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Leaf extracts as green substitute to toxic zinc chromate and zinc phosphate additives in Polyurethane primers for corrosion inhibition of steel

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ABSTRACT

Corrosion inhibition of steel by Polyurethane Extract-primer (PEP) containing plant leaf extracts was compared with Polyurethane Conventional primer (PCP) containing zinc phosphate and zinc chromate as inhibitors. The primers were investigated using gasometric technique in 5 °C steps of temperature increase from 25 to 50 °C in 1.0 M HCl as corrodent. The PEP of 34.24 percent actives compared with PCP of 56.35 percent actives gave the same inhibition efficiencies of 82.4%. Extract primers of low percent active concentration were more effective and less expensive than that of conventional primers.

KEYWORDS

Jatropha curcas, *Sida acuta*, Polyurethane Conventional primer, Polyurethane extract primer, mild steel, percent active

1. INTRODUCTION

Electropositive purified metals are unstable in moist or dry air dissolved in oxygen, chlorine or bromine gas. They tend to exist in combined state or disintegrate into their constituent atoms due to chemical reactions with surroundings [1]. Their instability and reactivity often lead to recombination of elements or compounds of affinity to forming compounds in the medium or environments of existence. This aesthetics devaluation with depreciation of technical values of the metal is corrosion. The manufacturing and construction industries suffer setbacks in the course of improper consideration of the redox process that will set in with time. Selective prevention and specific maintenance are being incorporated to the metallic structures based on corrosion phenomena. The kind coating formulations designed against the causative agents is a function of intent for corrosion prevention. The active protective constituents of the coating material break the reaction path of redox reaction. The barrier or insulator materials which serve as inhibitor adhere to the metal surface to impede transfer of electrons initiated from the anode and captured by the cathode due to corrosion aiding agent present in the environment.

Plant extracts are multifunctional due to their constituents which have numerous applications in human life, specifically corrosion inhibition of metals. Their specific inhibition mechanisms due to variation in phytoconstituents are yet to be established. Adsorption mechanism may either be through protonated organic specie or heteroatoms with lone pairs of electron. Since chloride ions from HCl used in the preparation of extract solution have a tendency to adsorb first on the surface of metals, it may get the protonated organic extract inhibitor attracted to the surface for adsorption. This therefore made HCl medium favor protonated organic inhibitor adsorption than other media [2]. Protonated organic extract

constituent in solution has been found to readily adsorb on cathodic sites of metal, thereby retarding the release of hydrogen gas so that the molecules components of the solution impinge anodic dissolution of the metal [3, 4].

In the case of halide (KI) addition as synergistic compound, I^- ion replaces Cl^- from the metal surface because of its higher electronegative potentials. This will therefore increase the power of attraction of protonated organic extracts. It will bring about higher surface coverage leading to increase in inhibition efficiency than it could have been if higher electronegative halide ions have not been introduced. Halide ions aid the adsorption of inhibitors mostly from organic origin on steel corrosion in acidic media by creating electrostatic environment within the metal surface. Synergism results from high surface area coverage that occurs when ion-pairs, that is, positive ions of the organic inhibitor and halide ions interact and are adsorbed on the metal surface [5, 6]. On the other hand, when a plant extract of higher number of inhibitory secondary metabolites but lower concentrations of phytochemicals as in the case of *Jatropha curcas* [7, 8] determined qualitatively was synergized with another extract of fewer phytoconstituents but of higher concentration, increasing the quantity of the extract with lower concentration resulted to increases in their inhibitory potentials as synergistic compound.

J. curcas plant can be propagated by both stem and seed. Among its importance are its use as grave and boundary demarcations of fields or farmlands. The stem and twigs are still being used in villages of Nigeria and Cameroun as chew stick. The watery sap can be used to treat fresh cut and sores in some nations in Africa. It also serves as medicine to ease stomach ache. The fruit and the seed are reported to contain a contraceptive principle [9].

