^{-2}M $HClO_4$ in ethanol. When MBT is added the inhibition of anodic copper dissolution and cathodic reaction of hydrogen evolution is observed. The concentration of MBT of 0.001M lead to reduction of current density 4 times that is associated with formation of complex between metal ions and inhibitor. MBT is oxidized to 2,2'-dithiobis(benzothiazole) and/or 2,2'-thiobis(benzothiazole) and forms a complex involving its ionized thiol form and Cu(II) ions. The characteristics of adsorption and the influence of MBT and tetrazole (TTA) on the growth of oxide film on copper in 0.1M NaOH are also investigated [12]. The inhibition efficiency is strongly dependent on the structure and chemical properties of the species formed under the specific experimental conditions. MBT contains three atoms available for coordination i.e. N and S atoms in the ring and S atom of the thiocarbonyl group. The S atom of the thiocarbonyl group (C=S) that is ionized in alkaline medium can react with Cu and form thick polymeric film. The surface coverage is 0.89 which is the highest value recorded among all the investigated compounds. TTA does not act as a copper corrosion inhibitor in 0.1M NaOH.

The effect of 3-benzylidene amino 1,2,4-triazole phosphonate (BATP), 3-cinnamyledene amino 1,2,4-triazole phosphonate (CATP), 3-salicylalidene amino 1,2,4-triazole phosphonate (SATP), 3-para nitro benzylidene amino 1,2,4-triazole phosphonate (PBATP) in the neutral environment and its interference with biocides is studied. The synthesized triazo phosphonates are used as inhibitors together with molybdate and cetyl trimethyl ammonium bromide (CTAB) as biocide. SATP is the most efficient due to the presence of electron releasing character of OH group, PBATP is the least effective due to the coplanarity of p-NO_2 group with the phenyl ring which imparts maximum electron withdrawal. Molybdate act as corrosion inhibitors in neutral and alkaline solutions. There is synergism between molybdate and inhibitor which may be related either to interaction between the inhibitor compounds or to interaction between the inhibitor and ions present in the aqueous media. The reason for selecting CTAB as biocide is that CTAB is not only the cationic surfactant but is also a quaternary ammonium salt with a long hydrocarbon chain whose homologues are used as inhibitors and biocides. The halides are the most effective derivatives since they increase inhibiting tendency of the positive quaternary ammonium ions through a synergistic effect. Inhibitor and biocide are added to the system at the same time as well with the 24h time difference in order to evaluate interference between them. The most effective treatment is the application of 15ppmCTAB+4ppmSATP+5ppmMo. Maximum efficiency is noticed for the compounds with the methoxy phenyl substituents, since the basicity of the coordinating atoms are increased by electron donating groups. The electron withdrawing groups such as p-nitro group retards this electron transfer process, which results in decreased inhibition efficiency. Regarding the protective films structure the following can be said: there is P-O-Cu bond, polymeric 5- and 6-membered copper-inhibitor ring complex is formed on the copper surface via reaction between the triazole ring and the metal surface, and in addition the CTAB-Cu^{2+} complex can be deposited as a layer and as a part of the protective film. [13]

Table 5. The results of the treatment with triazo phosphonates [13]

inhibitor	media		concentration	IE (%)
BATP	lake water	+Mo 5ppm		71.25
				72.50
		+CTAB 15ppm		73.12
				81.25
CATP	lake water		4ppm	73.12
		+Mo 5ppm		74.37
		+CTAB 15ppm	inhibitor added at the same time	75.62
			inhibitor added after 24h	82.50
SATP	lake water		4ppm	75.00
		+Mo 5ppm		76.25
		+CTAB 15ppm	inhibitor added at the same time	78.12
			inhibitor added after 24h	83.75
PBATP	lake water			62.50
		+Mo 5ppm		65.62
		+CTAB 15ppm	inhibitor added at the same time	71.25
			inhibitor added after 24h	76.25
CTAB	lake water		15ppm	77.50
Mo	lake water		5ppm	50.40

El-Sayed M.Sherif [14,15] investigated the effect of 3-amino-1,2,4-triazole (ATA) on the copper corrosion in 0.5M HCl [14] and in 3.5% NaCl [15]. It is found that ATA strongly adsorbs on the Cu surface in chloride solution, forms a complex with Cu^+ and inhibits copper corrosion by preventing the formation of $CuCl_2^-$ through which Cu dissolution occurs. The maximum inhibition efficiency in the HCl solution in the presence of $5 \bullet 10^{-4}$M ATA is achieved after 48h and it is ~60% that increases to ~67% and ~72% when the concentration is $1 \bullet 10^{-3}$M and $5 \bullet 10^{-3}$M ATA, in the NaCl solution in the presence of 1mM it is 94.4%, and after 50h it is 96.1%. The effect is long-term and the maximum inhibition efficiency after 24days is 83% for 0.5mM ATA, and increases to 90% in the presence of 1.0mM ATA.

In the paper published by A.Lalitha et al. [16] the influence of derivatives of 1,2,4-triazole and surfactants in the aqueous solution containing potassium hydrogen phthalate and hydrochloric acid (pH 2) is examined. The inhibitors are 3-amino 1,2,4-triazole (ATA), 3-amino mercapto 1,2,4-triazole (AMT), 3-amino 5-methylthio 1,2,4-triazole (AMTT) and cetyl trimethyl ammonium bromide (CTAB) and sodium dodecyl sulphate (SDS). The performance can be ranged as ATA<AMT<AMTT, and SDS exhibits higher inhibition than CTAB. Azole compounds get adsorbed on the metal surface by forming a chemisorbed protective film, and surfactants by virtue of its hydrophobic character of the hydrocarbon chain may then plug the defects in the triazole film. The combination AMTT+SDS exhibits the highest synergism parameter which is in accordance with effective corrosion inhibition. The results are presented in table 6.

Table 6. The results of the study of the triazole action in acidic aqueous solution [16]

inhibitor	medium		concentration	EI (%) weight loss	EI (%) potentiodynamic polarisation	synergism parameter
ATA	KH phthalate +HCl pH=2		100ppm	62.50	63.08	
		+CTAB	10ppm	89.71	90.00	1.42
		+SDS	2500ppm	92.36	93.08	1.72
AMT			100ppm	68.91	70.00	
		+CTAB	10ppm	91.17	92.31	1.50
		+SDS	2500ppm	92.48	94.31	1.70
AMTT			100ppm	78.40	79.23	
		+CTAB	10ppm	91.50	94.62	1.48
		+SDS	2500ppm	93.32	96.15	1.74
CTAB			10ppm	61.22	61.54	
SDS			2500ppm	66.35	67.69	

The efficiency of two newly developed triazole type organic compounds: bis [4-amino-5-hydroxy-1,2,4-triazol-3-yl]methane (D_1) and bis[4-amino-5-hydroxy-1,2,4-triazol-3-yl]butane (D_2) as copper corrosion inhibitors in 4.0M HNO_3 solution at 25°C is investigated. It is noticed that they act predominantly as cathodic inhibitors with long-term effectiveness whereat the inhibition efficiency is over 99%. D_1 is more efficient than D_2 and that is attributed to the screening effect of the $–CH_2$- chain of compound D_2, the efficiency increases with concentration and the mechanism is different at lower and at higher concentration. The adherent film of low solubility is formed which prevents the components of solution to reach the metal and ensures optimum protection. [17]

The most commonly used copper corrosion inhibitor of azole type is benzotriazole. There are numerous investigations of inhibitive action of BTA on copper corrosion in various media such as solutions containing chloride ions [18-22], nearly neutral solutions [23,24], strongly acidic [21,25-27] and strongly alkaline media [12] and atmosphere [28,29]. Besides the common applications it is shown that BTA is the only inhibitor that provides effective protection of copper archeological artifacts during preservation process [24,29], although it is not the most efficient it exhibit some protection of electrodeposited copper powder [28]. However, it is noticed that BTA action is weaker in highly acidic and highly alkaline media as well as in media containing aggressive ions, so the investigation of its derivatives action is also conducted.

