Journal of Applied Electrochemistry **30**: 595–600, 2000.

Cleaning of copper foil coated with sodium hexanoate as corrosion inhibitor

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Received 15 December 1998; accepted in revised form 23 November 1999

Key words: copper, corrosion inhibitor, gliding arc plasma, humid air plasma, non-thermal plasma, sodium hexanoate, surface cleaning

Abstract

Sodium hexanoate is proposed as corrosion inhibitor for copper when the metal is situated in an aggressive aqueous or gaseous environment. The efficiency of the inhibitor, measured by electrochemical techniques in the ASTM 1384 standard solution, depends on the hexanoate concentration. Copper foils immersed in a (0.1 M) sodium hexanoate conditioning bath, and later exposed to a strongly oxidizing gliding arc plasma in humid air, yield oxide layers, the thickness and the nature of which differ from the unconditioned samples since the voltammograms show no CuO at the surface. The organic salt thus limits the oxidation process induced by the gaseous species. The organic layer remains active for at least 30 min. For longer exposures, the salt begins to degrade to carbon dioxide, which makes the plasma treatment a useful tool to clean metallic surfaces.

1. Introduction

Metallic copper is widely used in the electronics industry as a chip-level and board-level conductor. However, an unprotected copper surface is subject to corrosion and the subsequent effects are damaging to the copper circuitry. Copper is a relatively noble metal; nevertheless it easily reacts in an ordinary oxygen containing environments [1]. Under ambient conditions, the copper surface is covered with a thin layer consisting of a mixture of metallic copper, cuprous oxide and other corrosion products yielding a high electrical resistance [2, 3].

Due to the harmful effects of corrosion, protection measures must be taken and among them the use of corrosion inhibitors is one of the most common. Organic corrosion inhibitors are usually classified on the basis of their interactions with the metal surface. 'Interface inhibitors' function primarily by delaying the surface reactions through direct adsorption, while 'interphase inhibitors' alter the metal surface reactivity by forming a barrier layer at the metal–solution interphase following the initial adsorption step. For a long time, heterocyclic compounds, such as 1 H-benzotriazole (1H-BTA), triazole and imidazole derivatives were used as inhibitors of copper corrosion and thermal oxidation [4–6]. However, the environmental regulations relating to the disposing of cooling waters are becoming stricter; toxicity has become a critical character for any inhibitor [7] and the occurrence of nitrogen containing heterocycles is unsuitable. Thus, great efforts have been made during the last decade to find good alternatives for the inhibition of copper corrosion. Several long chain carboxylic acids have been thus considered (e.g., the *N*-capryl glutamic acid (CGA), 4-chloro-benzhydroxamic acid (*p*-CBHA)), as well as 1-amino 3-methoxypropane and 2-dimethylaminoethanol, which provide good protection for copper in neutral model water [7, 8].

As part of our research programme on plasma–solid interactions, we focused on the formation of oxide layers on the surface of various metal foils exposed to an oxygen-containing plasma gas. Most of our work in the field was performed on low-pressure inductively coupled oxygen plasma. The oxidising power of inductively coupled oxygen plasma had previously been investigated on copper, zinc and brass foils [9–11]. We found that the main characteristics of the resultant oxide layers depended on the plasma treatment parameters [9–11]. Such treatments were much more efficient than thermal ones, even those performed in pure oxygen, if we consider the growth rate of the oxide layers.

However, in the present work, we used a new plasma set-up, the gliding arc or 'glidarc', proposed by Czernichowski et al. [12]. This kind of arc was modelled by Fridman et al. [13] more recently and was classified as a nonthermal plasma because the energy of the electrons is markedly higher than that of the heavy species. The glidarc results from an electric arc burning between two diverging electrodes, which is blown by a gas flow along the axis of the electrodes. The gas pressure is close to 1 atmosphere. The feed gas used for the present study is water saturated air. The resulting plasma presents, among others, the interesting characteristic of being a source of highly oxidizing species [14, 16], that is, of $^{\circ}$OH radicals which were identified by emission spectroscopy.

Due to the high standard potential of the OH/H_2O system ($E^{\circ} = 2.85\,V$), the glidarc in humid air is a very convenient tool to examine most of the oxidation phenomena and in particular the corrosion of metals. This device is being developed in the laboratory, and the oxidation studies of zinc and even stainless steel are under progress.

