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Research Paper

POLYETHYLENE GLYCOL AS A CORROSION INHIBITOR FOR LEAD AND LEAD FREE SOLDERS IN ACIDIC MEDIUM

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The inhibition effect of Poly Ethylene Glycol (PEG) as corrosion inhibitor for lead and lead free solders in 1 N HCl solution was investigated by weight loss method and electrochemical methods. The inhibition efficiency was increased with increase in inhibitor concentration up to optimum concentration for lead and lead free solders in acidic medium. Polarization measurements reveal that PEG acts as a mixed-type inhibitor. PEG was found to be better inhibitor for lead free solders.

Keywords: Inhibitor, Polyethylene glycol, Inhibitor efficiency, Polarisation

INTRODUCTION

Soldering is a low temperature process of joining metallic materials by using a filler material known as solder that melts below 450 °C. There are several advantages of soldering compared to other joining methods such as simplicity of the process, economy, easy repair works, etc. In the electronics filed, solder plays a crucial role by providing electrical, thermal and mechanical continuities. Sn-Pb alloys have been used as solders in electronic packaging for many years (Schwartz and Aircraft, 1991; and Manko, 1992).

However, lead being highly toxic and with the arrival of legislative restrictions on the use of leaded solders there arose a need to initiate the search for acceptable alternate joining materials for electronic assembly (Abtew and Selvaduray, 2000; Titus Chellaih *et al.*, 2007; and Girish Kumar and Narayan Prabhu, 2007). Responding to the urgent need for green electronic products, lead-free solders have emerged as substitutes for traditional Sn-Pb solder alloys as major interconnecting materials in electronic packaging processes (Uhlig and Winston Revie, 1985). The study of

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lead free solder has become a hot subject in the recent years. In this regard now electronic industry is rapidly implementing lead free assembly strategies.

Many lead free solders have been studied as replacements for Sn-Pb solders, and among them Sn-3.5Ag, Sn-0.7Cu and Sn-3.8Ag-0.7Cu solders are the most promising candidates owing to their appealing overall properties. Also Sn-Zn eutectic solder has been recommended as a substitute for Sn-Pb solder due to its low melting point which is close to eutectic Sn-Pb solder, low cost, wide raw material sources, and superior strength. Sn-3.5Ag solders are the most promising candidates due to their overall properties, including mechanical properties, wettability, reflow properties and reliability (Townsend and Borzillo, 1995; and Dezhi Li *et al.*, 2008).

These alloys are also easily undergoes corrosion in aqueous media. Corrosion is the gradual destruction of materials, usually metals, by chemical reaction with its environment. In the most common form it is the electrochemical oxidation of metals in reaction with an oxidant such as oxygen (Prabhu *et al.*, 2008; and Rajappa *et al.*, 2008). The investigation of corrosion mechanism and its inhibition or prevention is a major challenge for electrochemists, material scientists and researchers in the field of science and technology. This corrosion can be controlled by painting, cathodic protection, metal coating or by the use of corrosion inhibitors.

Among these types the use of corrosion inhibitors is a well known method to control the corrosion rate. Many of the well known inhibitors are organic/inorganic compounds containing nitrogen, sulfur and oxygen atoms (Shankaresha *et al.*, 2007; and Praveen and Venkatesha, 2009). It has been observed that many of the organic inhibitors adsorbed on the active sites of the metal which reduce the corrosion rate. This adsorption phenomenon is influenced by the nature and surface charge of metal, type of aggressive medium and chemical structure of inhibitors. The adsorption of corrosion inhibitor depends mainly on physico-chemical properties of the molecule such as functional groups, steric factor, molecular size, molecular weight, molecular structure, aromaticity, electron density of the donor atoms and p-orbital character of donating electrons and also on the electronic structure of the molecules.

The aim of the present study is to determine the inhibition efficiency of PEG for the corrosion of Sn-37Pb, Sn-9Zn and Sn-3.5Ag in 1 NHCl medium containing different concentration of inhibitor.