Benzotriazole is an organic compound consisting of benzene and triazole ring, which formula is $C_6H_5N_3$. The presence of nitrogen atoms in triazole ring enables bonding with copper and is a basis for inhibitive effect of BTA. Generally about BTA action it can be said that it is anodic [21,23,30,31] copper corrosion inhibitor which action mechanism includes chemisorption [12,23,31-34], rearly physisorption [27,35] on the copper surface that follows Langmuire isotherm [12,23,26,27,32,35] followed by the formation of complex Cu(I)BTA[12,18-20,22,23,25,26,32,36-38]. Coordination between BTA molecule and Cu electrode surface occurs via nitrogen atom of triazole ring [12,23,27,32,38]. BTA molecules can be oriented parallel [12,23] or vertical [33,34] regarding surface. The orientation of inhibitor molecule is important because of the possibility of formation of stronger bond if the orientation is parallel due to interaction of π electrons of the ring with vacant d orbitals of copper. [12]

The mechanism of complex formation is proposed and described by the following reactions [18]:

$$Cu_{(s)} + BTAH_{(aq)} = Cu{:}BTAH_{(ads)} + H^{+}_{(aq)}$$

where $Cu{:}BTAH_{(ads)}$ stands for BTAH adsorbed on Cu surface. In the presence of oxidants or by anodic polarization it can be oxidised to protective complex:

$$Cu{:}BTAH_{ads} = Cu(I)BTA_{(s)} + H^{+}_{(aq)} + e^{-}$$

From this reaction it can be seen that increase of BTA concentration shifts the reaction towards formation of larger amount of protective complex Cu(I)BTA, that is confirmed in numerous experiments [12,18,22-24,27,29,30,35-38]. Also it can be observed that pH increase favours complex formation. [12]

Based on the characteristics of BTA itself the inhibition efficiency in the specific media can be explained. BTA can be found in three forms dependently on pH value of solution [36]. In strongly acidic media it has protonated form $BTAH_2^{+}$, in weakly acidic, neutral and weakly alkaline media its form is BTAH, while in strongly alkaline media it is BTA^{-}. Considering that Cu surface is positively charged in the solution it can easily be concluded which form is more, and which is less favorable. Tromans [37] constructed the E-pH diagrams for systems containing Cu and BTA that provide an indication when the protective action can be expected, and when not, dependently on pH, potential and inhibitor concentration. The action mechanism is adsorption on Cu surface that is an exothermic process so it is obvious that temperature increase has an adverse effect on the inhibition efficiency [23,33,34].

The behavior of BTA derivatives is very similar. The introduction of the substituent groups has no effect on the mechanism of the inhibitive action while it has influence on inhibition efficiency [23,27,30,32,35,39].

P.Yu [23] and B.H.Loo [32] investigated influence of benzotriazole (BTA) and tolytriazole (TTA) on copper corrosion inhibition in deionized water [23] and in chloride solutions [32]. TTA has three isomers with the methyl group substituted in 4-, 5- or 6-position on the benzene ring. Both compounds exhibit inhibiting action, but TTA is more efficient. It can be concluded that the introduction of nonpolar methyl group increases the film hydrophobicity hence improving the copper corrosion prevention. A.Frignani [30] evaluated the effect of the introduction of alkyl chains of various lengths on the efficacy of the copper corrosion inhibition in 0.1M Na_2SO_4 and 0.1M NaCl solutions, pH=2.5. 1,2,3-benzotriazole (BTAH) and 5-alkyl-derivatives of benzotriazole, methyl-benzotriazole (C1-BTAH), butyl-benzotriazole (C4-BTAH), hexyl-benzotriazole (C6-BTAH), octyl-benzotriazole (C8-BTAH) and dodecyl-benzotriazole (C12-BTAH) are used. In Na_2SO_4 solution the inhibition efficiency increases with introduction of alkyl groups from BTAH to C6-BTAH while C8-BTAH has almost the same effect as C6-, and C12-BTAH does not have remarkable influence because of low sollubility. More aggressive media, such as NaCl solution, hinders the action of the less effective inhibitors thus only C4-BTAH and C6-BTAH act as highly effective inhibitors while C6-BTAH is the most efficient. It can be concluded that introduction of the alkyl chain in the 5- position of benzotriazole improves the action of the base molecule mostly towards the anodic reaction. Positive effects are more significant as the chain length increases up to 6 C atoms.

A.Arancibia [35] conducted a research of the effect of BTA and its derivatives 5-methyl BTA and 5-chloro BTA on the copper corrosion inhibition in aerated 0.1M HCl solution. BTA and 5-methyl BTA act as cathodic inhibitors and their action is associated with adsorption of $BTAH_2^+$ on Cu. 5-chloro BTA dependently on concentration has mixed, and at higher concentration anodic action mechanism associated with passivation and CuBTA formation. Chloro in 5-position enables formation of the partially protonated species BTAH while nitrogen is responsible for bonding with copper. It is noticed that the interaction between inhibitor and metal surface enhances with substituents in 5-position of inhibitor molecule, while electron acceptor groups have better effect that electron donor.

V.Otieno-Alego [38] studied the inhibiting action of 4- and 5-carboxybenzotriazole (4- and 5-CBT) and BTAH on copper corrosion in 0.1M Na_2SO_4 solutions (pH 0 and 4) as well as in $Na_2S{\bullet}9H_2O$ solution. It is noticed that the inhibition efficiency is lower in pH=4 solution compared to that in pH=0 solution, but it increases with exposure time. The optimum concentration is approximately $7{,}5{\bullet}10^{-4}$M, and in mixture of 4- and 5-CBT the component having the inhibiting properties is 5-CBT. The mechanism of action is the same as for BTAH and includes adsorption and coordination with copper through N atom of triazole ring. It is found that the introduction of the electron withdrawing group (-COOH) in 4- position decreases the strength of coordination while in the 5- position the electrophilic effect is less effective and leads to stronger chemisorption and better corrosion inhibition. J.Bartley [27] conducted a research on the series of alkyl esters (methyl, butyl, hexyl and octyl) synthesised from the mixture of 4-CBTAH and 5-CBTAH in aerated pH~0 solution. It is observed that the inhibition efficiency increases with hydrocarbon chain length. This is attributed to increased physisorption of the alkyl chain as more methyl groups are introduced and chemisorption through azole ring N. In order to obtain the same degree of surface coverage concentration of inhibitor required becomes progressively less as the molecule is larger due to more efficient surface blocking. Based on the presented data it can be said that esterification of BATH particularly with the introduction of the longer hydrocarbon chains is beneficial. The same results were reached by N.Huynh et al. [40] investigated the inhibition action of coatings formed dipping copper in solutions of alkyl esters (methyl, butyl, hexyl and octyl) of carboxybenzotriazole (mixture of 4- and 5-CBTAH, and separately 4- and 5-CBTAH-OE) in 0.5M Na_2SO_4 solutions with pH 0 and 8. The inhibition efficiency depends on type of solvent used in the coating solution (water, alcohol, acetone), temperature (30-100°C) and period of immersion (5min-6h). Pretreatment by immersing copper in hot (70°C) aqueous solution ($1 \bullet 10^{-4}$M) for aproximately 2-3h gave a film with the highest degree of corrosion protection. Film formed in aqueous solutions of inhibitors can be stable in acidic solution (pH~0) for up to three days, and in near-neutral sulphate solution (pH~8) for up to 10 days. In both acidic and neutral solution the inhibition efficiencies of the protective film increase with the length of the alkyl ester chain in the order: methyl<butyl<hexyl<octyl. It can be said that alkyl esters of carboxybenzotriazole are efficient copper corrosion inhibitors both when they are added to the solution or when the film is formed during pretreatment in the inhibitor solution.

Guo-Ding Zhou [20] investigated the effect of 1-(2,3-dicarboxypropyl)benzotriazole (BT-250) which is a derivative of BTA but is less efficient as copper corrosion inhibitor in NaCl solution. Da-quan Zhang [41] investigated the effect of a novel corrosion inhibitor bis-(1-benzotriazolymethylene)-(2,5-thiadiazoly)-disulfide (BBTD) on copper corrosion in 3% NaCl and 0.5M HCl solutions. BBTD contains two BTA moieties and one thiadiazole moiety. It is found that BBTD is a good inhibitor for copper in both neutral and acidic solution, but it has greater influence in 3% NaCl then in 0.5M HCl solution. This can be attributed to the stability of cuprous oxide in neutral solution. BBTD adsorbs on the Cu surface and forms protective complex with Cu(I) ion. The complex is identified as BBTD-Cu(I) and protects copper surface from aggressive Cl^- ions. BBTD is more efficient then BTA under this conditions, that can be seen based on data from table 7. M.A.Elmorsi et al. [42] investigated copper corrosion inhibition in aerated 0.5M H_2SO_4 solution in the presence of two classes of heterocyclic compounds, namely phenylazo-pyrazolones (PAP) or hydroxy quinoline and bromobenzyl-carboxy-1,2,3 triazole (BCT) derivatives. Inhibition efficiency (IE) of BCT is 75-97%, and IE of PAP 90-97% while there is no regular change of IE with inhibitor concentration. The influence of temperature was investigated in the range form 300 to 343K and negative influence of high temperature is observed. Influence of PAP is attributed to adsorption, followed by Cu-chelates precipitation on copper surface via the interaction of C=O and N=N groups of the inhibitor molecule with the Cu ions of polarized surface. Effect of BCT can be a result of π-complex formation between adsorbed triazole ring of inhibitor and Cu ions. Both PAP and BCT are cathodic inhibitors with significant difference in adsorption degree or protective Cu-complex formation.

