

**1, 5-BIS [(4-DITHIOCARBOXYLATE-1-DODECYL-5-HYDROXY-3-METHYL)PYRAZOLYL] PENTANE AS COPPER CORROSION INHIBITOR IN 0.1 M SULPHURIC ACID**

**Rosa Vera\*, Alfonso Oliva and Aurora Molinari**

*Institute of Chemistry, Faculty of Sciences, Pontificia Universidad Católica de Valparaíso, Campus Curauma, Avda. Universidad 330, Placilla, Valparaíso, Casilla 4059, Chile.  
email: rvera@ucv.cl*

**Abstract:** The ability of tetradentate ligand 1,5-bis[(4-dithiocarboxylate-1-dodecyl-5-hydroxy-3-methyl)pyrazolyl]pentane (H<sub>2</sub>BDTCPP) as organic surface coating to inhibit the copper corrosion in 0.1 M H<sub>2</sub>SO<sub>4</sub> have been studied. The inhibitory properties were studied by immersion assays and the results show that H<sub>2</sub>BDTCPP behaves as a mixed inhibitor in 0.1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution, with an inhibition efficiency of 62.1 %, increasing the corrosion potential and decreasing the corrosion current of copper when it is coated over the metal surface. These properties can be attributed to the planar aromatic structure of the pyrazolyldithiocarboxylate group and to the high  $\pi$ /lone-pair electron density due to nitrogen, oxygen and sulphur which favour its physical and chemical adsorption.

**Keywords:** copper, corrosion inhibition, sulphuric acid, 1,5-bis(4-dithiocarboxylate-1-dodecyl-5-hydroxy-3-methylpyrazolyl)pentane coating.

### **Introduction**

Copper and its alloys are widely used in industry due to their convenient mechanical properties, high electric and thermal conductivity, resistance to wear, and resistance to corrosion. However, incrustations and corrosion products adhered to the metal surface have a negative effect on heat transfer equipments, causing a decrease in efficiency. This brings about the necessity of periodic cleaning of the oxidized copper using acidic solutions of H<sub>2</sub>SO<sub>4</sub> or HCl. This process is also the most commonly employed method to clean copper and its alloys during the processing and fabrication of copper materials. Under these conditions it is necessary to use inhibitor compounds which when added to the acidic media in small quantities, slow down the corrosion rate of copper or its alloys [1-4].

It is known that organic compounds containing heteroatom like oxygen, sulphur or nitrogen as well as aromatic rings in their structure have inhibitory effects on corrosion of copper and others metals. These inhibitory properties depend among others, on their molecular structure, the size of the molecule, the type and number of adsorption centres with high electron density, the ability to form protective layers of metallic complexes and the type of electrolyte used. The compounds act mainly displacing water molecules, forming a barrier film by an adsorption process or by a strong coordination bond on the metal surface; they interact with the anodic and

cathodic reactions sites to retard the oxidation and/or reduction corrosion reactions [5]. A great number of studies on organic molecules with inhibitory properties are related to nitrogen heterocyclic compounds and among them the most widely used in copper corrosion are benzotriazole (BTAH) [6-12], benzimidazole [13] and tetrazole [14]. BTAH and related derivatives are used in copper corrosion in alkaline or neutral media but, in acidic solutions its inhibition efficiency is low, due to the fact that the coated surface film which is formed is fragile, porous, with a certain degree of solubility and low level of polymerization [15]; furthermore, its toxicity and carcinogenic properties are also important disadvantages [16].