The gliding arc device also provides a suitable technique to examine the efficiency of a corrosion inhibitor. We report here on the efficiency of sodium hexanoate to prevent or at least to limit the corrosion phenomena of copper.

2. Nonthermal humid air plasmas

Nonthermal plasmas are characterized by a large difference in the energies of the electrons and those of the heavy species (atoms, radicals, molecules and ions). Most of these plasmas are operated at a low temperature and pressure. However numerous plasmas such as the corona discharge, the barrier discharges or the gliding arc are operated at atmospheric pressure and belong to this family of plasmas. These low temperature and high pressure plasmas generate activated gaseous species which are very reactive even at room temperature. This feature makes them invaluable tools for the treatment of materials. It is related to the chemical properties of the gaseous species formed, which are not well known yet and must be carefully investigated. We selected the gliding arc system to generate plasma because we wished to investigate the oxidising properties of this kind of humid air plasma. Recent work has shown that the gliding arc is more efficient than the corona discharge for air treatment, and very attractive due to its wide operating conditions.

In plasma, the energy transfer from the electromagnetic field to the gaseous matter induces a number of processes to take place (e.g., ionization, dissociation by electron impact and attachment phenomena), and in particular the formation of activated species in their fundamental or excited states. The spectroscopic investigation of the emission bands of a gliding arc discharge in humid air in the 230–650 nm range showed the occurrence of the radicals NO and OH as the main heavy species present in the plasma [14–16]. Due to a strong modification of the electron distribution, these activated species show an enhanced chemical reactivity and in particular some of them behave as strong oxidising agents. The strength of the relevant oxidation–reduction systems is quantified by the normal oxidation–reduction potential in standard conditions, for example:

$$\mathrm{OH^{\circ} + H^{+} + e^{-} = H_2O} \quad E^{\circ} = 2.85\,\mathrm{V\ vs\ NHE}$$

$$\mathrm{O + 2\,H^{+} + 2\,e^{-} = H_2O} \quad E^{\circ} = 2.42\,\mathrm{V\ vs\ NHE}$$

$$\mathrm{O_3 + H_2O + 2\,e^{-} = O_2 + 2\,OH^{-}} \quad E^{\circ} = 1.24\,\mathrm{V\ vs\ NHE}$$

$$\mathrm{2\,HNO_2 + 6\,H^{+} + 2\,e^{-} = N_2 + 4\,H_2O} \quad E^{\circ} = 1.45\,\mathrm{V\ vs\ NHE}$$

The oxidising properties of the activated species generated in the gliding arc discharge in humid air are used to examine the efficiency of the protective films obtained by immersing copper samples in a sodium hexanoate solution. The aim of the present work is to study the ability of sodium hexanoate as an inhibitor of copper, both in aqueous solution and in an oxidising atmosphere. Two series of experiments were thus performed and involved different electrochemical techniques:

(i) With the first, we intended to show that sodium hexanoate actually acted as a corrosion inhibitor for copper. Accordingly we compared the Tafel plots for copper in a standard solution (ASTM 1384) with and without sodium hexanoate. Copper samples were thus immersed in the corrosive solution (ASTM 1384) with and without sodium hexanoate; they were later examined by potentiostatic polarization measurements. The comparison of the results, according to the occurrence of hexanoate, indicated the inhibitor efficiency.

(ii) The second series of experiments involved the use of air plasma as a corroding medium for the copper foils. Some of the metal samples were first immersed in an hexanoate solution and some were not. Then all these samples were exposed to the plasma. Oxide layers developed at the plasma treated surface. The nature of the oxides was identified by linear sweep voltammetry.

3. Experimental details

3.1. *Plasma device*

An electric arc was created between two diverging aluminium electrodes raised to a convenient voltage. The a.c. generator delivered a suitable energy (100 mA; 9 kV). A gas flow along the axis of the reactor blew the arc and made it glide along the electrodes before breaking. After breaking, a new arc formed and the cycle resumed. Plasma was generated by the arc in a volume at the tips of the electrodes.