The existence of a synergistic effect on copper corrosion inhibition in sulphuric acid solution in the presence of BTA and iodide ions is observed by D-Q.Zhang [25] and Y-C.Wu [43]. Synergistic effect is assumed to be a result of initial contact adsorption of iodide anions on copper, followed by a decrease in positive in the metal that facilitates the adsorption of protonated BTA on Cu surface [25] or Cu(IBTA) complex polymer film formation [43]. R.F.V.Villamil [26] also noticed synergistic effect on inhibition of copper corrosion in sulphuric acid solution in the presence of BTA and sodium dodecylsulfate (SDS).

When considering the data presented above, the following conclusion is imposed, the introduction of substituent groups into the BTA molecule leads to improvement of its inhibition properties and protective action. Withal, the synergistic action of BTA with some compounds or ions, that significantly improves BTA efficiency, is perceived to be of great importance. The results of the research are summarised in table 7.

Table 7. The values of the inhibition efficiency obtained by using BTAH and its derivatives

inhibitor	concentration	media	IE %	references
BTAH	10ppm	Deionized water	84.48	[23]
TTA	10ppm		95.48	
BTAH	10^{-5}M	0.1M Na_2SO_4; pH 2.5; exposure time 3h	83.30	[30]
C1-BTAH	10^{-5}M		83.30	
C4-BTAH	10^{-5}M		97.30	
C6-BTAH	10^{-5}M		99.30	
C8-BTAH	saturated solution		99.00	
BTAH	10^{-2}M	0.1M HCl	90.80	[35]
5-methyl-BTAH	10^{-2}M		97.87	
5-chloro-BTAH	10^{-2}M		99.79	
4-CBT	$7\bullet10^{-4}$M	0.1M Na_2SO_4; pH 0; 3 days	20.00	[39]
5-CBT	$7\bullet10^{-4}$M		70.00	
BTAH	$7\bullet10^{-4}$M		40.00	
4-CBT	$5\bullet10^{-4}$M	0.1M Na_2SO_4; pH 4; 10 days	10.00	
5-CBT	$5\bullet10^{-4}$M		55.00	
BTAH	10^{-4}M	pH 0	58.00	[27]
CBTAH-ME	10^{-4}M		57.00	
CBTAH-BU	10^{-4}M		67.50	
CBTAH-HE	10^{-4}M		85.00	
CBTAH-OE	10^{-4}M		98.00	
BTAH	10^{-4}M	0.5M Na_2SO_4 pH 0	45.10	[40]
		0.5M Na_2SO_4 pH 8	63.40	
CBTAH-ME	10^{-4}M	0.5M Na_2SO_4 pH 0	30.20	
		0.5M Na_2SO_4 pH 8	60.20	
CBTAH-BU	10^{-4}M	0.5M Na_2SO_4 pH 0	58.20	
		0.5M Na_2SO_4 pH 8	76.20	
CBTAH-HE	10^{-4}M	0.5M Na_2SO_4 pH 0	63.60	
		0.5M Na_2SO_4 pH 8	86.80	
CBTAH-OE	10^{-4}M	0.5M Na_2SO_4 pH 0	95.10	
		0.5M Na_2SO_4 pH 8	99.00	
4-CBTAH-OE	10^{-4}M	0.5M Na_2SO_4 pH 0	94.80	
		0.5M Na_2SO_4 pH 8	99.10	
5-CBTAH-OE	10^{-4}M	0.5M Na_2SO_4 pH 0	95.10	
		0.5M Na_2SO_4 pH 8	99.10	
BTAH	0.1M	atmosphere	99.00	[29]
BTAH	10^{-3}M	0.5M HCl	26.20	[21]
BTAH	0.1M	1M HCl; pH0	99.73	[38]
BTAH	10^{-3}M	0.5M H_2SO_4	58.20	[25]
BTAH + KJ	$5\bullet10^{-4}$M+$5\bullet10^{-4}$M		67.60	
BBTD	10^{-3}M	3% NaCl	87.60	[41]
BBTD	10^{-3}M	0.5M HCl	79.20	

Another azole type compound that also received plenty of attention is imidazole as well as its derivatives. Imidazole is a planar, aromatic heterocyclic organic compound containing two nitrogen atoms that form fivemembered ring. One of the nitrogen atoms is a pyrole type, and the other of pyridine type. Based on the structure it can be seen that imidazole molecule has two places convinient for bonding with surface: N atom with lone sp^2 electron pair and aromatic ring. It is favourable due to its non-toxicity and high inhibition efficiency.

Action mechanism is the same as for other azole compounds, adsorption of molecules on copper surface and formation of protective complex with copper. The efficiency increases with concetration increase, while the temperature increase has a negative effect. Introduction of groups influences the efficiency but not the inhibition mechanism. Following groups showed to be especially favourable phenyl group, mercapto group, presence of more heteroatoms as potential centres for bonding with copper as well as benzene ring.

They are revealed to be efficient copper corrosion inhibitors in various media such as: nitric acid [44], sulphuric acid [25,45], hydrochloric acid [21,46], sodium chloride [47], atmosphere [48], sodium hydroxide [12].

Synergism has become one of the most important effects in the inhibition processes and it serves as the basis for all modern corrosion inhibitor formulations. D-Q.Zhang [25] investigated the influence of 2-mercapto benzimidazole (MBI) and KI on copper corrosion in 0.5M sulphuric acid. The results indicate that MBI and KI have a synergistic effect to prevent copper corrosion. This effect is atributed to formation of couprous iodide (CuI_2) complex that is relatively stable and cuprous ions can react with protonated MBI and form (Cu^+MBI) film that is the best protection against corrosion. Based on that the inhibitor film (Cu^+MBI) formation may be acomplished through the following steps:

$$Cu + I^- \rightarrow (CuI)_{ads} + e^-$$

$$(CuI)_{ads} + I^- \rightarrow CuI_2^- + e^-$$

$$CuI_2^- + p\text{-}MBI^+ \rightarrow (CuMBI) + 2I^- + p^+$$

Iodide is not incorporated into the MBI inhibitive film on the copper surface. Synergistic effect is a result of initial contact adsorption of iodide anions on copper, followed by a decrease in the positive in the metal that improves the adsorption of protonated MBI on Cu surface. Organic molecule MBI has better inhibition effect on copper corrosion in comparison to BTAH in aerated sulphuric acid solution, it is about 20% more efficient.

The coordination property of imidazole derivatives with metals is used to construct higher-ordered hierarchical mesostructures in large scale [49]. In this order 4,5-diphenylimidazole (DPI) is used. Different characteristics can be obtained by changing the assembly conditions. The mesostructures can endow the copper surface with superhydrophobic property and significantly inhibit copper corrosion. The stucture is influenced by the solvent, time and concentration of DPI. It is shown that complex formed by the coordination of DPI with Cu plays a decisive role in providing a centre of layer nucleation and growth.

