# Protection of Zinc Alloy in $H_3PO_4$ using Extract of *Lantana Camara*

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**Abstract:** The inhibitive effect of *lantana camara* leaf extract on the corrosion of Zinc alloy in phosphoric acid solution has been studied using gravimetric methods. Inhibition increases with time and concentration of extract and temperature. This observation implies that lantana camara leaf extract is an effective and non-toxic inhibitor of the corrosion of zinc alloy. Adsorption of the extract on the surface obeyed the Langmuir adsorption isotherm. The kinetic parameter B, measured for the reaction has a high negative value which implies that lantana camara becomes more effective as the temperature increases. The free energy calculated for adsorption is small and negative in magnitude which suggests that the mechanism of adsorption is physical. The Brinell hardness test which is a measure of the tensile strength shows that lantana camara provides protection for Zn alloy in acid solutions.

[Nkiko M. O, Oguntoyinbo E. S, Bamgbose J.T. **Protection of Zinc Alloy In $H_3PO_4$ Using Extract of *Lantana Camara*.** *Life Sci J* 2014;11(11):899-904]. (ISSN:1097-8135). http://www.lifesciencesite.com. 160

**Key words**: corrosion inhibition, gravimetric methods, adsorption, hardness, lantana camara, Brinell hardness, tensile strength.

## l. Introduction

Corrosion of metallic materials in acidic media causes considerable economic and material loss. Corrosion processes develop fast after disruption of the protective barrier and are accompanied by a number of reactions that change the composition and properties of both the metal surface and the local environment (Rani and Basu, 2012). The use of corrosion inhibitors is one of the proven methods for preventing and controlling corrosion. Corrosion inhibitors reduce the corrosion rate by modifying the corrosion potential, retarding the cathodic and anodic corrosion reactions via polarization or passivation of the metal surface. These inhibitors have been found to function by adsorption of their ions or molecules onto metal surface (Sharma et. al, 2010). The hazardous effect of most synthetic corrosion inhibitors has made researchers to focus on the use of natural products as they are biodegradable, non- toxic and environmentally friendly. They are also readily available and cheap. Extracts from several plants have been reported to inhibit the corrosion of metals in acidic media; Ocimum gratissimum, (Nkiko and Bamgbose, 2011) Occimum viridis (Oguzie, 2006), Opuntia (El – Etre, 2003), Phyllanthus amarus (Okafor et.al, 2008), Sanseviera trifasciata (Oguzie, 2008), Ipomea involcrata (Obot et.al, 2010), Allium sativum (Okafor et. al, 2009), Azadirachta indica (Ekpe et. al, 1994), to mention a few.

This paper, in continuation of our earlier work on the development of green inhibitors (Nkiko and Bamgbose, 2011) reports the investigation of the inhibitive effects of the leaves extracts of lantana camara on the corrosion of Zinc (Zn) alloy in Phosphoric acid.

L. camara known as Spanish flag belonging to the family verbenacea is a low subscandent shrub with stout recurved prickles and strong currant fragrance. It is used as herbs for the treatment of various ailments, as firewood and can also be planted as a hedge to keep away livestock. (Venkatachalam et. al, 2011) and (Germplasm Resources, 2010).

Studies on the chemical composition of lantana camara have shown that the plant contains pentacyclic triterpenoids, flavanones, fatty acids such as oleanic acid, the leaf contains various high percentage of sesquiterpenes. Major components of essential oils obtained from the leaves include (E) – nerolidol, γ-cardinene, α –humulene and β- caryophyllene (NSWNPR, 2010).

Zinc is a bluish- grey metal covered by a protective transparent layer of basic carbonate in air. It is twice as heavy as aluminium. It has a strength of about 4 -12ksc and the cold work of rolling is 28 – 36 ksc, hard - drawn (Kissel and Ferry, 2002) and (Degarma et. al, 2003). Zinc has its major application in corrosion in the plating of steel as a sacrificial metal. Zinc alloy is used in fabrication of materials such as roofing sheets and head pans. The alloy consists of varying compositions of Zinc and other metals such as copper, aluminium. Distinguishing features of the alloy have been reported to include as-cast strength, excellent bearing properties and low energy requirements for melting (Kissel and Ferry, 2002) and (Degarma et.al, 2003).