In this work the glidarc was fed with humid air. The air flow provided by an air compressor was saturated with water by bubbling in a Durand flask before entering the reactor through a nozzle (dia. 0.99 mm). The airflow rate was fixed at 22.5 L min^{-1}. The copper foils with and without inhibitor on their surface were exposed to the plasma flux as shown in Figure 1.

3.2. *Samples and inhibitor*

All the copper samples were supplied by Alcatel–Cuivre. They were 0.3 mm thick discs (area 110 mm^2) and were cut off from A-grade copper foils which originally contained 100 ppm of oxygen in the form of Cu_2O. They were polished with grinding paper (400, 800 and 1200 grade), washed in absolute ethanol and dried in nitrogen according to standard metallurgical techniques. Some samples were then dipped in a 0.1 M sodium hexanoate solution for 2 h, and nitrogen dried to allow the protective layer to form and fix on the substrate. The samples were later exposed to the plasma for various exposure times under controlled conditions.

Hexanoïc acid was purchased from Atochem. The sodium hexanoate solution was prepared by neutralizing hexanoïc acid with a NaOH solution.

The medium selected for the electrochemical measurements at room temperature, (20 ± 1) °C, is referred to as the ASTM solution 1384, (i.e., 148 mg L^{-1} Na_2SO_4, 165 mg L^{-1} NaCl, 138 mg L^{-1} $NaHCO_3$) [17].

3.3. *Instrumental techniques*

The potentiodynamic polarization curves were obtained on a PAR (model 273) potentiostat/galvanostat linked to a Softcorr (model 342) corrosion measurement software (potential sweep rate 0.1 mV s^{-1}; starting potential −0.200 V vs SCE). The electrolyte used was the ASTM solution. The electrochemical reduction curves were determined on a PAR 273 potentiostat associated with IBM PC, which provided the characteristic values of the Tafel plots. The selected electrolyte was a 0.1 M Na_2BO_7 solution, (pH 9.2), because the solubility of the various copper oxides and hydroxides is minimum at this pH. The potential sweep was fixed at 0.5 mV s^{-1}.

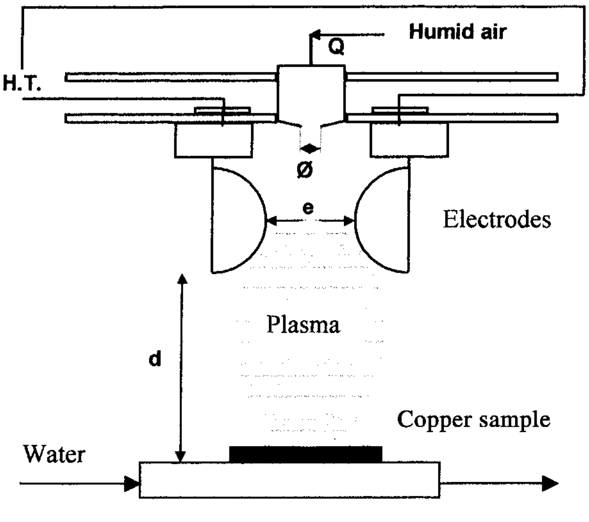

Fig. 1. Experimental set-up.

A classical three-electrode cell was used; all the potentials are referred to the SCE. Before each run the electrolyte was carefully purged with nitrogen.

Standard procedures were used to measure the chemical oxygen demand (COD).

4. Results and discussion

4.1. *Corrosion of copper in aqueous medium: inhibition by sodium hexanoate*

The potentiostatic polarization data were processed as the current density (j) against the applied potential (E) and as $\log(j/\mathrm{A\,cm^{-2}})$ vs E/V. The relevant plots allow the determination of the corrosion potentials by means of the Tafel plots for large overvoltages.

Polarization curves were recorded for the copper samples in the ASTM solution with and without sodium hexanoate. The efficiency of the inhibitor results from the comparison between the relevant E_{corr} values. Without hexanoate, E_{corr} is close to −0.075 V vs SCE (Figure 2(a)) while it increases to −0.054 V vs SCE in the ASTM solution with a 0.075 M sodium hexanoate solution added (Figure 2(b)). The corrosion potential thus moves towards positive potentials, so that sodium hexanoate behaves as an anodic inhibitor, and this effect is related to a decrease in the corrosion current density.

