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Determination of the Durability of Polyurethane Coating on Mild Steel in Various Soil Media

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Abstract: In this paper, effort has been made to determine the durability of polyurethane coating on mild steel in acid, alkaline and neutral soil. A total of 42 mild steel coupons were used. Out of the 42 coupons, 21 were coated with polyurethane and the remaining 21 were left uncoated. Acid soil (pH = 4.5), Alkaline soil (pH =13.5) and neutral soil (pH = 6.8) were used as the test media. Seven each of the coated and uncoated coupons were buried in each soil media. On weekly basis, one coated and one uncoated coupon were withdrawn from each of the soil media and reweighed. The durability of the coating in each soil media was calculated using a proposed model. From the results obtained, the durability of polyurethane coating was found to be 7.0yrs, 4.5yrs and 2.9yrs in neutral, acid and alkaline soil respectively.

Keywords: Durability, Polyurethane coating, Mild steel, Soil media.

1. Introduction

Corrosion is the gradual degradation of engineering materials when exposed to aggressive environment [1]. It is also defined as the product of the interaction between metallic materials and their environment [2]. In a typical corrosion cell, there must be two metals connected by a conductor in aggressive environment. One of the metals must have higher electrode potential than the other. The metal with higher activity called anode decomposes into positively charged ion (cations) and release mobile electrons which flows to the other metal (cathode). The reaction at the anode is oxidation while the reaction at the cathode is reduction process. The cations in the system migrate to the cathode while the anions (negatively charged ions) migrate to the anode. A typical anodic reaction is stated in Equation (1).

$$M = Mn+ + ne \qquad (1)$$

where M is the corroding metal, Mn+ is the cation produced, e- is the released electron and n is the number of electrons released by M due to its oxidation. The two basic types of corrosion circuits are shown in Figure 1.

There are different forms of corrosion, which includes Pitting corrosion, Inter-granular corrosion, Crevice corrosion, Erosion corrosion, Stress corrosion, and uniform corrosion [3]. Erosion corrosion occurs when a flowing fluid containing solid particles rapidly impinges on a metal surface [4]. It is common with elbow of pipelines through which crude oil flows [5].

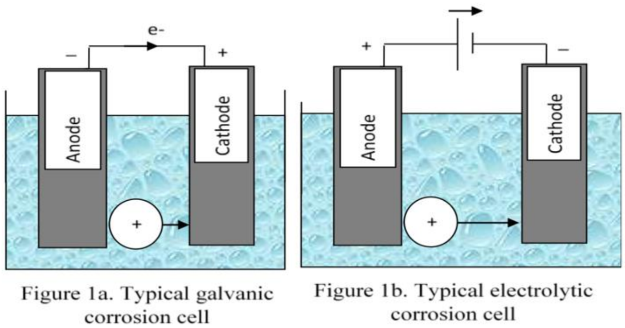

Figure 1 Two basic types of corrosion circuits.

Corrosion is common to most metals and alloys, including steel. Steel is an alloy of iron and carbon. It has improved mechanical properties. Steel is often used where good strength, ductility, creep resistance and dimensional stability are needed. It is used in virtually all aspect of engineering such as buildings, automotive, hospitals equipment, railways, aircrafts, pipelines, overhead tanks, ships, submarines, underground tanks, boilers etc. Four classes of steel are Carbon Steel, Alloy Steel, Stainless Steel and Tool Steel [6]. The alloying elements in steel may include manganese, chromium, vanadium, copper, aluminum nickel and tungsten [7]. The major problem associated with the use of steel is corrosion. Against its negativity, several methods have been developed for corrosion protection and mitigation. One of the most fundamental methods is proper selection of the elements at steel production stage.

Other effective methods include Cathodic Protection [8]. Sacrificial Anode Method, Pipeline Pigging, Use of Corrosion Inhibitors, Use of Protective Coatings and others [9].