The present study investigated the inhibitive properties of the leave of extract of Lantana camara on the corrosion of zinc alloy in phosphoric acid ($H_3PO_4$) using gravimetric method. It also evaluated the effect of lantana camara leaf extract on the hardness and hence, the strength of the metal. The result obtained is aimed at developing an efficient, biodegradable and environmentally friendly protection that will prevent material loss and also reduce cost of corrosion control. Lantana camara plant is non - toxic and biodegradable and grows all year in the Nigerian flora.

## 2. Materials and Methods

Lantana camara was collected from the flora of Abeokuta and classified at the Forest Research Institute, Ibadan, Nigeria. Zn alloy plates supplied by Midland Galvanizing Company, Nigeria were cut into coupons dimension of 2 cm by 1cm, degreased with ethanol and acetone, weighed and stored in an airtight desiccator. Stock solution of plant extract was prepared by placing 400g of milled leaves in 100ml of 2.0M phosphoric acid ($H_3PO_4$) and refluxed for 3 hours. The resulting solution was cooled, filtered and stored. Inhibitor test solutions (V/V) of the extract were prepared in the concentration of 2.5mL – 12.5mL. Previously prepared Zn alloy were weighed and immersed into 50mL of different concentrations of the test solution. The coupons were retrieved every 1hour, washed and reweighed. The differences in the weight of coupons were taken as the weight loss evaluated in grams.

The inhibition efficiency of lantana camara was calculated using the equation:

$I\ \% = (w_0 - w_i)\ w_0^{-1} \times 100$.

The degree of surface coverage (θ) was calculated from the equation: $\theta = (w_0 - w_i)\ wo^{-1}$.

Corrosion rate per hour was evaluated using the formula, CR = WL/At

Optical Microscopy and hardness test was carried out by Nigerian Foundry Limited using Foundrax Brinell Microscope type 2BM15, Serial number 100332, and hardness tester 1, model BHD, serial number 1003402 respectively.

## 3. Results and Discussion

### 3.1. Metal composition and Percentage yield of Extract

Table 1 shows the result of the composition of Zinc alloy used for the experiments. Metal sample used for this experiment contains about 99% Zinc (Zn). The percentage yield obtained per 400g of lantana camara milled leaves per 100mL from equation 1 is 16.

$$\text{Percentage yield of extract} = \frac{\text{weight of plant material after extraction}}{weight\ of\ plant\ material\ before\ extraction} x\ 100 \qquad (1)$$

### 3.2. Weight loss and Inhibition Efficienccy of lantana camara extract

Weight loss of Zn alloy decreases as inhibitor concentration is increased. (Figure 1).

Inhibition efficiency of lantana camara increases with time and with increase in the concentration of the inhibitor (Figure 2a). This observation implies that more surface area of metal is covered as the concentration of inhibitor increases.

Inhibitor efficiency of lantana camara decreases as the temperature increases.

(Figure 2b) This suggests that adsorption of inhibitor on metal surface may be physical

Corrosion rate decreases with time and increase in inhibitor concentration. However corrosion rate increases with increase in temperature. (Figure 3a and 3b)

### 3.3. Adsorption isotherm and thermodynamic parameters of corrosion of Zn alloy in 2M $H_3PO_4$

Adsorption isotherm fitted perfectly into Langmuir (Figure 4) represented by equation1:

$$\frac{C}{\theta} = \frac{1}{Kads} + C \qquad (2)$$

Lantana camara leaf extract has a complex composition, the interaction between the metal surface and the components of the extract maybe attractive or repulsive. Adsorption may occur at the cathodic or anodic sites of the metal surface, thus adsorption of lantana camara on Zn surface is represented by the modified Langmuir (Villamil et.al, 1999) written as equation 3

$$\frac{C}{\theta} = \frac{n}{Kads} + nC \qquad (3)$$

Where C is inhibitor concentration, θ is surface coverage area, Kads is equilibrium constant for the adsorption process, n measures the effectiveness of the inhibitor

Assuming that the plot of corrosion rate (CR) of Zn alloy against concentration (C) obeys the kinetic relationship, k is defined as the rate constant and B is the reaction constant obtained from the intercept and slope of the graph obtained for the equation (4) below. Values of k and B and thermodynamic parameters are shown in tables 2 and 3. The free energy ( $\Delta G_{ads}$ ) of reaction is obtained from equation (5):

$$\text{Log CR} = \log k + B \log C \qquad (4)$$

$$lnKads = \ln(55^{-1}) - \Delta G_{ads}\,(RT^{-1}) \qquad (5)$$

Where R is the molar gas constant, T is temperature and the value 55.5 represents the concentration of water in solution

The inhibitor effectiveness or reaction constant B is high and negative depicting that the corrosion rate is inversely proportional to the concentration of lantana camara. The high negative value of B implies good inhibitive properties of lantana camara.