Sida acuta is a malvaceae family tropical plant considered as a common weed in most environments where found. It is a dicot genus with as much as 200 species, claimed to have probably originated from Central America that now spreads over the warm tropics. In Ivory Coast it is used for analgesic and to quell toothache, in vapor baths in cases of severe fever followed by embrocating of the body with the leave crushed with kaolin and to calm infantile convulsion. It is poisonous to goats, causing lysosomal storage disease if ingested. Cold infusion is common Yoruba remedy for gonorrhoea [10]. Compounds of Quidoline and Crytolepine5-methylindolo (2-3b)-quinolic are alkaloid compounds isolated from the extracts of *sida acuta*. The isolate was characterised and reported from an investigation to have possessed antibacterial activities in Burkina Faso [11].

Many quantitative works have been done extensively elsewhere on phytochemical screening of these two plant leave extracts [12–14]. Among several secondary metabolites present in green inhibitors, saponins, tannins and alkaloids have been reported to be their most active constituents.

Primers are the metal corrosion barriers applied on steel to inhibit or suppress the existing corrosion process [15]. They are formed as resins that bind other components of the solution. Epoxy, alkyd or 2-pack polyurethane are various types of primers used as vehicular media in most primers as coating compounds.

The nature of inhibitors used (e.g., corrosion pigments) and polymeric binders determines the classification of the prepared primer. It could be metallic, which may contain any of zinc, aluminium, tin, silver or gold. It could also be chemical compounds of any or a combination of iron oxide (Fe_2O_3), zinc chromate ($ZnCrO_4$) or zinc phosphate ($Zn_3[PO_4]_2$). These compounds can be singularly or in combination with others, contained in the primer recipe. A non-toxic zinc phosphate can be used for protection of steel when not alloyed with nickel. It is perceived that under damp conditions zinc phosphate supplies phosphate ions that bring about phosphating of the iron-based metal surface. Compounds such as zinc chromate impact yellow colouration in solution but are toxic and carcinogenic to human health.

These two compounds are complementary for effectiveness in both acidic and alkaline media in which their inhibition activeness exist in either [16]. The conventional additives were pure and ionic compounds. The oxidising power of Cr^{6+} in the chromate ion (CrO_4)²⁻ is responsible for inhibiting power in the primer. At the pH of the primer greater than 5, the chromium (VI) was reduced to Cr(III) per mole of zinc chromate. This occurs at the anodic sites where the release of two electrons from iron initiates it to become Fe^{2+} [17, 18]. The complimentary use of zinc phosphate as a highly soluble anticorrosive pigment in this batch was to maintain the activeness of the primer in acidic conditions [19, 20].

This work investigated corrosion inhibition effectiveness of leaf extracts of *J. curcas* (JC) and *Sida acuta* (SA) in polyurethane primer compared with conventional polyurethane primer containing zinc chromate and phosphate as inhibitor. The incorporation of the leaf extract into conventional primer recipe as additive substitute for inhibition enhancement and environmental conduciveness made the research unique from others in this area.

2. EXPERIMENTAL WORK

2.1. Materials used

Mild steel sheet was cut into coupons of dimension 18 mm by 9 mm with 3.0 mm thickness. The coupons were made free from grease by cleaning with ethanol and stored in a desiccator [21].

Metal Spectrometer Analyser, Model ARL Quanbo Desk OTD 226 (Optical emission) was used to determine the elemental composition analysis of the steel (Table 1).

J. curcas (JC) and *Sida acuta* (SA) fresh leaves were dried and powdered. 100 g of each of the processed plants were weighed separately into 2,000 ml conical flask filled with 1,000 ml ethanol. The flasks were covered and left to stand for 48 h and been shaken occasionally at regular intervals [22]. The resultant solutions were filtered and residue thoroughly washed with ethanol. The extracts were concentrated and the solvents recovered through rotary evaporator. The concentrated extracts were evaporated to



Table 1. Percentage elemental composition of mild steel

| Elements | C | Co | Mo | V | Fe | Si | Mn | Nb | Cr | Ni | Cu | S | P |
|----------|--------|--------|--------|--------|-------|--------|--------|--------|--------|--------|--------|--------|--------|
| % | 0.1551 | 0.0463 | 0.0106 | 0.0169 | 98.42 | 0.2378 | 0.5571 | 0.0823 | 0.0626 | 0.1499 | 0.0792 | 0.0445 | 0.0280 |

oily solid on a water bath by gently heating at 75° C to finally expel the leftover ethanol [23].