Another group of compounds with protective properties against metals or alloys corrosion in aggressive media are pyrazolic, bipyrazolic and tripyrazolic derivatives [5,17,18]. Related to copper corrosion, it has been reported that pyrazole behaves as a cathodic inhibitor and its presence in chloride media changes the mechanism of the metal dissolution, decreasing the rate of cuprous species formation and increasing that of cupric species; the action of pyrazole is due to a blockage of metal surface by copper-pyrazole species produced during the anodic sweep [19]. Others heterocyclic compounds contain mercapto groups; they show a higher level of copper inhibition than BTAH [6-12]. Studies with bismuthiol (1,4,4-thiadiazole-2,5-dithiol) in 0.5 M HCl at 25°C and  $1.0 \times 10^{-5}$  M inhibitor concentration level have shown that this compound is a mixed inhibitor with 84.1% corrosion inhibition. This protective effect is attributed to the formation of a Cu-bismuthiol complex on the metal surface which acts as a coating barrier against the corrosion progress, effect that is enhanced as the acidity is increased [4].

Searching for new heterocyclic organic compounds with chelating and extractive properties, we have described the synthesis, characterization and copper (II) extraction studies of 1,5-bis[(4-dithiocarboxylate-1-dodecyl-5-hydroxy-3-methyl)pyrazolyl]pentane ( $H_2BDTCPP$ ) [20,21]. This compound meets most of the requirements to be a good inhibitor of copper corrosion because it contains planar aromatic pyrazolyl groups, N, O, S heteroatom and reacts with copper (II) ions as a tetradentate ligand to form a square-planar complex stable in acidic media. Recently we have reported the behaviour of  $H_2BDTCPP$  as an efficient inhibitor of copper corrosion in aggressive 3.5% NaCl solution. It was proven that the inhibitor prevents copper corrosion by a two step physisorption-chemisorption coating process of the ligand onto the copper surface, followed by the formation of a protective Cu (II)- $BDTCPP$  complex layer over the metal surface. The Cu(II) arises from the oxygen oxidation of Cu(I) formed at the earlier stages of the corrosion process [22]. Taking into account that the search of new inhibitors of copper corrosion in acidic media is an active research area, we wish to report the efficiency of  $H_2BDTCPP$ , an organic coating, as copper corrosion inhibitor in 0.1 M  $H_2SO_4$ .

## Experimental

The ligand  $H_2BDTCPP$  was conveniently prepared and characterized according to a previously reported procedure [20]. A solution of the ligand containing 1.0 g/10 mL in  $CHCl_3$  was prepared and 100  $\mu$ L were deposited over the copper surface using the spin-coating technique, obtaining an adherent 1  $\mu$ m layer. Before and after inhibition experiments, the coated layer was analyzed by IR spectroscopy using a Perkin Elmer Spectrum One FT IR spectrophotometer, by UV/VIS spectroscopy with a Perkin Elmer UV/VIS Lambda EZ 201 spectrophotometer and by NMR spectroscopy using a Bruker Avance Digital spectrometer operating at 400 MHz for  $^1H$  and at 100 MHz for  $^{13}C$ .

Copper sheets of 99.9% purity and 1.0  $cm^2$  area previously polished with 600-1000 grip SiC paper and washed with acetone before applying over one of the faces, were used in this study.

The aggressive media used was 0.1 M H<sub>2</sub>SO<sub>4</sub> at room temperature, prepared from analytical grade reagent and deionized water.

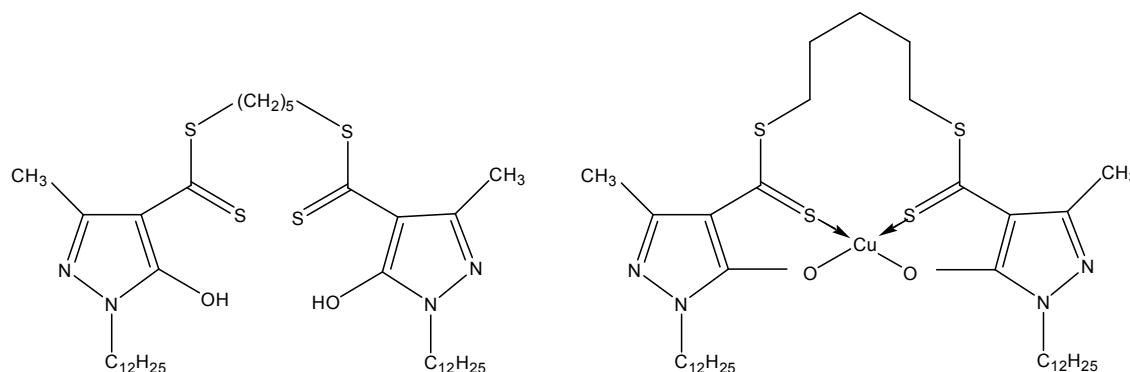
The morphology and thickness of the coated film of H<sub>2</sub>BDTCPP was analyzed using scanning electron microscopy (SEM) on a JEOL 5410 microscope coupled to a X-ray analyzer (EDS), and using atomic force microscopy (AFM) on a IIIA Digital Instruments Nanoscope. The samples, which were cut in order to be observed via SEM, were polished with aluminium to a width of 0.05 μm and metalized with Au-Pd.