The free energy obtained for the reaction are negative and small, which implies that adsorption of inhibitor on the Zn alloy is spontaneous and the magnitude of the free energy (< -20kJ/mol) obtained also indicates that adsorption of lantana camara is physical.

The enthalpy of adsorption $\Delta H_{ads}$ is obtained using the van't Hoff equation (6) and the entropy from equation (6).

$$\ln Kads = \frac{\Delta\text{Hads}}{RT} + constant \qquad (6)$$

The equilibrium constant of adsorption $K_{ads}$ decreases with increase in temperature which suggests that the adsorption of lantana camara on Zn alloy surface is physical. The inhibition efficiency n is positive and close to unity. The enthalpy of adsorption $\Delta H_{ads}$ is negative and and decreases with increase in temperature. This observation implies that the reaction is exothermic and the inbibition efficiency decreases as the temperature increases (Table 3).

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \qquad (7)$$

The apparent activation energy Ea was calculated using the Arrhenius equation:

$$log\frac{CR1}{CR2} = \frac{Ea}{2.303R}\left[\frac{1}{T1} - \frac{1}{T2}\right] \qquad (8)$$

$CR_1$ and $CR_2$ are the corrosion rates at temperature $T_1$ and $T_2$ respectively.

The apparent energy of activation in the presence of the inhibitor is higher than in the absence of inhibitor which implies lantana camara is an effective inhibitor (Table 2).

**3.4. Surface and Hardness Test**

Hardness is a measure of the resistance of a metal to permanent (plastic) deformation. It is dependent on the ease with which it is plastically deformed. The relationship between hardness and strength can only be determined empirically. (Smith and Hashem, 2010)

The Brinell hardness number of Zinc alloy obtained by conversion from the Foundrax Brinell Hardness table (Nigeria Foundry Limited, 2000) and the approximate tensile strength in the absence and presence of the inhibitor is shown in Table 4. The result shows that the hardness and the tensile strength of Zinc alloy are drastically reduced by immersion in acid solution in the absence of inhibitor.

The hardness number and approximate tensile strength obtained in the presence of the lantana camara (inhibitor) is higher than in the observed value obtained for the metal without inhibitor. This implies that lantana camara extract inhibits corrosion of Zinc alloy and may also be able to prevent to an extent its plastic deformation. Figure 5(a) Shows that the surface of Zinc alloy used as control has irregular pattern with some cracks undergoing deterioration. Figure 5b shows the metal in acid medium in the absence of inhibitor appears darker and wider showing due to corrosion of the metal by the acid when compare to figure 5a. However figure 5c shows the optical micrograph of the metal in the presence of the inhibitor.

The cracks depicted by the lines in figures 5a and b appeared to have been filled significantly. This implies that the inhibitor have slowed down the deterioration. This observation implies that lantana camara is adsorbed on the surface of Zn alloy thereby slowing down deterioration.

**Conclusion**

- Extract of lantana camara acts as an efficient inhibitor for Zn alloy in Phosphoric acid.
- The inhibition efficiency increases with concentration of lantana camara but decrease as temperature increases.
- Lantana camara extract improves the hardness and the strength of Zn and prevents it from deterioration in $H_3PO_4$
- Corrosion rate decreases with increase in the concentration of inhibitor.
- The adsorption of extract on the surface of the metal as observed, obeys perfectly the Langmuir.
- The yield of 16% of crude extract obtained from 100g of plant material suggests that lantana camara can be processed into inhibitor for commercial use.