Table 8. The results of imidazole application as the copper corrosion inhibitior

inhibitor	media	concentration	IE%	references
1-(p-tolyl)-4-methylimidazole	0.5M H_2SO_4	0.05M	86.00	[45]
1-phenyl-4-methylimidazole		0.50M	94.30	
4-methyl-5-hydroxymethylimidazole		0.30M	65.40	
Imidazole		0.50M	44.00	
MBI	0.5M H_2SO_4	1mM	74.20	[25]
MBI + KJ		0.75mM+0.25mM	95.30	
MBI	0.5M HCl	1mM	91.60	[21]
IM (imidazole)	1M HCl	10^{-3}M	33.00	[46]
TMI (1-(p-tolyl-4-methylimidazole))		10^{-3}M	54.00	
MMI (2-mercapto-1-methylimidazole)		10^{-3}M	87.50	
Imidazole	3% NaCl	10^{-4}M	49.79	[47]
4-methylimidazole		10^{-4}M	63.31	
4-methyl-5-imidazolecarbaldehyde		$3\bullet10^{-4}$M	71.24	
ethyl-4-methyl-imidazolecarboxylate		10^{-3}M	80.50	
4-methyl-1(4-methoxyphenyl)imidazole		$2\bullet10^{-4}$M	83.95	
1-(p-tolyl)-4-methylimidazole		$7\bullet10^{-4}$M	93.03	
1-phenyl-4-methylimidazole		$5\bullet10^{-3}$M	94.31	
imidazole	1M HNO_3	0.1M	94.93	[44]
BIMD (benzimidazole)	0.1M NaOH	2.0mM	82.00	[12]
MBIMD (mercaptobenzimidazole)		2.0mM	74.00	
IMD (imidazole)		2.0mM	46.00	

3.2. Amines

Copper corrosion inhibition in de-aerated, aerated, and oxygenated HCl [50] and NaCl [51] solutions by N-phenyl-1,4-phenylenediamine (NPPD) is investigated. The NPPD adsorbs on the copper surface whereat Cu undergoes oxidation to Cu^+ and form insoluble complex Cu^+-NPPD on the surface. The efficiency increases with time and inhibitor concentration. The inhibition efficiency (IE) values are shown in table and reveal that NPPD is a good copper corrosion inhibitor in HCl though the IE is somewhat lower than in NaCl solution. The results are presented in table 9.

Table 9. Copper corrosion inhibition efficiency in the presence of 10mM NPPD in 0.5M HCl solution [50]

	deaerated	aerated	oxygenated
IE(%), polarization curves	81.70	83.75	68.42
IE(%), Nyquist plots	79.80	73.60	83.00

The behavior of secondary amines as copper corrosion inhibitors in acid media, 0.5M hydrochloric acid and 0.5M sulphuric acid, is studied. [52] The homologous series of aromatic secondary amines with various substituents is investigated. All the investigated compounds contain amino group that has the ability of adsorption and co-ordination with metal as well as the polar and unsaturated bonds such as heterocyclic ring with oxygen (furan) substituted in 5- position and aromatic ring with methyl group in p-position. The nonsubstituted secondary amine (N-(2-furfuryl)-p-toluidine) is the least efficient while the substitution of a hydrogen atom (-Cl, -Br, -NO_2, -CH_3) in the 5-position by either the electrophilic -Cl, -Br, -NO_2, or the nucleophilic CH_3 substituent increases protective effect. In hydrochloric acid all the substituted secondary amines have good inhibiting characteristics while in sulphuric acid only the halide substituted ones show significant inhibition efficiencies as can be seen in table 10.

Table 10. The efficiency of copper corrosion inhibition in the presence of secondary amines [52]

Inhibitor 0.01M	N-2-furfuryl-p-toluidine	N-5-chloro-2-furfuryl-p-toluidine	N-5-bromo-2-furfuryl-p-toluidine	N-5-nitro-2-furfuryl-p-toluidine	N-5-methyl-2-furfuryl-p-toluidine
IE%, 0.5M HCl	36.00	78.00	62.00	84.00	86.00
IE%, 0.5M H_2SO_4	/	81.00	84.00	31.00	/

Schiff bases are condensation products of an amine and a ketone or aldehyde, with $R_2C=NR'$as their general formula. They contain heteroatoms and π electrons that enable bonding with copper. H.Ma [53] investigated copper corrosion inhibition in 0.5M NaCl and NaBr solutions by three Schiff bases N,N'-o-phenylen-bis(3-methoxysalicylidenimine) (V-o-Ph-V), N,N'-p-phenylen-bis (3-methoxysalicylidenimine) (V-p-Ph-V) and N-[(2-hydroxy-3-methoxyphenyl) methylene]-histidine (V-His). The inhibition efficiency is strongly dependent on the geometric structure and it decreases in the following order: V-o-Ph-V(around 90%); V-p-Ph-V(around 80%); V-His(around 40%). The inhibition action is a result of adsorption on the copper surface followed by complexation with Cu(I) or Cu(II) ions forming a blocking barrier to copper corrosion. It is noticed that these compounds strongy inhibit copper corrosion in chloride solutions of variuos pH values and they are environmentaly friendly. V-o-Ph-V is a compound with a planar structure and there are large conjugate bonds among the three aromatic rings and the two –CH=N- groups so it is inferred that it adsobs rapidly on the copper surface and forms a thin protective layer via the formation of a N-Cu coordinate bond or π electron interactions. Cu(I)-(V-o-Ph-V) chelate forms, and afterwards also Cu(II)-(V-o-Ph-V). A crystal of the chelate precipitates on the surface from the solution resulting in a thick protective film and the anodic dissolution is inhibited. Long immersion and high concentration favoure the inhibition effect.

$$\mathrm{Cu+V\text{-}o\text{-}Ph\text{-}V \rightarrow Cu\text{-}(V\text{-}o\text{-}pH\text{-}V)_{ads}}$$
$$\mathrm{Cu(I)+V\text{-}o\text{-}Ph\text{-}V \rightarrow Cu(I)\text{-}(V\text{-}o\text{-}Ph\text{-}V)_{ads}}$$
$$\mathrm{CuX_2^{-}+V\text{-}o\text{-}Ph\text{-}V \rightarrow Cu(I)\text{-}(V\text{-}o\text{-}Ph\text{-}V)_{ads}+2H^{+}+2X^{-}}$$

V-p-Ph-V is also a planar compound with a big conjugate π bond. The difference is in the arrangement of –C=N- groups. V-His is a non-planar compound so no big conjugate π bond can be formed. All the three Schiff bases can form chelates with Cu(I) or Cu(II), but Cu complexes with V-p-Ph-V and V-His are less compact. V-o-Ph-V and V-p-Ph-V in the halide solutions change the Cu dissolution mechanism or hinder the diffusion of dissolved oxygen towards Cu surface, they behave as mixed inhibitors but cathodic reaction is more influenced.

Maryam Ehteshamzadeh et al. [54,55] investigated the effect of novel the new series of Schiff base molecules on copper corrosion. The effect of N,N'-ethylen-bis(salicylidenimine) (S1), N,N'-isopropylen-bis(salicylidenimine) (S2) and N,N'-ortho-phenylen acetyl acetone imine (2-hydroxy benzophenone imine) (S3) on copper corrosion during treatment with 1M HCl solution is investigated [54]. It is shown that they are good inhibitors with inhibition efficiency up to 92%. The differences in the efficiency among molecules are correlated with their structure. S2 may assume a coplanar conformation which would provide optimal interaction of aromatic π electrons with the metal surface and thus show an advantage over S1 and S3. They act as cathodic inhibitors. They obay Langmuir isotherm while the adsorption energies indicate mixture of physical and chemical adsorption. The inhibitive action of Schiff bases N,N'-ethylen-bis(salicylidenimine) (S-E-S) and N,N'-ortho-phenylen-bis(salicylidenimine) (S-o-ph-S) self-assembled films on copper surface in chloride (0.88M NaCl) and acid (0.5M H_2SO_4) solutions is investigated [55]. It is found that S-o-ph-S is more efficient then S-E-S. When the concentration is increased the inhibition efficiency increases but that kind of application is not economical in industrial conditions, however film modification with propanethiol and 1-dodecanethiol significantly improves corrosion resistance at lower concentrations. $C_{12}H_{25}SH$ SAMs are better then C_3H_7SH SAMs. Synergetic parameter obtained in the presence of 25ppm Schiff bases and 5mM dodecanethiol is 1.92 for S-o-ph-S and 5.6 for S-E-S. Results are presented in table 11.