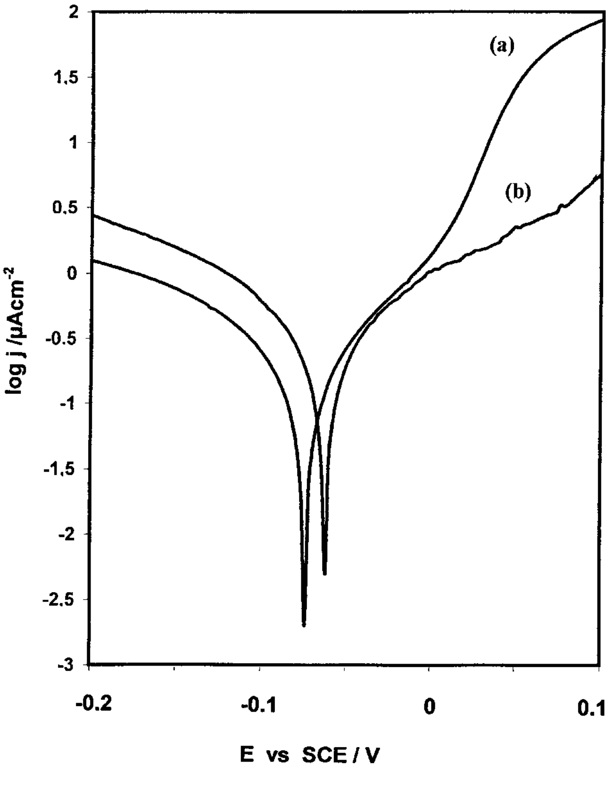

Fig. 2. Tafel plot of copper in ASTM solution no. 1384: 148 mg l^{-1} Na_2SO_4, 165 mg l^{-1} NaCl, 138 mg l^{-1} $NaHCO_3$ (potential sweep rate 0.1 mV s^{-1}). (a) without hexanoate: $E_{corr} = -0.075$ V vs SCE; (b) with (0.075 M) hexanoate: $E_{corr} = -0.054$ V vs SCE.

These features result from the adsorption of hexanoate at the copper surface.

The anodic and cathodic polarization curves of the copper samples were recorded under the same conditions in the ASTM solution with different sodium hexanoate concentrations in order to optimize the inhibitor concentration. Figure 3 shows that the corrosion potential is an increasing function of the hexanoate concentration, and the relationship between E_{corr} and C is nearly linear.

The particular concentration (i.e., $C = 0.1$ M) was selected as a standard hexanoate concentration to study the behaviour of copper samples exposed to a humid air plasma and to estimate the efficiency of the inhibitor.

4.2. *Corrosion of copper foils induced by humid air plasma*

Copper foils were covered or not with sodium hexanoate, before being exposed to an air plasma under controlled conditions. In particular, the gas flow and the distance between the treated sample and the tips of the electrodes were carefully fixed ($Q = 22.5$ L min^{-1}; $d = 1.5$ cm).

4.2.1. *Plasma treatment without corrosion inhibitor*

Figure 4 illustrates the typical curves (current intensity vs applied potential) recorded for the copper samples exposed to the plasma for various lengths of time. All the voltammograms present three peaks. They are identified by referring to a previous electrochemical study [9] of the oxide layers formed in the treatment of copper by inductively coupled oxygen plasma. The first peak, near -0.60 V vs SCE, is ascribed to the reduction of the precursor oxide Cu_xO [9] (i.e., $Cu^+ + e^- \rightarrow Cu$). The second peak, near -0.75 V vs SCE, is assigned to the first reduction of CuO (i.e., $Cu^{2+} + e^- \rightarrow Cu^+$) and the last one near -0.80 V vs SCE is related to the second reduction of CuO and the reduction of Cu_2O (i.e., $Cu^+ + e^- \rightarrow Cu$).