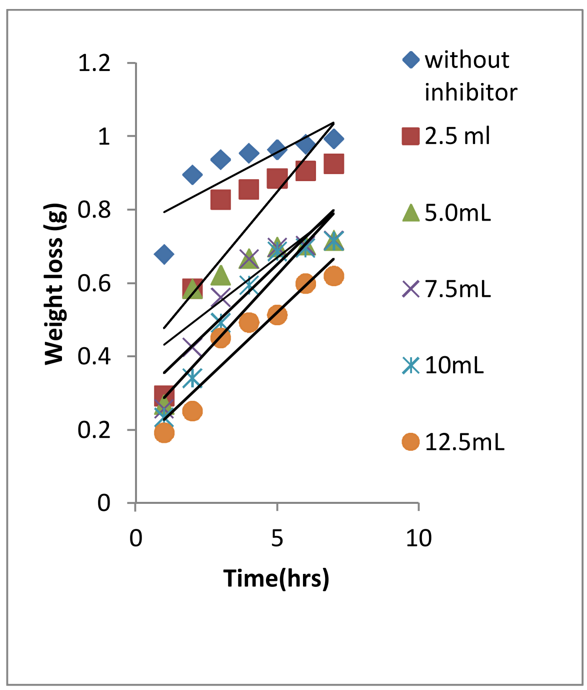
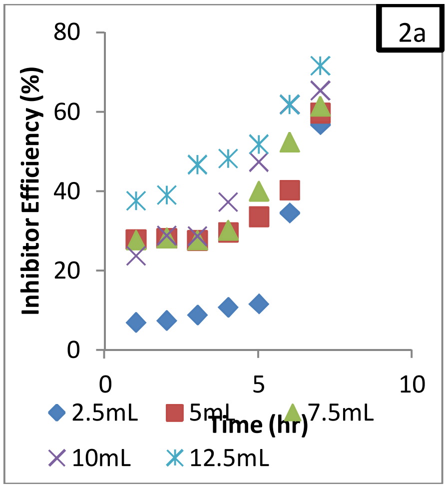



**Figure 1: Variation of weight loss of Zn alloy with time in the presence and absence of lantana camara at 303K in 2M $H_3PO_4$**



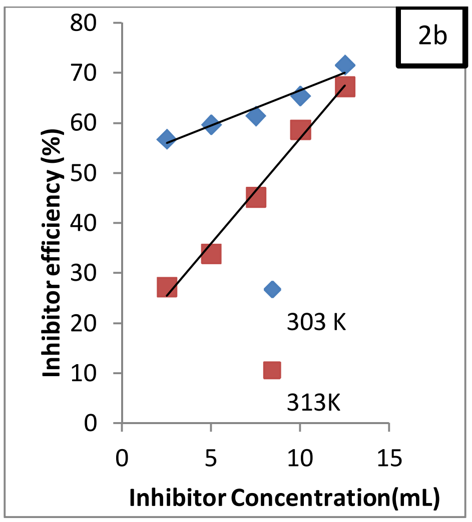
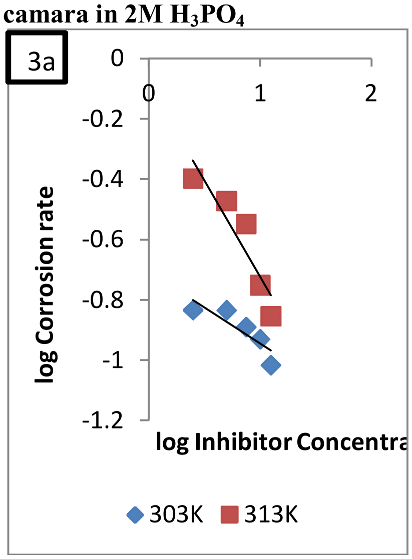




**Figure 2a: Variation of inhibition efficiency of lantana camara with time at 303K. Figure 2b: Temperature dependence of inhibitor efficiency of lantana camara in 2M $H_3PO_4$**