Characterization was made by use of Fourier-transform infrared spectroscopy [FTIR] method of analysis to determine the functional group present in the extract sample.

The two obtained plant extracts were mixed in ratio 3:1 (JC: SA). The zinc compounds were substituted with the mixture and were increased in weight steps of 25% to obtain PU-Extract primers in series of 3.94, 4.93, 5.91, 6.90 and 7.88 g in the recipe below:

2.2. Measurements

2.2.1. Coating procedure of coupons. The coupons of the same 18 mm by 9 mm were coated with the primer using sprayer to achieve 1 mm thickness confirmed with thickness probe. It was allowed to dry for 24 h. It was repeated twice to obtain 1 mm thickness and was then finally left to air dry for 48 h (1 control with 5 extract primed coupons, making up to 6 primed samples per set for each brand of primer).

2.3. Gasometric corrosion test

50 mL of 1.0 M HCl solution was measured and poured into Mylius cell. The coupon to be examined was introduced into the acid solution contained in the cell. It was corked and sealed with vaseline. The set up was lowered into a temperature regulated bath. The coated samples produced for set of weights for conventional and extract primer were subjected to gasometric corrosion test described elsewhere using the blank solution of 1.0 M HCl as the corrodent at 25 °C [24]. Evolved gases were recorded hourly for 8 h. It was repeated for 30, 35, 40, 45 and 50 °C in 1.0 M HCl. The investigation was carried with coupon coated with PU-Conventional primer as control. The schematic diagram of the experimental is a modified form of the apparatus used elsewhere [25] for similar measurement.

The Percentage Inhibition Efficiency (% I.E.) for the corrosion inhibition of plant extracts on the steel was calculated using the equation below [25].

$$\% \text{ I.E.} = 1 - \frac{V_{in}}{V_{uni}} \times 100 \quad (1)$$

where

V_{inh} = Volume of hydrogen evolved from solution containing inhibitor

V_{unih} = Volume of hydrogen evolved from uninhibited solution both at time t .

$$\text{Surface coverage } \theta = 1 - \frac{V_{in}}{V_{uni}} \quad (2)$$

3. RESULTS AND DISCUSSIONS

3.1. FTIR analysis

Fourier Transform Infrared Spectroscopy [FTIR] analysis shown in Fig. 1 confirmed the presence of functional groups in the mixed leaf extract. The O–H of carboxylic acid at 3,381 cm^{-1} strong band of 1,744 cm^{-1} was assigned to stretching vibrational frequency of C=O of esters and lactones. The weak band at 1,644 cm^{-1} was an indication of imines and oximes moieties. The weak bands at 1,463 and 1,376 cm^{-1} were for N=O of nitro group present. Weak bands at 1,240, 1,162 and 1,094 cm^{-1} depicts C–O stretching vibrational band of alcohol, ethers and esters that are present in the extract. The weak bands at 724 and 661 cm^{-1} confirmed that bending vibrational mode of amines were also present. All these groups present in the extract contained heteroatoms oxygen and nitrogen in the bonding structure of their secondary metabolites. These have been reported to act as binding centers with metals when acting as inhibitor [27–29].

3.2. Corrosion rate ($\text{mL}/\text{cm}^2\text{hr}^{-1}$)

$$\text{From } R \propto \frac{\partial \Delta W_m}{\partial t} \propto \frac{\partial \Delta V_{H_2}}{\partial t} (\text{mg}/\text{cm}^2\text{hr}^{-1}) \propto (\text{mL}/\text{cm}^2\text{hr}^{-1}) \quad (3)$$

Volume of hydrogen gas evolved at time t was determined using mathematical polynomial regression [26].

$$V_{in} = g \pm ft \pm et^2 \quad (4)$$

Differentiating Eq. (4) gave $R = \frac{\partial v}{\partial t} = f + 2et$ which could be rewritten as

$$R = 2et \pm f \quad (5)$$

For steel in HCl acid and the two different primers, Eqs. (4) and (5) were used to formulate and calculate rate of corrosion[®]. Where $t = x$