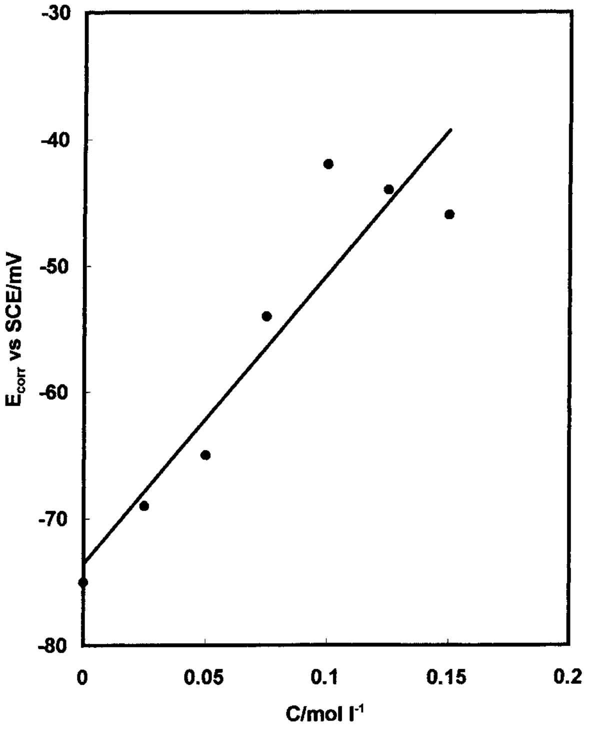

Fig. 3. Variations of the corrosion potential of copper as a function of hexanoate solution concentration.

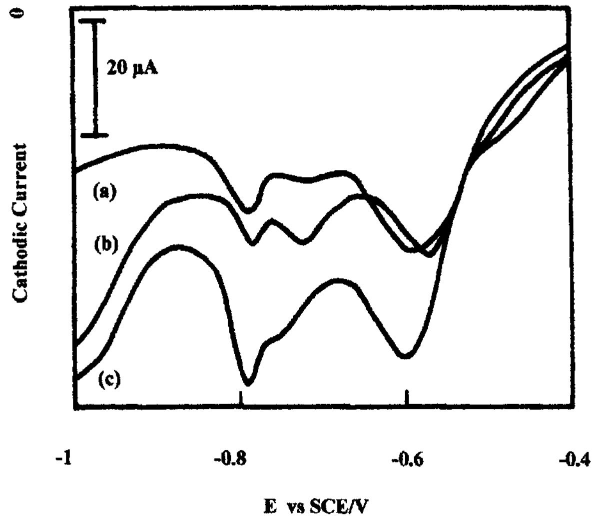

Fig. 4. Cathodic reduction curves of copper oxides formed by an air plasma oxidation of copper foils for different exposures ($d = 1.5$ cm): (a) 15, (b) 30 and (c) 60 min.

The copper oxides formed by air plasma treatment were identified by linear potential sweep voltammetry. The intensity of the reduction peaks of the different copper oxides depends on the exposure time (t) to the plasma (Figure 4). For example, the I_p values, relevant to the reduction peak of Cu_2O increase with the treatment time (t) and the plot I_p against t is reasonably linear (Figure 5(a)). Since the formation of oxide on the metal surface results from the plasma treatment, and since the peak intensity I_p is related to the quantity of oxide formed, the oxidizing effect of the plasma observed directly depends on the exposure time, in the same way as for the electrolysis processes.

We now consider the influence of the working parameters of the plasma treatment on the oxidation kinetics and special attention is devoted to the exposure time and to the distance (d) between the copper target and the electrode tips. As shown by Figure 5, the peak intensity for the reduction of Cu_2O is strongly affected by d: for a fixed treatment time, the I_p value increases as d decreases. Both effects are interpreted in terms of plasma efficiency, since for smaller d and longer time, the plasma efficiency is higher. This confirms previous results [14].