A protective coating is a material applied on the surface of a metal which creates a barrier between the metal surface and chemical environment in which the metals is exposed and hence protect the metal against corrosion. Such coatings may be polymeric materials, ceramic materials, cement and concrete, etc. Polymeric coatings include natural and synthetic rubber, urethane, polyvinyl chloride (PVC), acrylic epoxy silicone, phenolic resins and nitrocellulose [10]. Polyurethane has been discovered as an effective corrosion protective coating [11]. Based on practical experience, it is observed that various coatings in different corrosive media have varying degradation rates. It is also observed that the corrosion rates of the coated steel and the inhibition efficiency of the coatings vary with time. One other challenge associated with the use of coatings is how to estimate the durability of the coating in a giving corrosive environment. Several researchers have made attempt to estimate the durability of corrosion protective coatings in various aggressive environments. Weththimuni et al. [12] investigated the durability of nanocomposite coating with respect to well-known PDMS coating exposed two different ageing cycles: solar ageing (300W,1000h) and humid chamber ageing (RH > 80%, T = 22±3oC). The results obtained were in agreement with each other. In Vladimir et al. [13], a durability model was proposed in which coating thickness and strength of adhesion of the coating material were considered as main indicators of durability. According to Kreslova et al. [14], the durability of materials/coatings can be estimated using acceleration factor, in which the results obtained from accelerated test are related to the results obtained from long term exposure test in the real life environment. The acceleration factor in this case is the ratio of the accelerated test result to that obtained from long term test in the actual exposure environment from which the durability of the material or coating is deduced. However, the drop in coating efficiency due to degradation was not considered in any of the cited articles as durability factor.

On this note, this study is aimed at determining the durability of polyurethane coating on mild steel in acid, alkaline and neutral soil environments at ambient temperature. A model was proposed for calculating the durability of the coating in days or years. The result of this study may serve as a guide in selection of suitable coating on mild steel for underground works at ambient temperature. It may also be used to estimate how long a coating can serve effectively in a given soil medium. Using corrosion rate versus time graph, the corrosion behaviour of mild steel in various soil media may be studied through this research. In similar research by [15], it was shown that corrosion rate falls with exposure time.

2. Materials and Methods

2.1 Materials

The materials used in this study are:

i. Polyurethane; purchased from SAMEC Road, Ariaria Market Aba, Abia State, Nigeria.
ii. Mild Steel Coupons; produced with angle bar, purchased from Owerri Allied and Timber Market, Imo State, Nigeria.
iii. Acetone; purchased from SAMEC Road, Ariaria Market Aba, Abia State, Nigeria.
iv. Grades 60,120,220,400,800 and 1000 emery cloth; purchased from Owerri Allied and Timber Market, Imo State in Nigeria.
v. Soil used for preparation of the various test media was collected from a land portion at Umundula Orji, Owerri North Local Government Area (L.G.A.) of Imo State in Nigeria.

The equipment used includes:

i. (H20T) MettlerTolledo's Analytical balance: This was used for weighing the coupons.
ii. (HI-981030) Hana Soil pH Tester: This instrument was used for measuring the pH of the soil media.
iii. (Mitutoyo 500-196-30) Digital Caliper. The dimensions of coupons were measured using this equipment.
iv. PosiTector 200D1: The dry film thickness (DFT) of the coating was measured using this equipment.

2.2 Materials Preparation

a) Tagging of coupons and measurement of their initial masses: Each of the coupons was tagged for easy identification and proper recording of results. The coupons were tagged X_i, where i = 1, 2, 3, 4, 5, 6 and 7. The subscript, i denotes for the number of weeks the coupon was exposed in the test medium (exposure time in weeks). Thus, U_i denotes polyurethane coated coupon ; exposed for i number of weeks while X_i denotes uncoated coupon exposed for i number of weeks. The coupons were weighed using (H20T) MettlerTolledo's Analytical balance and their masses were recorded accordingly.
b) Preparation of coupons: The coupons were cut from a length of angle bar, ground and polished with grades 60,120,220,400,800 and 1000 emery paper accordingly. The coupons were polished to a final length of 50mm, width of 16mm and thickness of 4mm. A 4mm diameter hole was made on each coupon as shown in Figure 2a. They were washed with acetone and preserved in a desiccator. Uncoated coupon is shown as Figure 2b.
c) Application of Polyurethane: Polyurethane and thinner (curing agent) were mixed in a beaker at volume ratio of 5:1 respectively. Uncoated coupons were quickly dipped into the mixture in the beaker,

withdrawn and suspended in free air for 2hours curing and the dipping was then repeated. The second coat gave an average dry film thickness of 0.95mm was realized. A picture of polyurethane coated coupon is shown as Figure 2c.