- Steel $y = 0.059 x^2 + 1.588 x + 0.135$; $\frac{\partial v}{\partial t} = 0.118 x + 1.588$
- PU-Conventional primer: $y = 0.007 x^2 + 0.098 x + 0.223$; $\frac{\partial v}{\partial t} = 0.014 x + 0.098$.
- PU-Extract primer $y = 0.007 x^2 + 0.009x + 0.075$; $\frac{\partial v}{\partial t} = 0.024 x + 0.009 x$

3.3. Inhibition efficiency

In Fig. 2, I. E. of PU Conventional primer with anticorrosive agents remain constant at 82.4%. Increase in weight of plant extracts in various primers lead to increase in % I. E. At 50%



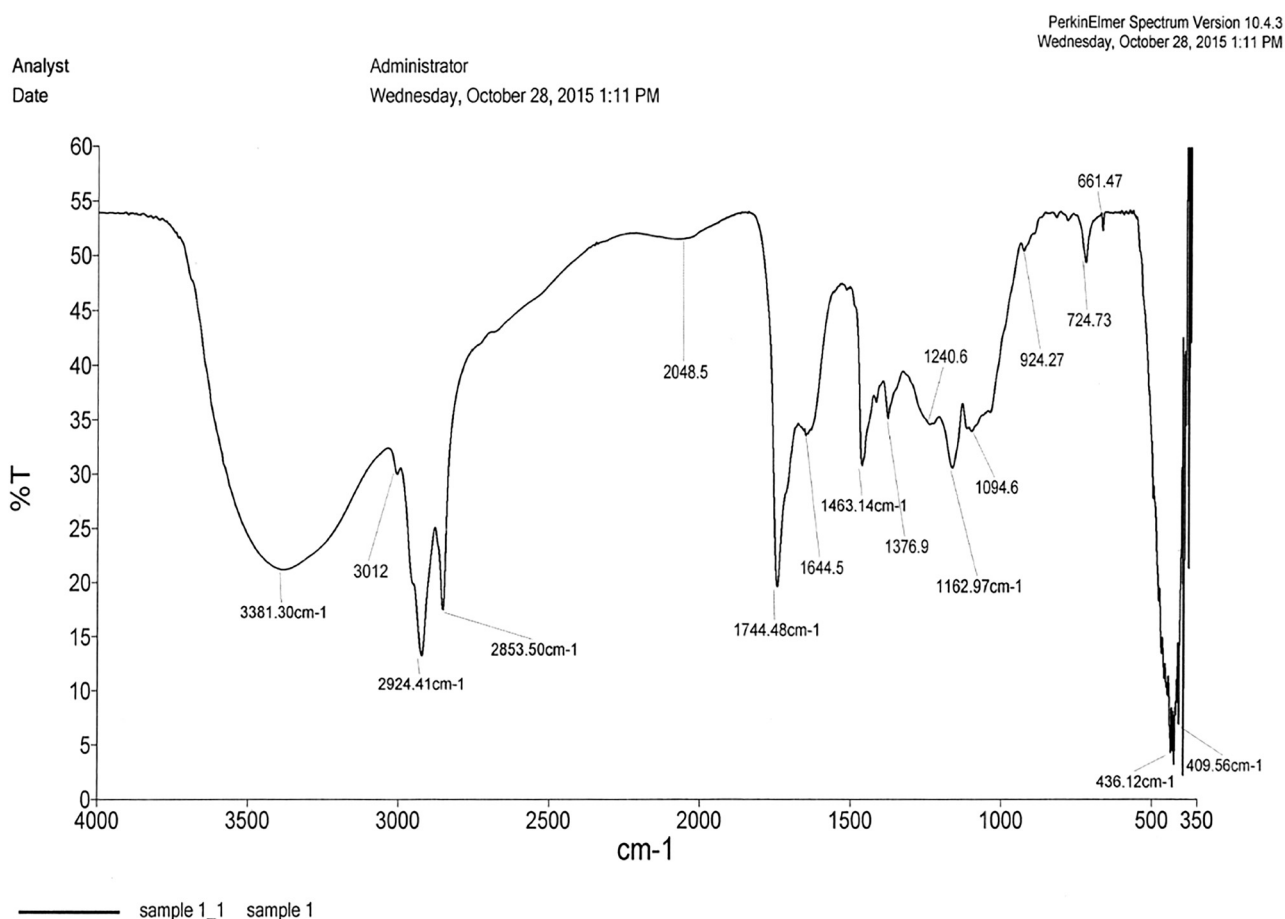


Fig. 1. Spectrum of mixture of *Sida acuta* with *Jatropha curcas* leaf extracts

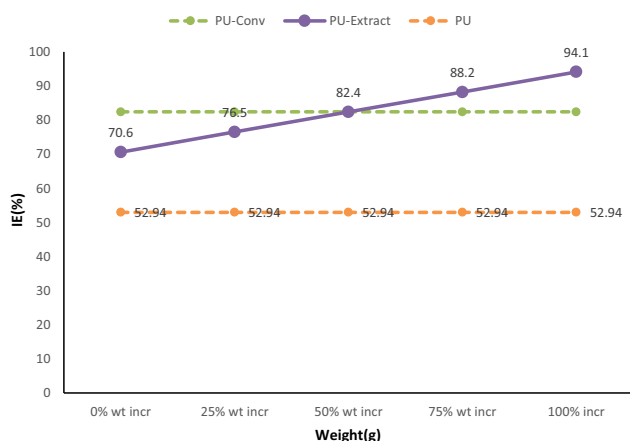


Fig. 2. Plot of inhibition efficiency against various weights of PU-Extract primer and Conventional PU-primer on steel in 1.0 M HCl at 30 °C

increase in weight of extract in PU primer to 5.91 g. Conventional PU-primer I. E. equals PU-Extract primer I. E. at 82.4%. At 75% extract weight increase in PU primer to 6.90 g Conventional PU-primer was at 82.4%. At 100% extract weight increase in PU primer to 7.88 g the I. E. of 94.1% and 88.2% were greater than the conventional primers. At double

extract weight concentration PU extract primer 94.1% is greater in % I.E. compared with PU conventional primer 82.4%.