Table 11. Copper corrosion inhibition efficiency in the presence of Schiff bases [55]

inhibitor	concentration, ppm	media	method	exposure time, min	IE,%
S-E-S	25	0.88M NaCl	EIS	30	87.00
	300	0.88M NaCl	EIS	30	96.00
	25	0.5M H_2SO_4	EIS	30	65.00
	300	0.5M H_2SO_4	EIS	30	92.00
	300	0.5M H_2SO_4	polarization	30	78.00
S-o-ph-S	25	0.88M NaCl	EIS	30	88.00
	300	0.88M NaCl	EIS	30	99.00
	25	0.5M H_2SO_4	EIS	30	69.00
	300	0.5M H_2SO_4	EIS	30	96.00
	300	0.88M NaCl	polarization	30	92.00

A.A.El Warraky [56] investigated the influence of ethylene diamine (EDA) on Cu in 0.01M HCl pH= 1.8-2 with and without presence of Na_2S additive. Inhibitor is added after the sample was immersed for 2h in the different Na_2S additive concentrations. In the presence of 2ppm Na_2S pits appeare because CuHS film is unable to protect Cu surface from attack. In the presence of higher concentrations there is no pitting. Complete surface coverage with strongly adsorbed HS^- is achieved at concentration of 10ppm Na_2S, that points out that S^{2-} ions concentration increase facilitates HS^- adsorption on copper surface that prevents pitting corrosion occurrance. The addition of various concentrations of ethylene diamine (EDA) increase promote the corrosion rate of copper due to autocatalytic dissolution process at the Cu surface. However there is a synergistic effect between EDA and Na_2S resulting from HS^- adsorption on Cu that facilitates EDA adsorption. It is noticed that different organic inhibitors become protonated in acid solution:

$$EDA+H^+ \rightarrow EDAH^+$$

Adsorption of $(EDAH)^+$ is facilitated in the presence of adsorbed HS^- thus the inhibitor film can be copper hydrogen sulphide EDA complex (CuHSEDA).

3.3. Amino acids

Amino acids form a class of non-toxic organic compounds that are completely soluble in aqueous media and produced with high purity at low cost. These properties would justify their use as corrosion inhibitors.

J.B.Matos [57] studied the effect of cysteine (Cys) on the anodic dissolution of copper in sulfuric acid, at room temperature using electrochemical methods. Cys ($HSCH_2CHNH_2COOH$) contains three dissociable protons, and in aqueous solutions ionization depends upon pH. Acording to the copper dissolution mechanism proposed for sulfate media in the absence of cys the main species present on the copper surface at low overpotentials is the intermediate $Cu(I)_{ads}$. This indicates that the inhibitory effect of cys originates from this intermediate and suggests that film formed at higher cys concentrations (0.001 and 0.01mol/l) is Cu(I)-cys complex. Film has inhibition effect since current density is aproximately 20 times lower in the presence of cys. At low cys concentration, cys is adsorbed on surface but complex can not be formed. Influence of cys is not significant at higher overpotentials where the main species present on copper surface is $Cu(II)_{ads}$. G.Moretti [58] investigated possibility to use tryptophan (Trp) as a copper corrosion inhibitor in 0.5M sulfuric acid in the 20-50°C temperature range. Trp has good inhibiting effect in the short-term tests and at the highest concentrations. Temperature increase has a negative effect on its efficiency.

Table 12. Inhibition efficiency values in the presence of 0.01M tryptophan at different temperatures calculated from potenciodynamicpolarization curves [58]

T(°C)	20	30	40	50
IE(%)	86.90	93.40	77.90	84.90

Trp adsorbs on copper surface maintaining a certain contact angle with the metal surface and it can be physisorption or chemisorption and obays Bockris-Swinkels' isotherm where x=2 that means that Trp is at least in short time adsorbed on copper surface by displacing two water molecules. In the presence of inhibitor copper dissolution mechanism is changed so Cu is primarely oxidized to Cu^+ and is able to form slightly soluble $[Cu\text{-}Trp_n]^+_{ads}$ complex as the main product of electrooxidation in the presence of a "clean" surface (Cu/Cu_2O system). This complex lowers the Cu^+ concentration making the successive oxidation to Cu^{2+} negligible. In the presence of inhibitor this may participate in the intermediate formation $[Cu^+_{(ads)}]$ depending on the chemical stability and oxidative property of the adsorbed $[Cu\text{-}Trp_n]^+_{ads}$ complex:

$$Cu^+_{ads} + nTrp \leftrightarrow [CuTrp_n]^+_{ads}$$

The inhibition sustaines until the compex is adsorbed. Even if Trp suffers a certain photodegradation process at least for those Trp molecules present in the solution, the molecules of inhibitor adsorb well on active sites of the metal and/or the passivation layer at 20°C that is proved by inhibition percentage (IP) that is 80% for the solutions kept in dark as well as those kept in light.

3.4. Triphenylmethane derivatives

Two nitrogen containing organic compounds which are triphenylmethane ($(C_6H_5)_3CH$) derivatives, fuchsin basic FB (rosaniline chloride) ($C_{20}H_{19}N_3$•HCl) and fuchsin acid sodium salt FA ($C_{20}H_{17}N_3O_9S_3Na_2$), are tested as new copper corrosion inhibitors. [33,34] These compounds are thought to be good candidates due to the presence of chloride ion in FB and the polar or charged nature of the more complex FA surfactant molecule. Investigation is performed in sulphuric acid [33] and hydrochloric acid [34] solutions at various concentrations and temperatures in the presence of different inhibitor concentrations. FB is more efficient than FA that can be attributed to different molecular structures. The Frumkin isotherm gives the best fit while inhibitor ocupies more then one active spot. The inhibition mechanism of FB and FA can be explained by the $Cu(inhibitor)_{ads}$ reaction intermediates:

$$\mathrm{Cu+inhibitor} \leftrightarrow \mathrm{Cu(inhibitor)_{ads}} \leftrightarrow \mathrm{Cu^{n+}+ne^{-}+inhibitor}$$
$$\mathrm{inhibitor_{aqu}}+\chi \mathrm{H_2O_{ads}} \leftrightarrow \mathrm{inhibitor_{ads}}+\chi \mathrm{H_2O_{aqu}}$$

At first, when there is not enough $Cu(inhibitor)_{ads}$ to cover Cu surface, because the inhibitor concentration is low or because the adsorption rate is slow, metal dissolution takes place at sites on the Cu surface free of $Cu(inhibitor)_{ads}$. With a high inhibitor concentration a compact and coherent inhibitor overlayer is formed on the copper, which reduces chemical attacks on the metal. FB addition introduces chloride ions that are primarely adsorbed so afterwards by synergetic effect FB cations are electrostaticaly adsorbed on the Cu surface covered with primarily chemisorbed chloride ions. The inhibition action of FA in an H_2SO_4 acid solution may result from the blocking effect due to physical adsorption of the negatively charged $C_{20}H_{17}N_3O_9S_3^{2-}$ to the positively charged copper surface by the electrostatic attraction force. Temperature negatively effects inhibition efficiency. Comparison of these results with those obtained using BTA under the same conditions reveals that in sulphuric acid solution BTA is the most efficient, while in hydrochloric acid solution FB is the most efficient and the inhibition efficiency of BTA is close.

3.5. Thiole group compounds

H.Baeza [59] studied copper corrosion inhibition by 1,3,4-thiadiazole-2,5-dithiol (bismuthiol) in 0.5M HCl at 25°C. The efficiency is increased as the inhibitor concentration is increased reaching maximum value of 84,1% at $80 \cdot 10^{-5}$M. The inhibitor is chemisorbed on the copper surface obaying Langmuir isotherm, and since the peaks corresponding to the formation of complexes bismuthiol-Cu(I) and bismuthiol-Cu(II) are observed, it is concluded that inhibition mechanism originates from these complexes on metal surface.

Y.S.Tan [60] studied the effect of self-assembled monolayers (SAM) of a series of substituted benzenethiol (BT) $X\text{-}C_6H_4\text{-}SH$ (where X=meta-NH_2 3-aminobenzenethiol 3-A-BT, ortho-NH_2 2-aminobenzenethiol 2-A-BT, para-NH_2 4-aminobenzenethiol 4-A-BT, para-$NHCOCH_3$ 4-acetamidobenzenethiol 4-AA-BT, para-F 4-fluorobenzenethiol 4-F-BT, para-CH_3 4-methylbenzenethiol 4-M-BT and para-$CH(CH_3)_2$ 4-isopropylbenzenethiol 4-IP-BT) molecules. SAMs are prepeared by adsorption from 5mM solution in ethanol, during 1h at room temperature, onto a fresh copper surface. The hydrophilic mercapto group (-SH) in the BT molecule has a strong affinity for copper and the inhibitor molecules anchor on the copper surface via the thiolate bond, while the hydrophobic benzene ring with different substituents constitutes the ultra thin protective monolayer. The formation of the benzenethiolate-Cu complex requires the loss of the –SH hydrogen though it is not yet determined whether this proton is lost as H_2 or H_2O:

$$X\text{-}C_6H_4\text{-}SH + Cu^0 \rightarrow X\text{-}C_6H_4\text{-}S^{-}Cu^{+} + 1/2H_2$$
$$X\text{-}C_6H_4\text{-}SH + Cu^0 + \text{oxidant} \rightarrow X\text{-}C_6H_4\text{-}S^{-}Cu^{+} + 1/2H_2O$$

The loss of the –SH hydrogen is enchanced by the electron withdrawing groups though according to the results it can be inferred that any substitution in the BT benzene ring regardeless of whether electron-donating or electron-withdrawing, improves the corrosion inhibiting properties of the chemisorbed films. Self-assembled monolayers of benzenethiols chemisorbed on Cu surface are good copper corrosion inhibitors in 0.5M sulphuric acid. The structure of the inhibitors influences their inhibition efficiency and is strongly affected by the type and the position of the substituent functional group on BT. The results indicate that the inhibition efficiencies (IE) of the para substituted BT molecules increase in the following order: $–CH(CH_3)_2 > –CH_3 > –F > –NHCOCH_3 > –NH_2$. The effect of the ring position of the substituent on IE is ortho > meta > para, relative to the –SH position. These results are important in providing the rationale for the selection and the molecular design of inhibitors against Cu corrosion in aqueous media.