d) Soil Preparation and experimentation set up: Three heaps of subsoil, each weighing 20kg was collected from a land portion at Umundula Orji, Owerri North Local Government Area (L.G.A) of Imo State in Nigeria. The pH of the soil was measured using (HI-981030) Hana Soil pH Tester and 6.8 was read and recorded. One heap of the soil was treated with dilute HNO_3 to a pH of 4.5; one other heap was treated with slaked lime to a pH of 13.5 and the other heap was left untreated (neutral). These three soil portions make up the acid, alkaline and neutral soils used as the test media in this study.

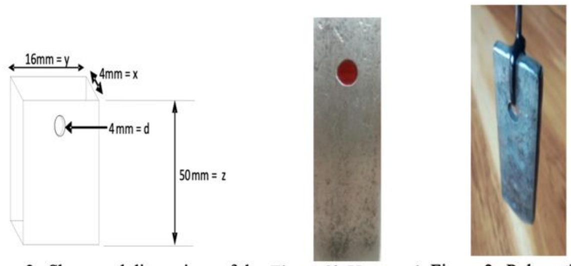

Figure 2a Shape and dimensions of the uncoated coupon Figure 2b Uncoated coupon Figure 2c Polyurethane coated coupon

Figure 2 Coupon design and coating

Each of the prepared soil media was poured into a rectangular plastic basin of dimension 30cm x 60cm x 90cm and properly leveled to uniform height. Seven coupons, each of polyurethane coated and the uncoated were carefully buried in each of the soil media to about half the soil depth, maintaining coupon spacing of about 15cm.The setup was kept under a shed to avoid rain water. On weekly bases, i.e. 7, 14, 21,28,35,42 and 49days, one coupon, each of the polyurethane coated and uncoated were withdrawn from each of the test media. The coating was removed and the coupons were washed with acetone to remove corrosion product on them and then sum dried for 2 hours. The dry coupons were reweighed and their new masses $m(x_i)$ were recorded accordingly.

2.3 Characterization

The corrosion rate, corrosion inhibition efficiency and durability of the coating of the coating were calculated as follows:

i. Corrosion Rate

$$CR(x_i) = \frac{365\Delta m(x_i)}{\rho A t_i} \quad (2)$$

where CR = corrosion rate (mmyr^{-1}), $\Delta m(x_i)$ = mass loss, ρ = density of the steel (g/mm^3),A = exposed surface area of coupon(mm^2) and t_i= exposure time (days).

ii. Average corrosion rate

$$\overline{CR} = \frac{CR(x_1)+CR(x_2)+CR(x_3)+CR(x_4)+CR(x_5)+CR(x_6)+CR(x_7)}{7} \quad (3)$$

iii. Corrosion Inhibition Efficiency

The expression for the corrosion inhibition efficiency is given in [16]:

$$\%E(x) = \frac{CR^o(x_i) - CR(x_i)}{CR^o(x_i)} \times 100\% \quad (4)$$

where $CR^o(x_i)$ = corrosion rate of uncoated specimen, $CR(x_i)$ = corrosion rate of coated specimen, $\%E(x_i)$ = corrosion inhibition efficiency.

iv. Average corrosion inhibition efficiency

$$\overline{E} = \frac{E(U_1)+E(U_2)+E(U_3)+E(U_4)+E(U_6)+E(U_7)}{7} \quad (5)$$

v. Durability

Durability of the coating was calculated using a proposed model given by:

$$D = e^{\alpha} \quad (6)$$

Where, D = Durability of the coating in the medium, n = number of sample points.

$$\alpha = \left(\sum Int + \sigma \sum E\right)/ n \quad (7)$$

$$\sigma = -\left(\frac{n\sum EInt - \sum E \sum Int}{n\sum E^2 - \left(\sum E^2\right)}\right) \quad (8)$$