The % I. E. were of lower values at corresponding weights at 50 °C compared to the situation at 30 °C, due to temperature rise that resulted in desorption but followed the same trends as indicated in Fig. 3. Also with weight 3.94 g of conventional inhibitor in PU, I.E. of 60% and 46.67% were attained for PU with conventional and PU without inhibitor primers, respectively, at temperature of 50 °C. No increase in I.E. was obtained beyond that amount of inhibitor. At that same 3.94 g of extract weight in primer, an optimum I.E. of 76.67% was achieved, further increase of extract weight led to subsequent decrease in efficiency at that same temperature of 50 °C.

The % I. E. of PU primer without anti corrosive agents (i.e., without any form of inhibitor) remain constant at 52.94%. The ketone group C=O in the glyptal resin have both σ sigma and π bond which are rich in π electrons. These electrons tend to reside more on oxygen atom which can be donated to the empty orbital of the Fe^{2+} , thereby forming adsorption.

In the PU 52.94% I. E., the lone pair of electrons on the hydroxyl oxygen: OH can be donated to the emptied orbital of the Fe^{2+} . Also isocyanate group $\text{O}=\text{C}=\text{N}^-$ which can get

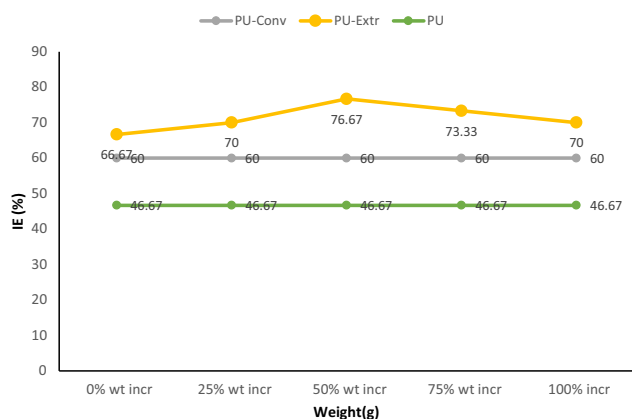


Fig. 3. Plot of inhibition efficiency against various weights of PU-Extract primer and Conventional PU-primer on steel in 1.0 M HCl at 50 °C

adsorbed to the steel surface through nitrogen or oxygen. Chellate adsorption could also occur through the two heteroatoms to the surface of the steel [30, 31].