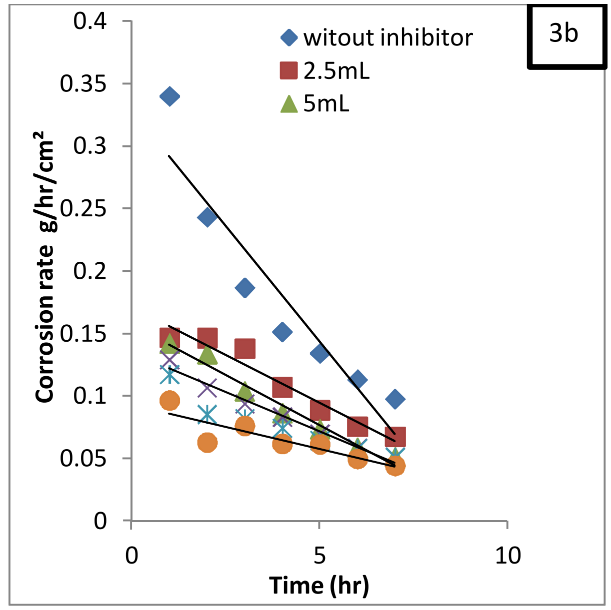




**Figure: 3a) Temperature dependence of corrosion rate of Zn alloy and 3b) is Corrosion rate of Zn alloy at 303K in 2M $H_3PO_4$**

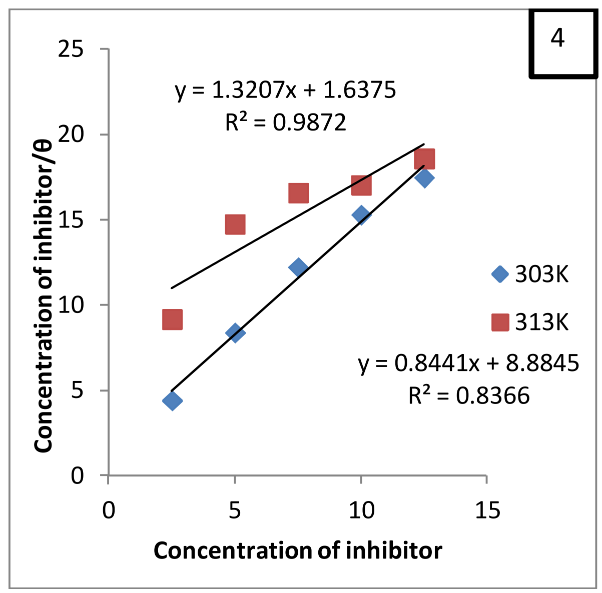



**Figure 4 represents Langmuir isotherm for Corrosion of Zn alloy in the presence of lantana camara in 2M $H_3PO_4$**

**Table 1: percentage composition of Zinc alloy sample**

| Element | Al | Cu | Fe | Mn | Ni | Pb | Sn | Mg | Ti | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| Composition of Zn alloy plate | 0.074 | 0.109 | 0.085 | 0.007 | 0.039 | 0.312 | 0.000 | 0.001 | 0.005 | 99.369 |

**Table 2: Kinetic and activation parameters of corrosion inhibition in the absence and presence lantana camara extract**

| | Temperature (K) | Rate constant k ($hr^{-1}$) | Inhibitor effectiveness B | $E_{a(app)}$ kJ/mol | $\Delta H_{app}$ kJ/mol |
|---|---|---|---|---|---|
| Absence of inhibitor | 303<br>313 | 0.329<br>0.389 | -<br>- | 13.2 | -15.7 |
| Presence of inhibitor | 303<br>313 | 0.197<br>0.828 | -0.239<br>-0.642 | 113.2 | -115.7 |

**Table 3: Thermodynamic parameters of corrosion inhibition in the absence and presence lantana camara extract**

| Temperature | Equibrium constant of adsorption ($K_{ads}$) $M^{-1}$ | Free energy of adsorption ($\Delta G_{ads}$) kJ/mol | Heat of adsorption ($\Delta H_{ads}$) kJ/mol | Entropy of adsorption ($\Delta S_{ads}$) J/mol | n | $R^2$ |
|---|---|---|---|---|---|---|
| 303 | 0.807 | -4.836 | - 0.542 | 14.172 | 1.321 | 0.987 |
| 313 | 0.095 | -10.224 | -6.125 | 13.096 | 0.844 | 0.837 |

**Table 4: Brinell Hardness Test value and Approximate Tensile Strength in the Absence and Presence of Lantana Camara**

| Sample | Brinell Hardness number (HB) | Approximate Strength of Metal (1000) Psi |
|---|---|---|
| Zinc alloy | 477 | 238 |
| Zinc alloy in the presence of Inhibitor | 429 | 212 |
| Zinc alloy in the absence of Inhibitor | 415 | 204 |