2.4 Proposed Durability Model

Under ideal conditions, everything exposed to nature deteriorates including corrosion protective coatings. This is why virtually everything made by man has expiry date. On this note, corrosion of metals will always occur irrespective of the mitigation method adopted. Both steel and the corrosion protective coatings are attacked by the exposure medium, therefore, as the steel corrodes; the coatings degrade alongside, hence the corrosion inhibition efficiency of the coatings fall over time. Mass loss or decrease in concentration occur in degradation process [17, 18]. In the cited articles it was shown that degradation rate is inversely proportional to time; thus, the rate at which corrosion inhibition efficiency falls is assumed to be inversely proportional to exposure time. Based on this assumption, the durability model proposed in this work was derived. Thus, the plot of corrosion inhibition efficiency against time may be represented graphically as shown in Figures 3a and 3b.

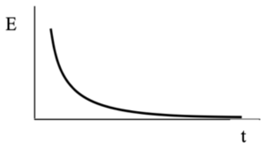

Figure 3a: Schematic diagram of the graph of Corrosion inhibition efficiency of coatings (E) against exposure time (t)

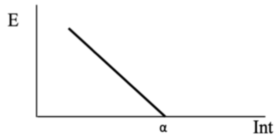

Figure 3b: Schematic diagram of the graph of Corrosion inhibition efficiency of coatings (E) against natural log of exposure time (Int) (linearized)

Figure 3 Schematic of corrosion inhibition efficiency graph against exposure time.

Looking at Figures 3a and 3b, the durability model was derived as follows:

$$-\frac{dE}{dt}=\frac{a}{t} \tag{9}$$

$$dE=-a\frac{dt}{t} \tag{10}$$

$$\int dE=-a\int\frac{dt}{t} \tag{11}$$

$$\therefore E=-aInt+\lambda \tag{12}$$

where $-dE/dt$ is the rate of decrease in coating efficiency, *t* = exposure time (in days or years), *E* = corrosion inhibition efficiency of coating expressed as fraction, a = constant of proportionality, λ is a constant of integration.

Rearranging Equation (12) gives:

$$Int=-\frac{E}{a}+\frac{\lambda}{a} \tag{13}$$

Taking 1/a to be a constant σ and λ/a to be constant α gives

$$Int=-\sigma E+\alpha \tag{14}$$

The graph of Int against E is deemed to be a straight line whose slope is -σ.

From Equation (14), t is obtained as:

$$t=e^{\alpha-\sigma E} \tag{15}$$

When $E=0, t=e^{\alpha}$ = Durability, D.

$$\therefore D=e^{\alpha} \tag{16}$$

To determine the values of α and σ, least square equation is stated as

$$\alpha n-\sigma\sum E=\sum Int \tag{17}$$

$$\alpha\sum E-\sigma\sum E^2=\sum EInt \tag{18}$$

α and σ were obtained by solving Equations (17) and (18) simultaneously, which gives Equations (19) and (20).

$$\sigma=-\left(\frac{n\sum EInt-\sum E\sum Int}{n\sum E^2-\left(\sum E\right)^2}\right) \tag{19}$$

$$\alpha=\left(\sum EInt+\sigma\sum E\right)/n \tag{20}$$

where α and σ are the durability parameters of the medium, E = corrosion inhibition efficiency of the coating (expressed as fraction of unity), t = exposure time (duration) of coupons in the soil medium, Int = logarithm of t in natural base, $\sum$ symbolizes summation and n = number of sample points. In this paper, the experimentation was monitored weekly for a duration of seven weeks, therefore, n = 7.

3. Results and Discussion

The results of mass losses, corrosion rates, corrosion inhibition efficiency and durability of the coating in all the test media are shown in Tables 1 to 4 and presented graphically in Figures 4 and 5.

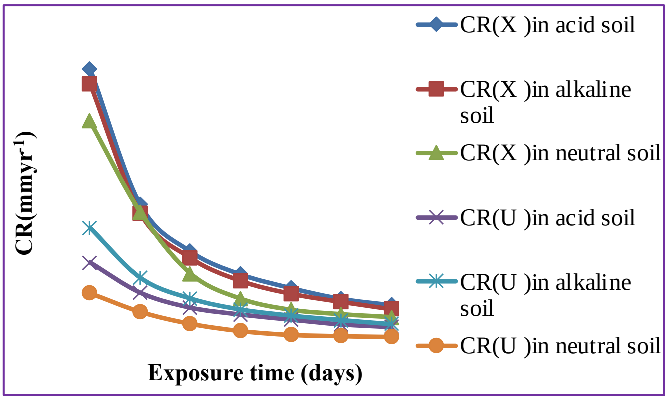

Figure 4 Corrosion rate of coupons (uncoated and coated) in various soil media.