The addition of the leaf extract containing heteroatoms into the batch matrix is to increase the electron donation capacity of the primer through the electron rich centres of the constituents.

The I. E. of the PU-primers both Conventional and Extract decreased with increase in temperature as indicated in Fig. 4. The I. E. of PU-Extract primer was 70.59% at 30 °C. Conventional PU-primer has I. E. 60.57% at 45 °C. Both PU conventional and extract primers % I. E. are reducing with increase in temperature. This might be attributed to the breakup of adsorbed nitrogen with Fe from the isocyanate group $O=C=N^-$ in the primer.

3.4. Phytoconstituents in the primer

Mixture of *Sida acuta* and *J. curcas* leaf extract used as anti-corrosive agent in the primer recipe contains different types of organic compounds [32, 33] of high molecular weight having heteroatoms and p-centers within molecular

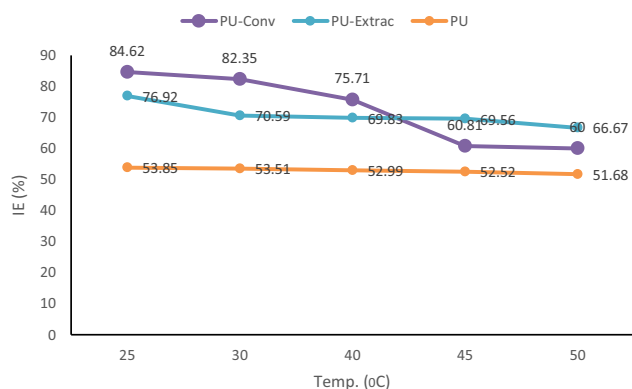


Fig. 4. Plot of inhibition efficiency against various temperatures for PU- Polyurethane Extract-primer and Polyurethane Conventional primer on steel in 1.0 M HCl at equivalent weight

structures. Some of them are tannins, flavonoids, alkaloids and saponins. Compounds such as tannins are water-soluble, esters of an aliphatic and phenolic acids or oligomers. Flavonoids are polyphenolic molecules which are polyhydroxyflavan-3-ol units of molecular weights that range between 500 and 3,000 [34, 35]. Alkaloids are naturally occurring organic nitrogen-containing bases. Some known alkaloids are morphine, strychnine, quinine, ephedrine, and nicotine [36, 37]. Saponins are characterized by the soap-like foam they produce when agitated in aqueous solutions. They are amphipathic glycosides grouped phenomenologically. Their structure was derived from combination of one or more hydrophilic glycone moieties with a lipophilic triterpene or steroid derivative.

Polyurethane is a polymeric organic unit joined with carbamate (urethane) links. On an average, it contains two or more functional groups per molecule that originated from two monomers: isocyanates and polyols [38] (Fig. 5).

Desmodur® N 75 Aliphatic polyisocyanate (HDI biuret) is a water-insoluble hydrophilic gel, which functions as a hardener component for fast curing polyurethane coating systems [39] (Fig. 6).

3.5. Adsorption isotherms

The conventional additives zinc chromate and zinc phosphate are ionic compounds. They are expected to be chemically bonded to the surface of the mild steel.