Table 13. The effect of benzenethiol SAMs on copper corrosion in 0.5M sulphuric acid [60]

inhibitor	BT	4-IP-BT	4-M-BT	4-F-BT	4-AA-BT	4-A-BT	3-A-BT	2-A-BT
IE%,polarization curves	74.39	86.47	82.53	80.53	66.01	53.51	60.25	72.30
IE%, EIS	74.10	90.60	89.10	87.10	82.60	76.80	78.00	80.40

The inhibition of copper corrosion in 1.5% NaCl solution is studied at 25, 35 and 45°C using three inhibitors: thiosemicarbazide (inh 1), phenyl isothiocyanate (inh 2) and their condensation product 1-phenyl-2,5-dithiohydrazodicarbonamide (inh 3). [61] It is concluded that all the three compounds are efficient corrosion inhibitors whereat the inhibition efficiencies follow the sequence: inh3>inh1>inh2. The enhanced effectiveness of the inh 3 can be correlated with the structure and size of molecule, inh 3 has four nitrogen atoms, two sulphur atoms and delocalised ð electron density acting as active centres and the largest surface area. Mechanism of inhibition is proposed as adsorption only in case of inh 2; inh 1 at lower concentrations inhibits corrosion through adsorption while at higher concentrations Cu(I) complex is formed that gradualy oxidises into Cu(II) complex. Complex films are responsible for corrosion inhibition. Inh 3 follows both the mechanisms simultaneously. It can be noticed that inhibition efficiency increases with temperature.

Table 14. Inhibitive action of thiosemicarbazide (inh 1), phenyl isothiocyanate (inh 2) and 1-phenyl-2,5-dithio hydrazodicarbonamide (inh 3) on copper corrosion in 1.5% NaCl [61]

Inhibitor	concentration (ppm)	Method	IE (%)		
			25°C	35°C	45°C
Inh 1	100	weight loss	72.00	76.00	84.00
		polarization	69.00	74.00	83.00
Inh 2	100	weight loss	62.00	66.00	70.00
		polarization	60.00	63.00	67.00
Inh 3	100	weight loss	82.00	88.00	93.00
		polarization	80.00	85.00	92.00

3.6. Phosphates as copper corrosion inhibitors

Copper corrosion by-product release to potable water is a complex function of pipe age, water quality, stagnation time and phosphate inhibitor type. Phosphates can be phosphoric acid, combination of orthophosphoric acid and zink orthophosphate, polyphosphate or blend of orthophosphoric acid and polyphosphate. It is noticed [62] that dosing of 1mg/l orthophosphate led to reductions in copper release ranging from 43-90% when compared to the same condition without inhibitor regardless of pipe age, water quality or stagnation period. Ortophosphate and hexametaphosphate have beneficial effects on copper release, but ortophosphate leads to greater reductions in copper release when compared to hexametaphosphate. Shiyin Li [63] investigated the adverse effect of organic matter on orthophosphate corrosion inhibition for copper pipe in simulated soft water. Sodium alginate and fulvic acid are selected to simulate extracellular polymeric substance produced by bacteria and natural organic matter in potable water. It is observed that organic matter markedly influence orthophosphate corrosion inhibition efficiency for copper pipes of various age (1mg/l as P), sodium alginate of low concentrations increases Cu dissolution but it decreases at concentration of 16mg/l, fulvic acid in concentration of 16mg/l strongly influences soluble Cu release (release increases and more from new pipes), at higher pH copper dissolution decreases.

Two kinds of phosphates, triethyl phosphate (TEP) and triphenyl phosphate (TPP), are used to form self-assembled monolayers, in $1{\bullet}10^{-3}$M ethanolic solution, for the inhibition of the copper corrosion in 0.2M NaCl solution. [64] The results showed that their inhibition ability first increases with increasing immersion time in ethanolic solutions of the corresponding compounds. However, when the immersion time is increased over some critical point, the inhibition effect decreases. The best effect is achieved after 12h immersion whereat the surface coverage is 93.80% for TEP, and 96.50% for TPP. Therefore, for the same immersion time the inhibition effect of TPP monolayer is more pronounced than that of TEP monolayer. The influence, on copper corrosion in 0.2M NaCl aqueous solution, of self-assembled monolayers (SAMs) of triethyl phosphate (TEP – $(C_2H_5O)_3PO$) and mixed SAMs of TEP with cetyltrimethyl ammonium bromide (CTAB – $(CH_3(CH_2)_{15}(CH_3)_3N^+Br^-$)) formed on copper surface is studied. [65] Films are formed from $1{\bullet}10^{-3}$M TEP ethanol solution, and

1•10^{-3}M CTAB aqueous solution. It is noticed that inhibition efficiency (IE) increases with an increase in the immersion time of copper in TEP-containing solution. When the TEP film is modified with CTAB, the efficiency improves markedly. External magnetic field improves the inhibition effect of SAMs and the inhibition efficiency increases with the increase in the field strength. TEP molecule reacts with copper surface via oxygen atom at the end of molecule.

Table 15. The results of the investigation of TEP self-assembled layers [65]

Inhibitor	exposure time (h)	magnetic field strength (mT)	IE (%)
TEP	1	0	81.00
TEP	20	0	95.00
TEP	1	160	97.60
TEP + CTAB	1 + 24	0	99.40

Inositol hexaphosphate (IP_6) also known as phytic acid and its salts, is suggested to be used as an environmentally friendly reagent to prevent metal surface from corrosion through a self-assembled monolayers (SAMs) method. [66] It is cheap and available as naturally polyphosphorylated carbohydrate widely occurring in beans, brown rice, corn, sesame seeds, wheat bran. For monolayer formation 10^{-2}M IP_6 aqueous solution was used. Polarization is conducted in 0.1M KCl solution at room temperature. Monolayers on the copper surface improve its corrosion resistance, but the efficiency is only 41.20% due to water co-adsorption.

3.7. Other organic compounds

The effect of potassium ethyl xanthate on the anodic dissolution of copper in 1.0M NaCl acidic solutions pH=1-3 is investigated. [67] Increasing the concentration and pH of the solution increases inhibition efficiency (IE) therefore in pH=3 solution in the presence of 5•10^{-3}M KEtX IE is 83%. Inhibitor action can be related to formation of an adherent and compact film of the Cu(I) complex on the copper surface:

$$EtX^-_{(aq)} + Cu^0 \leftrightarrow Cu(I)EtX_{(ad)} + e^-$$

$Cu(I)EtX_{(ad)}$ represents the surface dipol formed by chemisorption of EtX^- ion on Cu electrode or growth of multilayer Cu(I)EtX film. Considering that the first step in copper dissolution in presence of inhibitor is formation of $CuCl_2^-$ the process may follow the steps presented below:

$$Cu + 2Cl^- \leftrightarrow CuCl_2^- + e^-$$
$$CuCl_2^- + EtX^- \leftrightarrow Cu(I)EtX + 2Cl^-$$

Soluble $CuCl_2^-$ can either diffuse to the bulk solution or react with EtX^- to form a protective film. The restrained inhibition efficiency is probably caused by the formation of an untight Cu(I)EtX film on Cu surface that can be penetrated by chloride ions, which results in increasing the copper corrosion rate.