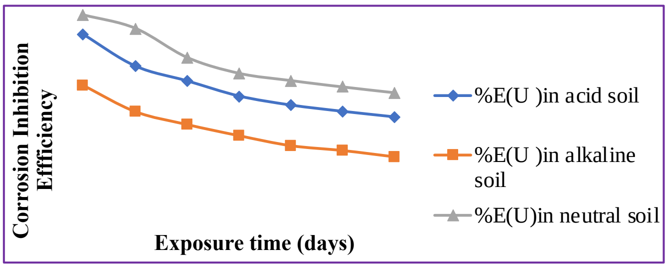

Figure 5 Corrosion inhibition efficiency of polyurethane coated coupons in various soil media.

Table 1 Corrosion rate and inhibition efficiency of coupons in the various soil media

Coupon tag(x_i)	t(days)	Corrosion rates CR($mmyr^{-1}$)			Corrosion Inhibition Efficiency %E(x_i)		
		Acid Soil	Alkaline Soil	Neutral Soil	Acid Soil	Alkaline Soil	Neutral Soil
X_1	7	0.3544	0.3359	0.2897	–	–	–
X_2	14	0.1864	0.1756	0.1772	–	–	–
X_3	21	0.1284	0.1202	0.1007	–	–	–
X_4	28	0.1001	0.0917	0.0693	–	–	–
X_5	35	0.0832	0.0758	0.0555	–	–	–
X_6	42	0.0698	0.0657	0.0500	–	–	–
X_7	49	0.0621	0.0568	0.0464	–	–	–
U_1	7	0.1140	0.1572	0.0770	67.83	53.21	73.40
U_2	14	0.0770	0.0955	0.0539	58.68	45.61	69.57
U_3	21	0.0585	0.0698	0.0390	54.40	41.88	61.22
U_4	28	0.0501	0.0562	0.0300	50.00	38.66	56.67
U_5	35	0.0438	0.0487	0.0252	47.41	35.77	54.57
U_6	42	0.0380	0.0431	0.0236	45.59	34.38	52.75
U_7	49	0.0348	0.0383	0.0227	43.97	32.56	51.09

Table 2 Durability parameters of polyurethane coating in various soil media

t (days)	Polyurethane in acid soil				Polyurethane in alkaline soil				Polyurethane in neutral soil			
	E	E^2	Int	EInt	E	E^2	Int	EInt	E	E^2	Int	EInt
7	0.6783	0.4600	1.9459	1.3198	0.5321	0.2831	1.9459	1.0354	0.7340	0.5388	1.9459	1.4284
14	0.5868	0.3443	2.6391	1.5485	0.4561	0.2081	2.6391	1.2038	0.6957	0.4839	2.6391	1.8359
21	0.5440	0.2959	3.0445	1.6562	0.4188	0.1754	3.0445	1.2751	0.6122	0.3748	3.0445	1.8640
28	0.5000	0.2500	3.3322	1.6661	0.3866	0.1494	3.3322	1.2881	0.5667	0.3211	3.3322	1.8882
35	0.4741	0.2247	3.5553	1.6855	0.3577	0.1280	3.5553	1.2718	0.5457	0.2978	3.5553	1.9403
42	0.4559	0.2078	3.7377	1.7039	0.3438	0.1182	3.7377	1.2848	0.5275	0.2782	3.7377	1.9715
49	0.4397	0.1934	3.8918	1.7113	0.3256	0.1060	3.8918	1.2671	0.5109	0.2610	3.8918	1.9884
Sum	3.6787	1.9762	22.1465	11.2914	2.8207	1.1682	22.1465	8.6261	4.1927	2.5558	22.1465	12.9167
D(yrs)	α = 8.08791 σ = 7.41423 D = 4.54662				α = 9.43603 σ = 6.96606 D = 2.90434				α = 7.82386 σ = 7.85000 D = 7.02978			