For the weight loss tests 1 cm<sup>2</sup> copper sheets, polished in the same way as mentioned before, with and without H<sub>2</sub>BDTCPP and their initial weight were measured. They were submerged in a solution of 0.1 M H<sub>2</sub>SO<sub>4</sub> for 2, 4, 6, 8 and 10 days and after the immersion period was completed, the samples were removed, in accordance with ISO regulation 8407 [23], dried with cold air and weighed.

## Results and Discussion

### Synthesis and characterization of ligand H<sub>2</sub>BDTCPP

H<sub>2</sub>BDTCPP (Fig.1) was synthesized by the reaction of 1-dodecyl-3-methyl-2-pyrazolin-5-one with sodium acetate, carbon disulfide and 1,5-dibromopentane in DMF, according to a described procedure [20]. It was characterized by <sup>1</sup>H and <sup>13</sup>C NMR as well as IR and High Resolution Mass Spectra (HRMS). Complexing reaction and solvent extraction studies with Cu (II) showed the formation of a Cu-BDTCPP square-planar complex (Fig. 1) [21]. After thin layer fixation of H<sub>2</sub>BDTCPP over copper surface and using AFM images it was observed that the film covers completely the topography of the metal, with a roughness (RMS) of 11.30 nm, which is less smooth than bare polished copper whose roughness is 6.06 nm (Fig. 2).



**Figure 1.** Structure of H<sub>2</sub>BDTCPP and its copper complex.

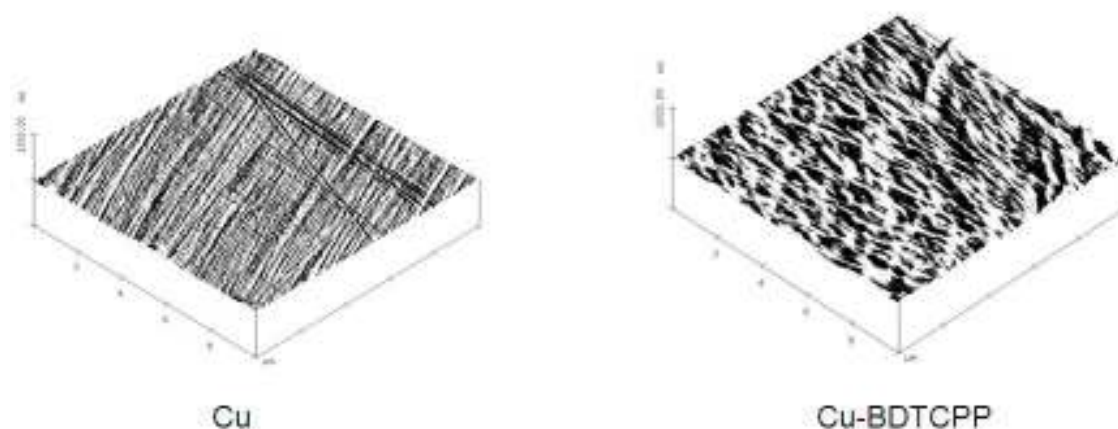


Figure 2. AFM images of Cu and Cu-BDTCPP.