The adsorption isotherm that best explains the effectiveness of the primers on mild steel was studied. The correlation coefficient (R) was deduced from plot of relationships of 5 different adsorption isotherms. This was

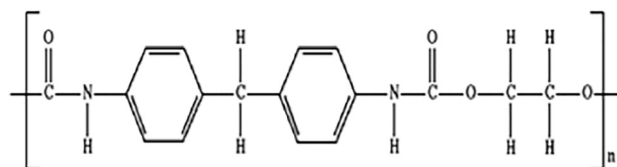


Fig. 5. Polyurethane chemical structure

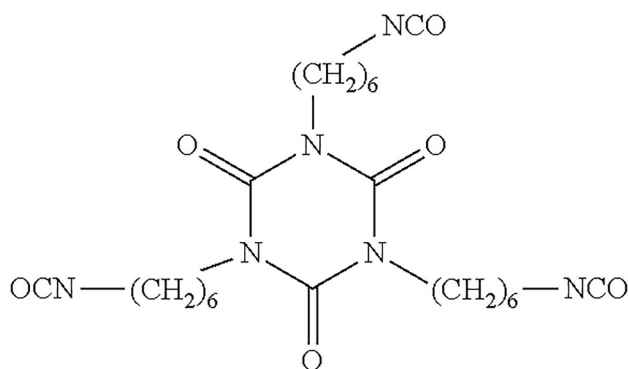


Fig. 6. Desmodur N75 (polysiloxane modified polyisocyanate)

Table 2. Primer recipe

| Components | %wt PCP | %wt PEP @ 0% increase |
|---|------------|--------------------------|
| <i>1st Pack</i> | | |
| Polyhydroxyl resin (PHR) | 31.38 | 31.38 |
| Toluene | 5.05 | 5.05 |
| Bentone | 1.10 | 1.10 |
| Zinc phosphate $Zn_3(PO_4)_2$ | 1.99 | – |
| Zinc chromate ($ZnCrO_4$) (yellow) | 1.95 | – |
| Plant extract | – | 3.94 |
| Magnesium silicate ($MgSi_2O_3$) | 2.88 | 2.88 |
| Talc | | |
| $CaCO_3$ (precipitated) | 5.43 | 5.43 |
| Butyl acetate | 9.96 | 9.96 |
| <i>2nd Pack</i> | | |
| Desmodur N75 | 28.50 | 28.50 |
| Toluene | 11.76 | 11.76 |
| Total | 100 | 100 |

considered at the percentage inhibition efficiencies of PCP = PEP = 82.4% at extract weight of 5.91 g in primer.

From Table 2, Langmuir isotherm, which is synonymous to physisorption, best explains the adsorption between the two primers and the mild steel at 50 °C with R^2 0.999 for

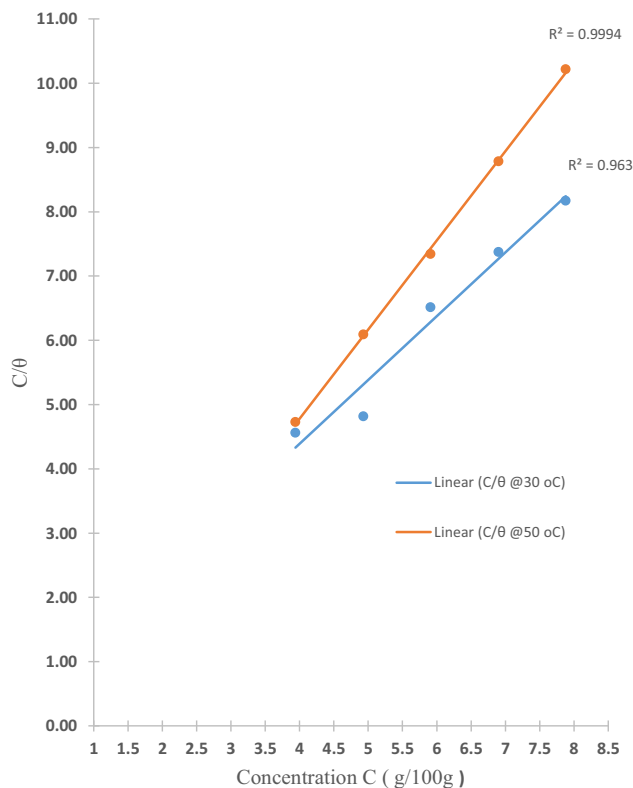


Fig. 7. Plot of C/θ versus Concentration C (g/100 g) of PEP at 50% extract weight increase in primer coats adsorbed on mild steel at 30 °C and 50 °C in agreement with Langmuir isotherm in the presence of 1.0 M HCl