4.2.2. *Plasma treatment of copper foils coated with corrosion inhibitor*

The reduction curves of the oxide layers formed on metal surfaces after the same plasma treatment ($t = 15$ min; $d = 1.5$ cm; $Q = 22.5$ L min^{-1}) differ due to the

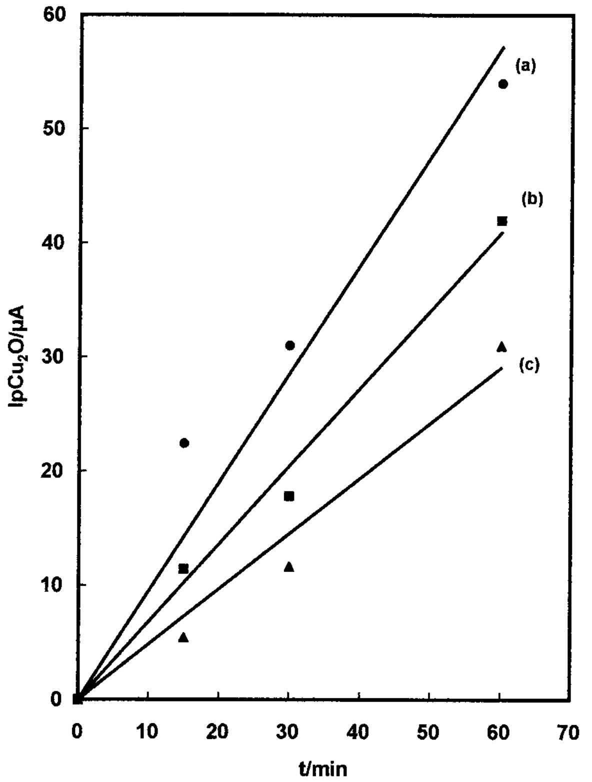

Fig. 5. Variation of the intensity of the reduction peak for given treatment time at different distances (d) between the copper target and the electrode tips. d: (a) 1.5, (b) 2.5 and (c) 3.5 cm.

occurrence of an initial hexanoate coating. Figure 6(a) refers to the noncoated sample and Figure 6(b) to the inhibitor coated metal. No reduction peak of CuO appears on Figure 6(b); hence no CuO is present on the plasma treated metal surface when the sample is initially immersed into the inhibitor solution. Moreover, the peak intensities for the reduction of the two oxides Cu_xO and Cu_2O are smaller than the corresponding ones for the noncoated sample. These features confirm that sodium hexanoate induces a protective effect against oxidising agents when it fixes on the metal surface.

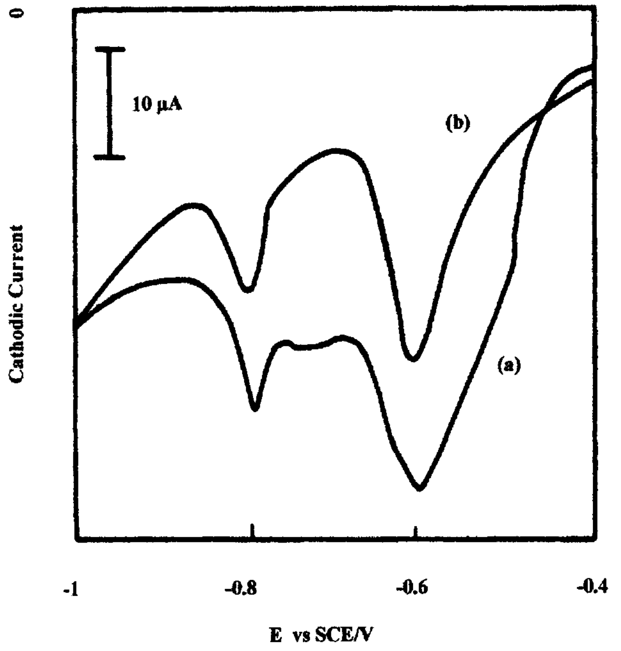

Fig. 6. Cathodic reduction curves of copper oxides formed by an air plasma oxidation of copper foils (t = 15 min, d = 1.5 cm). (a) without inhibitor, (b) with inhibitor.

The present study clearly shows that species fixed on the surface actually modify the oxidation kinetics. An important question is connected with the protective effect provided by sodium hexanoate at the copper surface under plasma conditions. Suitable information is provided by varying the exposure time of the samples to the plasma and by subsequently measuring the peak intensities on the corresponding voltammograms. The reduction peak intensities of Cu_2O with and without the inhibitor for various treatment times are shown in Table 1. They show that sodium hexanoate protects the copper surface when the plasma treatment lasted less than 30 min.