Table 3 Durability equations for polyurethane coating in various soil media

Durability Equations		
Acid Soil	Alkaline Soil	Neutral Soil
$t = 1659e^{-8.088E}$	$t = 1060e^{-9.436E}$	$t = 2566e^{-7.824E}$

Table 4 Summarized experimentation results

Specimen (coupon)	Acid Soil			Alkaline Soil			Neutral Soil		
	$\overline{CR}$	$\overline{E}$	D(years)	$\overline{CR}$	$\overline{E}$	D(years)	$\overline{CR}$	$\overline{E}$	D(years)
Uncoated	0.1406	-	-	0.1317	-	-	0.1127	-	-
Polyurethane coated	0.0595	52.6	4.5	0.0727	40.3	2.9	0.0388	59.9	7.0

4. Discussions

From Figure 4, it is seen that the corrosion rate of polyurethane coated coupons is relatively lower than those of the uncoated coupons. This is an indication that polyurethane is a good corrosion protective coating for mild steel in acid, alkaline and neutral soil. It is also observed that in each case the corrosion rate of the coupons fall with time. This might be caused by the formation of passive films (iron oxide) on the metal as corrosion product, which lowers the rate of corrosion. From Figure 4, it is also shown that the corrosion rate of polyurethane coated coupons are lowest in neutral soil, followed by acid soil but high in alkaline soil, indicating that polyurethane coating is more effective in acid soil than alkaline soil. The plots of corrosion inhibition efficiency of the coating presented as Figure 5 shows that the corrosion inhibition efficiency of polyurethane is quit high in neutral soil, followed by acid soil but very low in alkaline soil. This is an indication that polyurethane coating likely degrades faster in alkaline soil than in acid soil. The corrosion inhibition efficiency of polyurethane coating in the various soil media was calculated using the proposed model and the results obtained were compared with the corresponding values obtained, using equation 4. With the model, the efficiency of U_4 was 50.4% against 50.0% obtained with equation 4. Also, the efficiency of U_5 was 36.1% against 35.5% obtained with equation 4. These results, show in Table 4 indicates that the model has integrity. From the summarized experimental result shown in Table 4, polyurethane coating has a long life in neutral soil, fairly durable in acid soil but has a short life in alkaline soil. The exposure media used in this study were not natural; hence the result obtained in this research may not be reliable in practical sense. Thus, a field test is recommended within the actual exposure time in order to determine the acceleration factor relating the results of field test with those of laboratory test. Correlation Coefficient may also be used to compare the field test result with those of accelerated test.

In the event of occurrence of such unnatural soil presentations, for instance in situations of corrosion-induced ruptures of acid or alkaline storage tanks, polyurethane-coating could hold out for 4.5 years and 2.9 years for the acid and alkaline soils respectively. That portends that fast remedial interventions within months of spillage may salvage the carbon steel pipes without their being compromised. Such scenarios could also be obtained where acid-producing microorganisms may be actively metabolizing and the above inferences may also hold. A typical example of such case is stated in [19].

6. Conclusion

From the experimental results obtained in this study, it may be concluded that polyurethane is a good corrosion protective coating for mild steel in various soil media. It may also be concluded that polyurethane degrades faster in alkaline soil than acid soil. The integrity of the durability model was verified using different exposure times and the results obtained show that the model is reliable for all the test media. Comparatively, corrosion rate of coupons are low in neutral soil; thus, it may be concluded that deviation of soil pH from neutrality accelerates the rate of corrosion in the soil. It may be concluded that corrosion rate of steel decreases over time in acid, alkaline and neutral soil. Uncoated specimen witnessed almost the same corrode rate in the various soil media. Therefore, polyurethane coating should be utilized as corrosion protective coating in both acidic and alkaline soils, though its performance is better in acidic than alkaline soil. Within the scope of this study, it may be concluded that the durability of polyurethane coating on mild steel is 4.5years, 2.9years and 7.0years for acid, alkaline and neutral soil respectively with corresponding corrosion rates of $0.0595 mmyr^{-1}$, $0.0727 mmyr^{-1}$ and $0.0388 mmyr^{-1}$.

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