### Weight loss measurement

Figure 3 shows the variation in copper weight loss of the bare Cu and coated Cu-BDTCPP as a function of immersion time in 0.1 M H<sub>2</sub>SO<sub>4</sub>. It may be observed that for both cases the weight loss increases linearly with time but it is lower when copper is coated with the ligand. The chemical nature of the protective coating after the weight loss measurement experiments was analyzed by UV-VIS spectroscopy. After corrosion experiments the coating layer was removed by dissolution in chloroform and the UV-VIS spectra of this solution showed three absorptions at 324, 374 and 390 (shoulder) nm in complete agreement with the UV-VIS spectra of authentically synthesized Cu(II)-BDTCPP complex previously reported and discarding the action of the coating as a simple physical barrier [21,22].

Figure 4 shows the variation of the copper corrosion rate (CR) calculated from Eq. 1 as a function of immersion time for both bare and coated BDTCPP copper sheets, where  $\Delta m$  is the weight loss in mg, S is the area in cm<sup>2</sup> and t the immersion time period in days. In all the period studied, corrosion rates of bare sheet were higher, showing a decrease because of Cu (II) sulfur salt formation which acts as a protective barrier against the electrolyte; for the coated sheet, rates are lower and remain almost constant. These results are in agreement with the protective function of H<sub>2</sub>BDTCPP to copper corrosion in an acidic media of 0.1 M H<sub>2</sub>SO<sub>4</sub>.

$$CR = \frac{\Delta m}{S \times t} \quad (1)$$

$$\% IE = \frac{CR_1 - CR_2}{CR_1} \times 100 \quad (2)$$

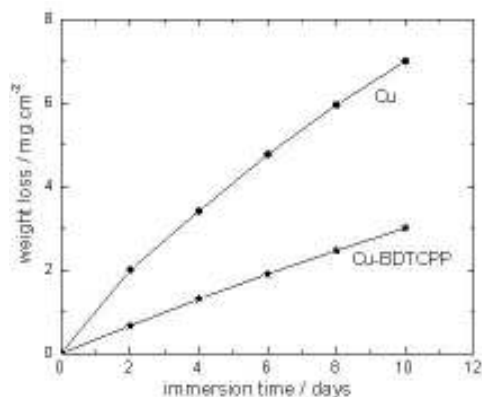


Figure 3. Variation of the weight loss with immersion time of a Cu and Cu-BDTCPP in 0.1 M H<sub>2</sub>SO<sub>4</sub>.

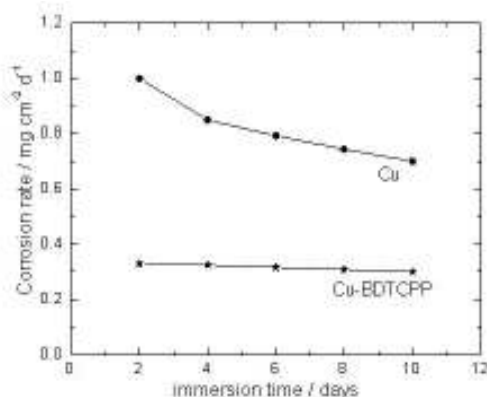


Figure 4. Corrosion rate of Cu and Cu-BDTCPP in 0.1 M H<sub>2</sub>SO<sub>4</sub>.

The variation of the inhibition efficiency percentage (% IE) as a function of immersion time were calculated according to Eq. 2 where CR<sub>1</sub> is the corrosion rate without coating and CR<sub>2</sub> is the corrosion rate with coating. After 10 days of immersion, this value decrease from 67.0% to 57.1% (62.1% overall) due to a partially solubilization of the coated Cu(II)BDTCPP complex in 0.1 M H<sub>2</sub>SO<sub>4</sub>. This explanation is supported by the fact that in solvent-extraction studies of Cu (II) with H<sub>2</sub>BDTCPP in chloroform, the metal ion present in the organic layer as Cu(II)BDTCPP complex is back extracted to an aqueous layer with a 2 M H<sub>2</sub>SO<sub>4</sub> solution [21] and therefore some small dissolution of the copper complex layer must occur in the 0.1 M acid. Previous research by the authors on H<sub>2</sub>BDTCPP in 3.5 % NaCl aqueous solution showed a 92.7% level of inhibition efficiency without any damage sign of the protective layer over time [22]. Consequently, the acidic media has a stronger negative influence than aggressive chloride ions on the protective corrosion degree of the H<sub>2</sub>BDTCPP/Cu(II)-BDTCPP layer.