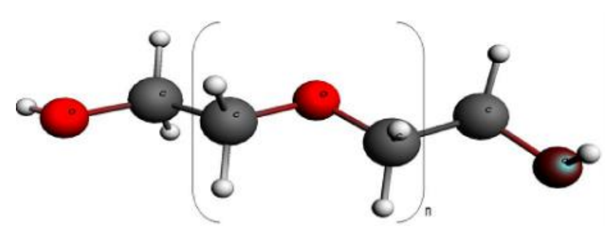
MATERIALS AND METHODS

Three solder materials Sn-37Pb (lead based solder), Sn-9Zn and Sn-3.5Ag (lead free solders) were used in this investigation. Solders were in the form of a rod machined into a cylindrical form embedded in epoxy resin. The exposed surface areas of Sn-37Pb, Sn-9Zn and Sn-3.5Ag solder rods were found to be 0.62 cm^2, 0.47 cm^2 and 0.35 cm^2 respectively. The samples were polished by emery papers (Grade No. 80, 120, 220, 320, 660 and 1200), washed thoroughly with double distilled water, degreased with acetone and dried at room temperature. The corrosive media 1 NHCl solution was prepared using AR grade HCl and distilled water.

Inhibitor

The compound Poly ethylene glycol (PEG) was purchased from Otto Chemie pvt ltd with 6000 molecular weight. IUPAC name of the PEG is alpha-Hydro-omega-hydroxypoly (oxy-1, 2-ethanediol). The Chemical formula of PEG is: $(C_2H_4O)_{n+1}H_2O$. The structure of PEG is shown in Figure 1. Inhibitor was soluble in 1 NHCl corrosive medium (Mahendra Yadav *et al.*, 2013).

Figure 1: Optimized Structure of Polyethylene Glycols



Weight loss Measurements

Weight loss measurements were performed by immersing solder alloys in glass beaker containing 100 cm^3 of corrosive media (1 NHCl) with different concentrations of inhibitor. After an immersion time of 4 hours, solder alloys were taken out and washed well with plenty of tap water followed by distilled water, dried and weighed accurately using digital balance (accuracy: ± 0.1 mg). All experiments were carried out in static and aerated condition. Each measurement was repeated thrice for reproducibility and an average value was reported.

Electrochemical Measurements

The electrochemical measurements were carried out in Electrochemical Work Station (Compactstat. e10800 from Ivium Technologies, Netherlands) at room temperature. The cell consists of three electrodes namely, the working electrode (solder alloy), counter electrode (platinum) and reference electrode (saturated calomel electrode). Before each electrochemical measurement, the working electrode was allowed to stand for 30 min in test solution to establish steady state Open Circuit Potential (OCP). In Tafel measurements, the potentio-dynamic current versus potential curves were recorded by polarizing the specimen to –250 mV cathodically and +250 mV anodically with respect to the Open Circuit Potential (OCP) at a scan rate of 1 mVs^{-1}.

The corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) cathodic Tafel slope ($_c$) and anodic Tafel slope ($_a$) were calculated from the software installed in the instrument. Impedance measurements were carried out using AC signal with amplitude of 5 mV at OCP in the frequency range from 100 kHz to 10 MHz. The impedance data were fitted to most appropriate equivalent circuit by using ZSimp Win 3.21 software. Nyquist plots were drawn to obtain the impedance parameters.

RESULTS AND DISCUSSION

Weight Loss Measurements

The corrosion inhibition efficiency (¦$_w$) of the PEG at room temperature was analyzed by weight loss measurement technique. ¦$_w$ of the PEG was calculated from following relation.

$$¦_w = \frac{W^o - W}{W^o} \times 100 \qquad ...(1)$$

where, $W°$ and W are weight loss of solders in absence and presence of inhibitor.