For longer plasma treatments the protective effect of sodium hexanoate decreases, since the I_p values tend to become independent of the occurrence of the coating. This feature may be related to the progressive degradation of the hexanoate coating when exposed to the active species of the plasma. Further work will investigate whether the plasma treatment induces some degrading effect on the corrosion inhibitor.

4.2.3. *COD measurements*

The assumption of the oxidizing effect of the plasma species on sodium hexanoate is easily verified. The chemical oxygen demands (COD) of a 10^{-3} M sodium hexanoate aqueous solution exposed to the plasma for various period of time were measured. Figure 7 shows the results and indicates that the COD is a decreasing function of time. It was shown in other work [14, 15] that the gliding arc treatment of aqueous solutions induced oxidizing effects; it is thus reasonable to suggest that hexanoate degrades to volatile organic compounds (VOC) and that the ultimate oxidation products are CO_2 and H_2O.

5. Conclusions

Sodium hexanoate fixed on copper foils and exposed to strong oxidizing agents acts as a corrosion inhibitor.

Table 1. Influence of the treatment time on the intensity reduction peak of Cu_2O with and without hexanoate (d = 1.5 cm)

t/min	15	30	60
Ip (Cu^+)/μA*	22	31	56
Ip (Cu^+)/μA†	14	23	52

* Without inhibitor
† With inhibitor

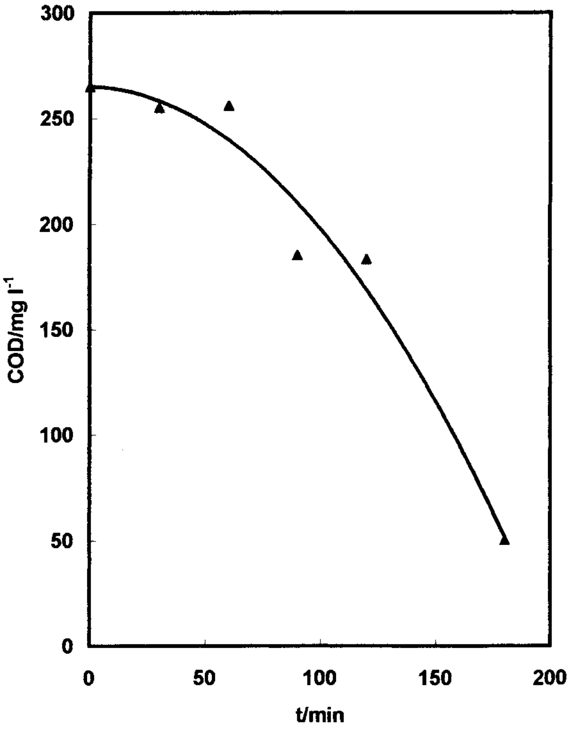

Fig. 7. Variation of the (10^{-3} M) hexanoate solution COD for given air plasma treatment time.

This first conclusion results from electrochemical investigations which showed an important change in the corrosion potential of the metal when it is dipped in a corrosive solution containing the inhibitor. The E_{corr} values increase linearly with inhibitor concentration.

The occurrence of an inhibitor on the copper foil prevents CuO from forming when the metal target is exposed to the oxidising plasma. It also limits the quantity of the lower copper oxides (e.g., Cu_2O, Cu_3O_2) yielded.

The inhibitor effect remains unmodified for 30 min under the harsh plasma conditions, so that we could conclude on its poor efficiency. However, the OH° radicals present in the plasma are among the strongest oxidizing agents known, so that the preceeding conclusion must be softened up, in particular with respect to 'usual' corrosion situations.

For plasma exposures longer than 30 min, the efficiency of the inhibitor decreases: the inhibitor is oxidized to carbon dioxide or to other volatile organic compounds. This ultimate step is ascertained by the decrease of the chemical oxygen demand (COD) of sodium hexanoate solutions for increasing exposure to the plasma.

Hexanoate also provides significant and durable corrosion protection for copper in aggressive aqueous solutions and in oxidising gaseous environments. The experiments show new and interesting features with numerous applications: a humid air plasma treatment is able to degrade aliphatic solutes with long carbon chains. Consequently, the plasma technique is likely to have application in the cleaning of materials.

Acknowledgements

This study was performed within the framework of the France–Algeria Cooperation Program 97-MDU 384.

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