The influence of sodium dodecylsulfate (SDS) on copper corrosion in 0.5M H_2SO_4 + xSDS solution is studied.[68] It is found that the critical micelle concentration is 8•10^{-4}M, and that the inhibition efficiency increases as the concentration increase and in presence of 5•10^{-2}M SDS it is 97.80%. SDS is a good anodic inhibitor very close to the rest potential. Adsorption obays Langmuir isotherm. The values of ΔG suggest that the inhibitive action results from the electrostatic adsorption of $C_{12}H_{25}SO_4^-$ ions onto the positively charged copper surface. The free energy of adsorption is more negative when SDS concentration exceedes critical micelle concentration due to formation of highly charged micelle and because of higher electrostatic attraction the adsorption increases and consequently the corrosion rate is reduced.

Phthalazin derivatives are studied as copper corrosion inhibitors in 1M H_2SO_4. [69] This study monitors the evolution of the inhibitory effect of the phthalazin derivatives, according to their substituents. Following compounds are investigated: (I) 2-[(5-Mercapto-4H-1,2,4-triazol-3-yl)methyl]phthalazin- 1(2H)-one; (II) 2-[(6-Phenyl- 5H-[1,2,4]triazolo [3,4-b] [1,3,4]thiadiazin -3-yl) methyl] phthalazin- 1(2H)-one; (III) 2-[(7-Anilino- 5H-[1,2,4]triazolo [3,4-b] [1,3,4]thiadiazin- 3-yl) methyl] phthalazin- 1(2H)-one (IV) 2-({6-Methyl- 7-[(E)-phenyldiazenyl] -5H -[1,2,4]triazolo [3,4-b] [1,3,4]thiadiazin -3-yl} methyl) phthalazin- 1(2H)-one. The inhibitors are of mixed type, and the suppression in current increases as the inhibitor concentration increases. The inhibitor molecules are adsorbed on the metal surface via electron pairs on the sulphur, oxygen and nitrogen atoms as well as via π electrons on the aromatic rings, while the adsorption obays Langmuir's isotherm. The structure and composition of phthalazine derivatives influence their inhibiting efficiency, IE decreases in the following order IV>III>II>I. Compound IV is the superior among the investigated compounds, this may be due to the highest molecular weight, the presence of phenyl group and the presence of additional N=N, and CH_3 groups which have the electron donating ability to the vacant d-orbital of a metal. The conclusion is that IE of the phthalazin derivatives increases with the substitution. Table 16 presents results obtained at inhibitor concentration of 6•10^{-5}M at temperature of 303K.

Table 16. The influence of phthalazine derivatives on copper corrosion in 1M H_2SO_4 [69]

inhibitor	IE,% (Tafel extrapolation)	IE,% (polarization resistance)	IE,% (weight loss)
I	68.70	66.90	71.70
II	73.10	73.50	76.50
III	80.10	78.90	80.60
IV	82.80	83.80	84.30

The inhibition effect of gamma-pyrodiphenone (γ-PD) [6-(c-pyridil) 6,7-dihydro-5H-dibenzo[a,b] cyclo-heptendion-5,7, called c-pyro-diphenone (gamaPD)] on copper corrosion in sulphate solutions (0.1M sodium sulphate pH 5.6) is investigated. [70] It is noticed that γ-PD suppresses both active copper dissolution and oxygen reduction. High IE, in the presence of 5mg/dm^3 it is 96.9%, is a consequence of γ-PD molecules adsorption as the first stage and the formation of a polymer-like structure film by coordination of γ-PD with Cu_2O on prolonged expusure. The presence of three donor atoms and the steric conformation of the molecule determine the chemical properties and adsorption on Cu surface.

Tannins, a class of non-toxic biodegradable organic compounds, are polyphenols of vegetal origin, extracted usually from the barks of trees. The basic components of tannins are sugars, gallic acid, ellagic acid and flavanoids. Extract characterization revealed the presence of main products: gallic acid, digallic acid, trigallic acid and various galloyl-O-D-glucose. The extract contains, in addition to gallic acid, a mixture of the polyphenolic compounds with complex structure and high molecular weight. J.Mabrour [71] studied copper corrosion inhibition in 0.1M NaCl solution pH=5.0 in the presence of vegetal tannin extracted from Takaout galls (Tamarix articulata). The gallic acid is used as a tannin representative. It is noticed that tannin are anodic inhibitors. The copper behaviour at free potential in the presence of tannin is similar to that in the presence of gallic acid but in the anodic domain contribution of other compounds present in tannins mixture is significant that is manifested by IE increase (93.2% at 2g/l tannin and 80.4% in the presence of 2g/l gallic acid E=0.15V) and current density decrease. Inhibition effect can be explained by the formation of Cu-tannin complex. The copper surface coverage increases with tannin concentration.

Substituted uracils are studied as copper corrosion inhibitors in 3% NaCl. [72] Following compounds are investigated: uracil (Ur); 5,6-dihydrouracil (DHUr); 5-amino-uracil (AUr); 2-thiouracil (TUr); 5-methyl-thiouracil (MTUr); dithiouracil (DTUr), so the substituent influence can be estimated. The inhibition efficiency decreases in the following order: DTUr>MTUr>TUr>Ur>DHUr>AUr. DTUr is the best inhibitor in the tested compounds and acts as a mixed-type inhibitor. DTUr is adsorbed on Cu surface according to the Frumkin isotherm. The inhibition efficiency may be explained on the basis on the existence of two SH groups in the molecular structure (the tautomeric equilibrium) and two nitrogen atoms. It may occur by means of the sulphur atoms and also by the delocalisation of electrons of the aromatic ring and by the pairs of the nitrogen electrons that enable formation of complex with copper. Results are presented in table 17.

Table 17. The effect of uracils on copper corrosion in 3% NaCl [72]

Inhibitor, 10^{-3}M	DTUr	MTUr	TUr	DHUr	AUr	Ur
IE,%	95.40	82.00	44.10	22.50	-72.20	39.20

The effect of propargyl alcohol (2-propyn-1-ol) on electrochemical behavior of copper in 0.5M H_2SO_4 is studied. [73] It is noticed that the electrodissolution decreases in the presence of the inhibitor. The interaction between the electrode surface and the organic compound is a relatively fast process and depends on the adsorption potential and alcohol concentration. The adsorption occurrs via triple bond π-electrons without the polymer film formation, whereat the effect is more distinct at higher concentration. Longer exposure to inhibitor has no effect. The influence of propargyl alcohol is more significant on nickle and Cu/Ni alloys in comparison to Cu.

Inhibitor action of aniline derivatives is investigated. [74] Aniline, p-chloro aniline, p-nitro aniline, p-methoxy aniline and p-methyl aniline are studied. Calculations show that the aniline molecules are preferentially adsorbed on highly reactive sites such as defects. The interaction is favoured by a deficiency of charge on metal surface. The electron donor substituents ($–CH_3$, $–OCH_3$) in the para position in the aniline molecule produce more effective interaction with surface that is due mainly to an increase of the net charge of the amino group. In the case of electron acceptor substituents ($–NO_2$, –Cl), the opposite is observed. When chloride ions are present as well, the protonated aniline from AH-Cl ion pair is the species most susceptible to interact with the adsorption sites on the copper surface liberating the chloride and H^+ ions and leaving behind the aniline adsorbed on the copper surface. The reaction is:

$$\text{anilineH-Cl} + \text{Cu(surface)} \rightarrow \text{aniline-Cu(surface)} + \text{HCl}$$

It is also noticed that Langmuir-Blodgett (LB) films of poly(N-hexadecylaniline)/docosanol deposited on copper inhibit corrosion in sea water. Even after 8 weeks inhibition efficiency is ~95%. [75]

The effect of N-(3-metoxyphenylaminomethyl)phthalimide (a); N-(3-methylphenylaminomethyl)phthalimide (b) and N-(phenylaminomethyl)phthalimide (c) on copper corrosion in 2M HNO_3 is investigated. [76] Inhibition efficiency decreases in the following order a>b>c, it increases with concentration, while at higher temperatures it decreases. Inhibitor action is attributed to physical adsorption on copper surface that obays Temkin's isotherm. Efficiency is higher when compound has higher molecular weight (size) and more centers for bonding with copper.