The rate of corrosion °(g cm^{-2} h^{-1}) was calculated from fallowing equation,

Table 1: Corrosion Parameters Obtained from Weight Loss Measurements for Solders Alloys in 1 NHCl at Various Concentrations of PEG

Corrosive Medium of PEG in (ppm)	Corrosion Value for Sn-37Pb in (gm/cm² hr)	Inhibition Efficiency ¦$_{w}$	Corrosion value for Sn-3.5Ag in (gm/cm² hr)	Inhibition Efficiency ¦$_{w}$	Corrosion value for Sn-9Zn in (gm/cm² hr)	Inhibition Efficiency ¦$_{w}$
1 NHCl	0.00753	–	0.0075	–	0.01250	–
05	0.00500	33.33	0.0062	17.33	0.00310	75
10	0.00350	53.33	0.0054	28	0.00125	90
20	0.00250	66.67	0.0051	32	0.00560	55

$$° = \frac{W^{o} - W}{st} \times 100 \qquad ...(2)$$

Here, S is the surface area of the solder alloys and T is the immersion time in hours. Corrosion parameters for solder alloys in 1 NHCl in presence of different concentrations of the PEG is provided in Table 1.

It clearly shows that, weight loss decreases significantly with the addition of PEG inhibitor since Inhibition Efficiency (¦$_{w}$) is increased with increase in PEG concentration. The decrease in corrosion rate with increase in concentration of PEG is due to the fact that the surface coverage of metal increases by the adsorption of inhibitor molecules. Maximum ¦$_{w}$ was achieved at 20 ppm of the PEG and above this concentration marginal/ no changes were observed in çw values. So it is considered as optimum concentration for achieving maximum inhibition efficiency.

Electrochemical Measurements

Polarization Measurements

The anodic and cathodic polarization curves of three solder alloys in 1 NHCl in the presence of different concentrations of PEG at room temperature is given in Figure 2. The corrosion current densities were calculated by extrapolation of the linear parts of these curves

Figure 2: Tafel Plots for Solder Alloys in 1 NHCl at Different Concentrations of Inhibitor (A) Sn-37Pb Alloy, (B) Sn-3.5Ag Alloy, (C) Sn-9Zn Alloy

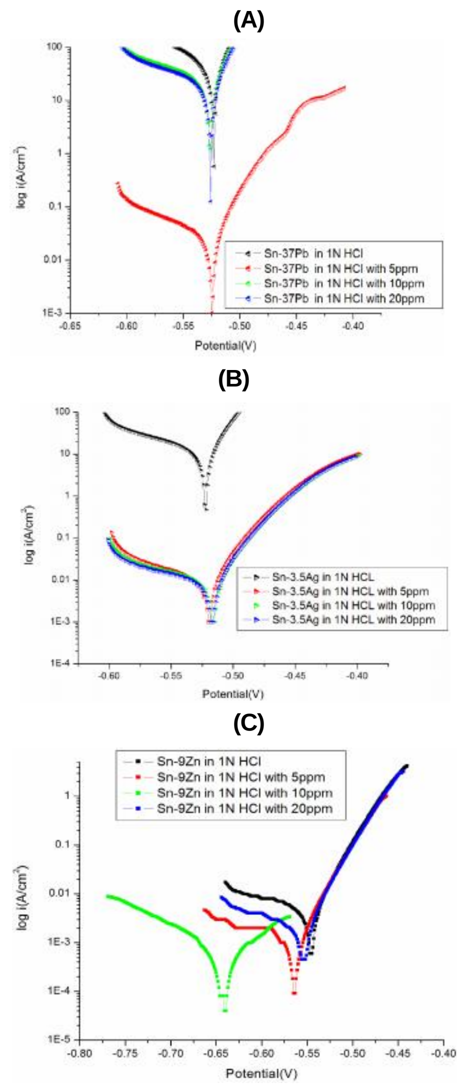


Table 2: Tafel and EIS Results for the Corrosion of Solders in 1 NHCl at Different Concentrations of PEG at Room Temperature