This corrosion inhibition behaviour may be attributed to sufficient physical adherence of the inhibitor to the copper surface at locations where the active sites of union of the Cu(II), are the aromatic pyrazole ring, and the dithiocarboxylate group. Each planar pyrazole moiety contributes with an aromatic sextet of  $\pi/n$  electrons (two double bonds and lone electron pair of the nitrogen at 1 position), lone electron pairs of nitrogen at position 2 and hydroxyl group at position 5, while the planar dithiocarboxylate group at position 4 contributes with the  $\pi$ -electrons of the thiocarbonyl group and the lone-pair electrons of sulphur; furthermore the electron density of the pyrazole is increased by the electron donor effect of the methyl group attached to carbon 3. The physical adsorption can occurs on the basis of donor-acceptor interaction between the  $\pi$  electrons of the planar aromatic pyrazolyl group and the lone pair electrons of heteroatom (N, O, S) present in the heterocyclic and dithiocarboxylate groups with the surface of copper atoms (Fig. 5A). This adsorption can be followed by a chemisorption process where, afterwards as the corrosion reaction start, the cupric ions generated by oxidation of Cu(I) form the Cu-BDTCPP complex at the earlier steps of the corrosion process which is also adsorbed over the copper surface, acting as a protective coating against corrosion (Fig. 5B).

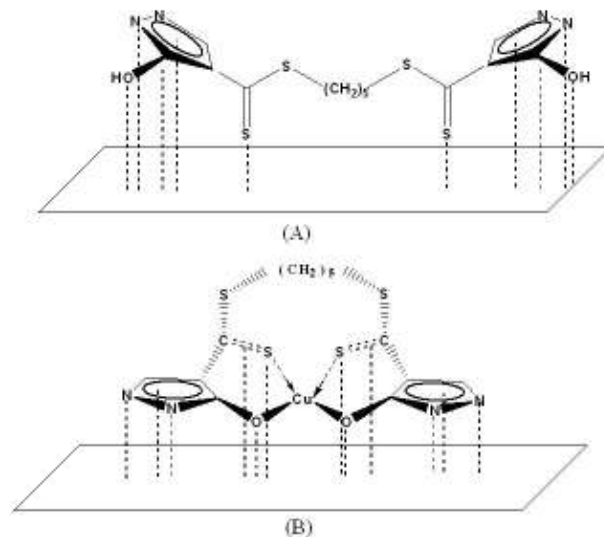


Figure 5. Mode of adsorption of H<sub>2</sub>BDTCPP (A) and the Cu-BDTCPP complex (B) on the surface of copper.

## Conclusions

From the results of this investigation, it is possible to establish the following conclusions: a) The data obtained from weight loss experiments, show that the compound 1,5-bis(4-dihtiocarboxylate-1-dodecyl-5-hydroxy-3-methylpyrazolyl)-pentane (H<sub>2</sub>BDTCPP) is a good organic coating inhibitor of copper corrosion in 0.1 M H<sub>2</sub>SO<sub>4</sub>. b) The inhibition efficiency percentage of H<sub>2</sub>BDTCPP was determined at 68.0% and this protection capacity is attributed to a physisorption of the compound to the copper surface, followed by a chemisorption process of the Cu(II)-BDTCPP complex, which blocks the active sites on the copper surface. This behaviour is attributed to the planar aromatic structure of the H<sub>2</sub>BDTCPP and the high density of free electron pairs due to the presence of nitrogen, oxygen and sulphur atoms which possess high affinity with the copper atoms.

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