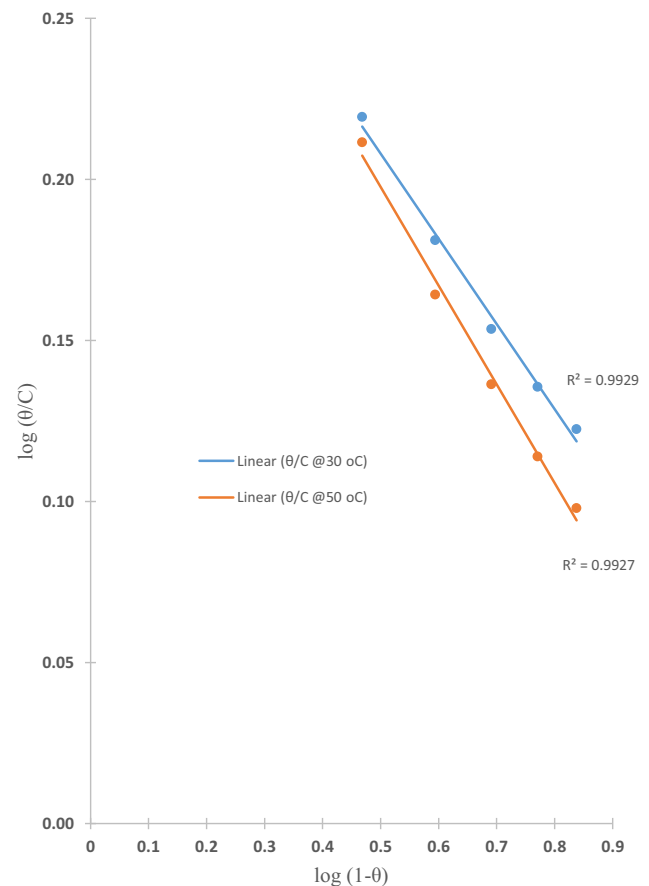
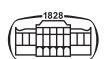


Fig. 8. Plot of $\log \theta/C$ versus $\log(1-\theta)$ (g/100 g) of PEP at 50% extract weight increase in primer adsorbed on mild steel at 30 °C and 50 °C in agreement with Florry- Huggins isotherm in the presence of 1.0 M HCl

PEP primer and graphed in Fig. 7. And that of Temkin known for chemisorption was about 0.970 at both temperatures. For the same PEP adsorption at 30 °C in Fig. 8, Florry-Huggins isotherm with Coefficient of determination R^2 0.992 significantly tends to 1.0 best suited. The presence of other components in the primer batch might have contributed to overall improvement over that of extract alone for adsorption of the extract primer on the steel. This

Table 3. Adsorption isotherms of PEP at which % I. E. of PCP = PEP

| Isotherms | Relationship plots | PEP ← R^2 → | |
|------------------|---|--------------------------------|----------------|
| | | 30 °C | 50 °C |
| 1 Langmuir | C/θ versus C | 0.963 | 0.999 |
| 2 Freundlich | $\log \theta$ versus $\log C$ (x-axis) | 0.975 | 0.969 |
| 3 Frumkin | $\ln\{\theta/C(1-\theta)\}$ versus θ | @ 30 °C 0.796 @ 50 °C 0.539 | 0.623 0.736 |
| 4 Temkin | θ versus $\log C$ | 0.971 | 0.970 |
| 5 Florry-Huggins | $\log \theta/C$ versus $\log(1-\theta)$ | 0.992 | 0.992 |



effect brought about both chemisorption and physisorption in the adsorption process of the primers (Table 3).

4. CONCLUSION

From the studies of corrosion inhibition characteristics of the primers, the substitution of conventional additives with leaf extract in PEP gave 34.25% activity, which is lower than the 56.35% activity for PCP at the same 82.4% Inhibition efficiency reduced potential toxicity threat to the environment at lower cost to PCP. PCP extract primer of the Polyurethane extract primer is of higher inhibitory effectiveness compared with Polyurethane conventional primer. The substituted chromate additives in the primer with leaf extract eliminated toxicity as potential threat to the environment and sourced at reduced cost.

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