Type of Alloy	Inhibitor Con^n (ppm)	E_{corr} (V)	I_{corr} A cm^{-2}	Corrosion Rate (mm/y)	$_c$ mV/ Decade	a_c mV/ Decade	¦ $_p$	R_p and t cm^2	C_{dl} (μF cm^{-2})	¦ $_z$
Sn-37Pb	1 NHCl	–0.528	0.000088	2.307	0.000088	2.307	–	0.29	0.04	–
	5	–533	0.000053	1.38	0.12	0.038	40.3	0.45	0.022	35.6
	10	–0.534	0.000042	1.091	0.14	0.036	52.7	0.56	0.019	49.2
	20	–0.535	0.000037	0.9641	0.140	0.037	58.18	0.85	0.239	66
Sn-3.5Ag	1 NHCl	–0.535	0.000042	1.106	0.119	0.040	–	2.15	0.067	–
	5	–0.534	0.000031	0.9328	0.104	0.041	15.62	2.79	0.211	23
	10	–0.531	0.000032	0.8377	0.130	0.040	24.28	3.03	0.005	29.1
	20	–0.531	0.000029	0.7622	0.132	0.039	31.01	3.30	0.49	34.8
Sn-9Zn	1 NHCl	–0.544	0.000012	0.287	0.298	0.033	–	1.498	0.00002	–
	5	–0.562	0.000003	0.06477	0.0234	0.032	77.59	5.01	0.00024	70.1
	10	–0.622	0.000001	0.02763	0.117	0.052	90.51	10.12	0.00003	24.26

to the corresponding corrosion potential. Table 2 gives the electrochemical corrosion kinetic parameters, namely, corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic Tafel slope ($_c$), anodic Tafel slope ($_a$) and inhibition efficiency (¦$_p$) obtained by extrapolation of the Tafel lines.

The inhibition efficiency in this case is calculated by using following relation.

$$¦_p = \frac{I^o_{corr} - I_{corr}}{I^o_{corr}} \times 100 \quad ...(3)$$

where, I^o_{corr} and I_{corr} are corrosion current in the absence and presence of inhibitor, respectively.

Table 2 clearly shows that, the corrosion current density (I_{corr}) values decreases with increase in concentration of inhibitor. It is due to the adsorption of the inhibitor molecule over the metal surface. Figure 2 shows the nature of the polarization curves in the absence and presence of different concentration of the inhibitor for different solder alloys. The curves shifted towards lower current density in the presence of inhibitor and it can be concluded that the inhibitor molecule retard the corrosion process without changing the mechanism of the corrosion process in the medium of investigation (Mahendra Yadav *et al.*, 2013). The presence of the inhibitors caused small changes in the E_{corr} value indicating that they act as mixed-type inhibitors (Jayaperumal, 2010). It is known that, if the displacement in E_{corr} is more than ±85 mV/SCE with respect to the corrosion potential of the blank, the inhibitor can be considered as cathodic or anodic type (Ferreira *et al.*, 2004). On the other hand, if the change in Ecorr is less than 85 mV, the corrosion inhibitor can be regarded as mixed type inhibitor. The maximum displacement in the present study was less than 07 mV, which indicates, PEG acts as mixed-type inhibitor. Furthermore, there is no significant variation in $_a$ and a $_c$ value, which indicates that the presence of PEG in corrosive media does not alter the corrosion reaction mechanism but it act as an adsorptive inhibitor, retarding both the anodic and cathodic reactions by blocking the active sites. Maximum inhibition was achieved at 20 ppm concentration of the inhibitor for Sn-37Pb and Sn-3.5Ag solders and at 10 ppm concentration of the inhibitor for Sn-9Zn solder alloy. Above this concentration almost same inhibition efficiency values were observed. Hence, these values may be considered as optimum concentration for achieving maximum inhibition efficiency.