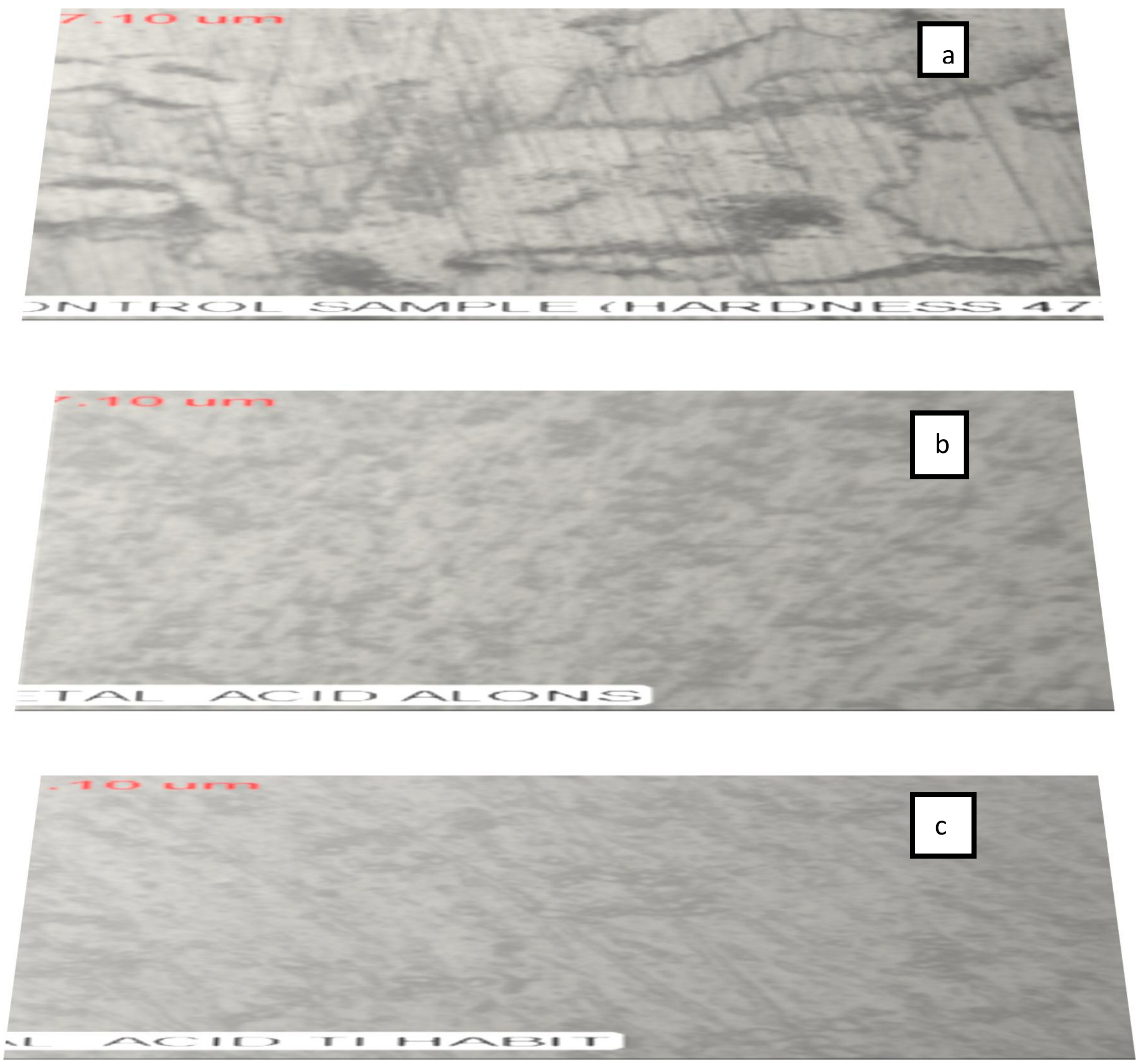



**Fig 5: Optical Micrograph of Zn alloy, (a) unpolished metal (b) metal in acid medium alone and (c) metal in test solution of acid and inhibitor.**

**Acknowledgement**

The authors are grateful to Midland Galvanising Company especially Mr Adams, Abeokuta for supply and determining the metal composition of Zinc alloy, and Mr Habib of Nigerian Foundry Limited, Sango-Ota, Nigeria for carrying out the optical microscopy and hardness test using Foundrax Brinell Microscope type 2BM15, Serial number 100332, and hardness tester 1, model BHD, serial number 1003402 respectively.

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11/9/2014