Table 18. EI values obtained by polarization method at 30°C in the presence of $1 \cdot 10^{-4}$M phthalimide derivatives in 2M HNO_3 solution [76]

inhibitor	a	b	c
IE (%)	93.10	80.90	79.10

The influence of purine (PU) on corrosion of copper in 1.0M NaCl solution pH=6.8 is studied. [77] The inhibition efficiency increases with an increase in the concentration of PU. An adherent protective layer is formed by chemisorption of purine on electrode surface according to the Langmuir isotherm. Mechanism is presented through the following reactions:

$$Cu^0_m(OH^-)_n + nH^+ + pPU \leftrightarrow Cu^0_m(OH^-)_{n-x}(PU)_p + (n-x)H_2O$$
$$CuCl_2^- + PUH \leftrightarrow (Cu\text{-}PU)_{ads} + H^+ + 2Cl^-$$

In the presence of $1 \cdot 10^{-2}$M PU inhibition efficiency (IE) is 76% (polarization curves) or at $5 \cdot 10^{-3}$M IE= 97% (weight loss). Purine is relatively cheap and easely produced with high purity. It is non-toxic and biodegradable and hence environmentaly friendly. Caffeine (1,3,7-trimethylxanthine) is studied as copper corrosion inhibitor in 0.5M KNO_3 as well as in the presence of chloride ions. [78] It is revealed that caffeine adsorption and interaction with copper occurr whereat inhibition efficiency in the presence of 1.5mM cafeine is around 60%.

The effect of isatin on copper corrosion in aerated 0.5M H_2SO_4 solution in the temperature range 25-55°C is investigated. [79] It exhibits inhibitive action in the whole temperature range whereat inhibition efficiency reaches 94% at $7.5 \bullet 10^{-3}$M of isatin. The action is attributed to the adsorption and formation of complex with copper through the following reaction:

$$Cu^{+}_{(ads)} + n \bullet isatin \leftrightarrow [Cu \bullet (isatin)_n]^{+}_{(ads)} + 1e^{-}$$

The adsorption behaviour of isatin suggests both physical and chemical adsorption.

3.8. Effect of self-assembled monolayers on copper corrosion inhibition

Self-assembled monolayers of numerous compounds proved to be a good way to protect metal surface against corrosion. Main characteristic is low consumption of chemical to achieve high efficiency, so industrie and nature are not too much burdened.

The ability of self-assembled layers of organothiols to protect copper surface from corrosion is studied. The following compounds are investigated: n-dodecanethiol (DT) [80]; (3-mercaptopropyl)trimethoxysilane (MPTS) [80]; 11-perfluorobutylundecanethiol (F_4H_{11}) [80]; octadecanethiol (ODT) [81] and dodecanethiol [82]. It is revealed that they have good protective effect during exposure to air [82], water [80], alkaline media [80,82] as well as to chloride ions [80,82].

The effects of layers of poly(o-anisidine) (POA) [83,85], poly(o-toluidine) (POT) [84,85] and poly(o-anisidine-co-o-toluidine) (OAOT) [85] formed on copper surface on copper behavior in 3% NaCl solution are investigated. It is revealed that they are efficient corrosion inhibitors and at concentration of 0.1M high inhibition efficiency is reached whereat the values are: POA-85.81%, POT-98.00%, OAOT-99.66%. [85] The copolymer film is more efficient and the best protection is achieved when the proportion of o-anisidine and o-toluidine is 1:1.

It is noticed that films formed in the presence of polyaniline (PANI) and poly(methyl methacrylate) (PMMA) protect copper surface against corrosion [86,87]. Polyaniline (Pani) and poly(orto-metoxyaniline) (Poma) are studied in 0.1M NaCl. The best results are achieved with Pani because polymer film is involved in formation of oxide film on polymer-metal surface, the fenomenon not observed with Poma. This oxide film increases the barier effect of polymer film. [88]

The effect of films formed from polypyrrole (PPy) and polyindole and polypyrrole (PPy/PIn) [89] and polypyrrole and polythiophene (PPy/PTh) [90] on copper corrosion in 3.5% NaCl is investigated. It is revealed that PPy protects copper surface against corrosion as well, but PPy/PIn and PPy/PTh films are more efficient. F.Zucchi et al. [91,92] studied the effect of 3-mercapto-propyl-trimethoxy-silane (PropS-SH), bis-triethoxy-silyl-ethane (BTSE), n-octadecyl-trimethoxy-silane (OctadecS), phenyl-trimethoxy-silane (PhS) on copper corrosion in 0.6M NaCl solutions of pH: 4, 7 and 10. The films are formed at the room temperature for different times, from 2 to 60min, in the solutions of the following composition: 90/6/4 v/v methyl alcohol/water/silane. The optimum treatement is acquired in solution pH=4, in presence of PropS-SH. The efficiency is enhanced by the presence of mercapto group and longer alkyl chain.

Table 19. The results of the investigation of the effect of silane on copper corrosion [91]

After 1h in 0.6M NaCl	pH	Time, min	PropS-SH	OctadecS	PhS	BTSE
IE, %	4	60	99.96	99.81	86.60	32.00
IE, %	7	60	99.59	99.49	/	/
IE, %	10	60	99.88	99.30	/	/

The self-assembled films of 1H,1H,2H,2H-perfluorodecyldimethylchlorosilane (PFMS) formed on copper surface are demonstrated to be a good and stable protection against corrosion as well. [93]

The influence of SAM formation time and chain length of hydroxamic acid amphiphiles molecules ($C_nH_{2n+1}CONHOH$, n=9-17) forming self-assembled molecular layer on the copper surface on its anticorrosive action is studied. It is noticed that inhibition efficiency increases with molecule chain length [94] and number of monolayers [95]. The results are presented in table 20.

Table 20. The results of the application of hydroxamic acid SAMs [94]

Media: 0.5M Na_2SO_4; pH 3; exposure period 1h [94]				
Inhibitor	[Cu+C_9CONHOH]SAM	[Cu+C_{11}CONHOH]SAM	[Cu+C_{15}CONHOH]SAM	[Cu+C_{17}CONHOH]SAM
IE, %	76.00	81.00	82.00	85.00

The formation of self-assembled monolayers from sodium S-alkyl thiosulfate ($CH_3(CH_2)_{n-1}S_2O_3^-Na^+$) (SAMs) on copper surface in aqueous and organic solvents is investigated. [96] Depending on the solvent, the efficiency decreases in the following order: ethanol > tetrahydrofuran > water > toluene. The influence of alkyl chain length is also noticed whereat thiosulfates with the longer chain can be used for copper corrosion inhibition in aqueous media.

It is revealed that nanoparticles of Au and Ag with sodium oleate can form self-assembled layer on the copper surface. They improve inhibiting action whereat Au nanoparticles more than Ag. In 0.5M NaCl solution after SAM formation for 1h following values of inhibition efficiencies are obtained: sodium oleate 91.20% < sodium oleate + Ag 98.00% < sodium oleate + Au 98.70%. [97]

4. CONCLUSIONS

Based on previously desplayed facts, it can be said that numerous compounds can be used as copper corrosion inhibitors and the possibility of their application depends on a few factors.

Media that inhibitor is used in is very important for selection. The presence of aggressive ions and pH are among the most important parametres.

Action mechanisms are different. Inorganic compounds act through oxide films formation. Organic compounds mostly act via adsorption on metal surface and complex formation. That is the basis of the adverse effect of high temperature on the efficiency of organic compounds.

Higher inhibitor concentration and longer exposure of copper in inhibitor solution lead to inhibition efficiency increase.

Molecular structure of inhibitor is the main factor determining its characteristics. Presence of heteroatoms (S,N,O) with free electron pairs, aromatic rings with delocalized π electrons, high molecular weight alkyl chains, substituent groups in general improves inhibition efficiency. The effect of electron-donor groups is particularly favourable. Group position is also important, 2- and 5-positions are shown to be more convinient.

It is noticed that higher inhibition efficiency is achieved by application of organic compounds related to inorganic. Thiazoles, benzotriazole, triazoles give good protection except in strongly acidic media, where tetrazoles and imidazoles are revealed to be good. However, introduction of substituent groups can change that. Amines show high inhibition efficiency in chloride and acidic solutions, but due to high concentration the application of that kind is not economic. Studies of derivatives of triphenylmethane, tannin, aminoacids reveal that it is possible to use compounds that are accessible, non-toxic and efficient. Self-assembled monolayers of inhibitor show high inhibition efficiency with low inhibitor consumption which is a great advantage of that kind of treatement.

There is no universal solution for efficient copper corrosion inhibition, corrosion inhibition efficiency using specific inhibitor is a complex function of numerous significant parametres.

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