Electrochemical Impedance Spectroscopy (EIS) Measurements

Figure 3 shows Nyquist plots recorded for the corrosion of Sn-37Pb, Sn-3.5Ag and Sn-9Zn solder alloys in 1 NHCl at different concentration of PEG at room temperature.

Inhibition efficiency (¦_z) was calculated using following equation (Bentiss *et al.*, 2009).

$$\text{¦}_z = \frac{R_p - R_p^o}{R_p} \times 100 \qquad ...(4)$$

where, R_p and R_p^o are polarization resistance values in the presence and absence of inhibitor.

The analysis of impedance parameters shows that R_p values increased with increasing PEG concentration. The increase in R_p value can be attributed to the formation of protective layer on the metal surface. Figure 4 shows equivalent circuit for calculating the electrochemical parameters.

Weight loss, Polarisation and Electrochemical impedance parameters show almost same trend with almost all the results matching with each other. Thus PEG

Figure 3: Nyquist Plots for Solder Alloys in 1 NHCl at Different Concentrations of Inhibitor (A) Sn-37Pb, (B) Sn-3.5Ag, (C) Sn-9Zn Solder Alloys

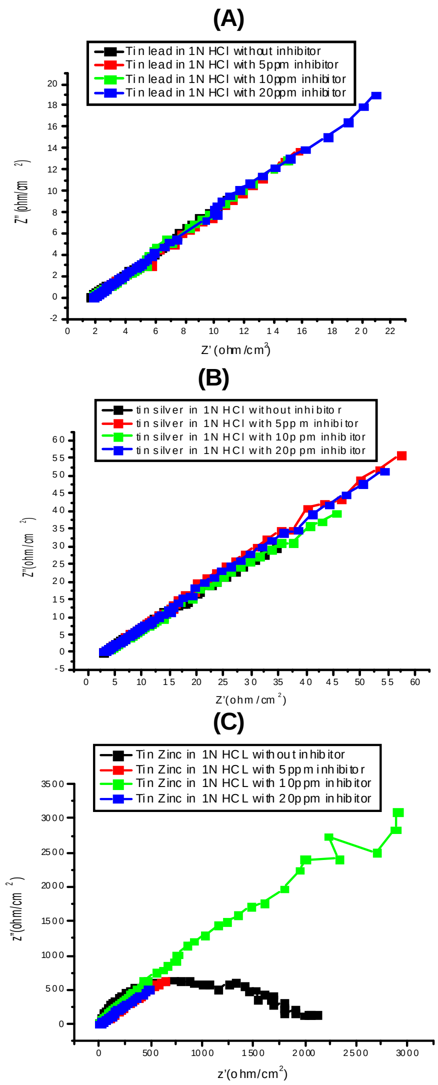
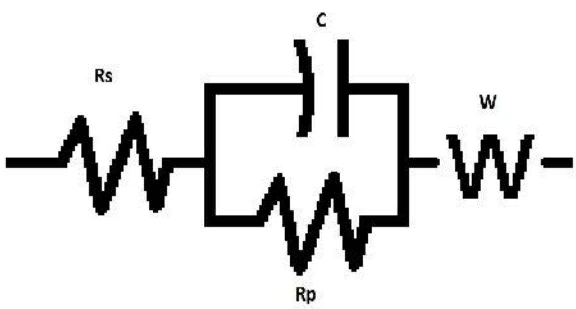


Figure 4: Equivalent Circuit



can be considered as good corrosion inhibitor.

CONCLUSION

From the investigation of corrosion of solder alloys in the acid media, following conclusions were drawn.

- PEG acts as an excellent mixed type inhibitor for the corrosion of solder alloys in 1 NHCl.
- The optimum inhibitor concentration for Sn-37Pb and Sn-3.5Ag solders was 20 ppm and 10 ppm for Sn-9Zn solder.
- Lead free solders exhibited lower corrosion rates than lead based solder in the acidic medium in the presence of inhibitor.
- Highest inhibitor efficiency was observed for Sn-9Zn solder alloy.

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