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Corrosion Inhibition Efficiencies of Polymeric Materials on Alloy Steel in Dilute Hydrochloric Acid and Sodium Hydroxide Solutions at Ambient Temperature

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Abstract. A corrosion control test was conducted on alloy steel, using polymeric coatings (polyurethane, bitumen (medium ailing), and high-density polyethylene) in dilute HCl solutions of pH values 4, 7, and 12, respectively for acid, neutral and alkaline solutions at ambient temperature. In the study, Eighty-four coupons of alloy steel were used. The coupons were mechanized, ground, polished, etched with natal, and weighed using a digital weighing balance (Beva 206B). The mass of each coupon was recorded according to the tag number on them. Twenty-one of the coupons were coated with polyurethane, 21 coated with medium curing bitumen (MC), and 21 coated with high-density polyethylene, while 21 were left uncoated. Seven polyurethane-coated samples, bitumen coating, and uncoated coupons were suspended in dilute HCl solutions of pH values 4, 7, and 12. Every week, one sample is taken from each of the solutions, the coatings and the corrosion products were removed, and the coupons were etched with natal. Then the coupons were reweighed, and their masses were recorded in accordance with their tag number. The weight loss per unit area of the coupons, corrosion rate, and percentage corrosion inhibition efficiencies of the coatings was calculated over seven weeks. The results obtained were tabulated and represented graphically. From the results obtained, it is seen that the corrosion inhibition efficiency of polyurethane coatings is higher compared with bitumen and polyethylene. It is also seen from the graphs that the corrosion rate of the coupons is higher in acid, a little bit lower in alkaline, and much lower in neutral solution. It is also observed that the corrosion rates fall with time as the inhibition efficiency also falls with time.

Keywords: alloy steel, ambient temperature, inhibition efficiency, polymeric coatings.

1 Introduction

Due to its improved mechanical properties, including yield strength, hardness, toughness, etc., alloy steel is widely used in engineering works. Alloy steel has a yield strength of up to 500 MPa, a density of about 7800 kg/m³, the melting point of about 1400 °C, and good creep resistance. It is used in structural fabrication, pipelines, concrete reinforcement, etc. However, alloy steel has low corrosion resistance. As a result of alloy steel's corrosive nature, its mechanical properties fall over time when exposed to an aggressive environment. This can lead to the poor performance of the steel in service, short durability, or catastrophic failure. To avert this problem, there is a need to mitigate corrosion.

Corrosion is the deterioration of materials in an aggressive environment. It occurs when there is a difference in electrode potential inside the material or between the material and chemical species within the metal exposure environment. It is a redox reaction process in which oxidation occurs at the anode and reduction occurs at the cathode. The cation usually produced at the anode often leads to loss of weight of the anode. On the other hand, the cathode's importance increases if the cation (positively charged ions) migrates to the cathode. The electrons released during the anode migrate to the cathode and reduce the cations at the cathodes, thereby making the cathode more stable against corrosion.

Corrosion is the product of the interaction between metallic materials and the environment in which they are exposed depending on the environment and the number of

prevailing conditions [1]. Corrosion is also defined as the degradation of metals due to a redox reaction between the metal to different substances in their environment, which produces an undesirable compound [2]. Corrosion occurs if the half-cell reaction that releases electrons is connected with the half-cell reactions that receive electrons. Corrosion occurs in various forms: uniform attack, galvanic corrosion, crevice corrosion, pitting corrosion, inter-granular corrosion, selective leaching, erosion, and stress-corrosion cracking [3].

Several researchers have made a reasonable effort, and significant results have been obtained on the appropriate measures for mitigating alloy steel corrosion in various corrosive media. Corrosion control of alloy steel can start from the liquid state of the steel. Corrosion-resistant elements are used to alloy the steel, such as chromium, which reduces the diffusion rate of carbon from the matrix to the steel's grain boundaries. This minimizes the chances of intergranular corrosion of the steel. This is achieved by the chromium tying itself with the carbon in the matrix, forming chromium carbide (Cr_3C_2) against carbon migrating to the grain boundary to form cementite or iron carbide (Fe_3C), which is a hard phase and corrosion site.

Inorganic coatings and organic inhibitors have been developed to fight the corrosion of metals. Material selection in design and electrical methods are also effective methods widely adopted in fighting the corrosion of metals. Inorganic inhibitors have an active group. They are amino which decreases the corrosion rate of metals [4].

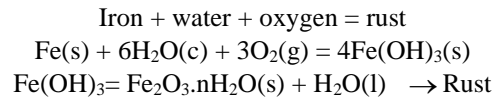
They include sodium Nitrite, Chromate, Phosphate, Zinc, etc. Sodium nitrite is not always recommended because it is required at a high concentration compared to others, usually (300–500 mg/L), so it is not economical. Chromate and zinc are toxic, and phosphate is considered a pollutant [5]. Other than the inorganic inhibitors, organic inhibitors are in use. They are classified into synthetic and organic from nature's extractions [6]. Compounds used as organic inhibitors usually consist of nitrogen, sulphur, or oxygen atoms having a pair of free electrons [7].

Metals are also protected against corrosion using polymeric coatings, ceramic coatings, and concrete coatings. Polymeric coating in use includes epoxy resin, high density and low-density polyethylene, polyurethane, bituminous coatings (slow curing (SC), medium curing (MC) and Rapid curing (RC), etc. Comparatively, polyurethane has several good qualities against corrosion even at elevated temperatures (up to 40 °C). Such qualities include good hardness, good flexibility, strong adhesion to a metal surface, good resistance against steam penetration, chemical resistance, etc. [8]. This investigation aims to determine the most effective polymeric coating against alloy steel in acid, alkaline, and neutral solutions, looking at the corrosion inhibition efficiencies of polyurethane, high-density polyethylene, and medium curing bitumen as the coatings.

2 Research Methodology

2.1 Rusting

Rusting is the most common form of corrosion. The oxidation of iron from iron (II) ion to iron (III) ion in water and oxygen gives a reddish-brown deposit called rust. Generally, rusting is given by the equations.



2.2 Corrosion rate

Generally, the corrosion rate is given by:

$$CR = \frac{\Delta W}{D \cdot A \cdot T} \quad (1)$$

where CR – corrosion rate, ΔW – weight loss, D – density, A – the surface area of metal exposed to corrosion environment, T – exposure time.

2.3 Corrosion inhibition efficiency

Corrosion inhibition efficiency is a parameter that shows the effectiveness and durability of corrosion control measures over a given time. It is generally expressed as follows:

$$\%IE = \frac{CR^o - CR}{CR^o} \times 100 \quad (2)$$

where $\%IE$ – percentage corrosion inhibition efficiency; CR^o – corrosion rate without inhibitor in the medium.

Al Aisha and Moubaraki [9] give the percentage corrosion inhibition efficiency:

$$\%IE_{WL} = \left(1 - \frac{e_{WL}}{e^o_{WL}} \right) \times 100 \quad (3)$$

where $\%IE_{WL}$ – percentage inhibition efficiency in terms of weight loss; e_{WL} – corrosion rate with inhibitor; e^o_{WL} – corrosion rate without inhibitor.

2.4 Experiment

Three coupons, each of dimension 4 mm x 40 mm x 45 mm were cut off from a bar of mild steel or alloy steel. The coupons were analyzed in a laboratory using a spectrometer (spectromax). The average composition of the coupons s was determined and recorded as shown in Table 1:

$$s = \frac{s1 + s2 + s3}{3} \quad (4)$$

Table 1 – Chemical composition of the mild steel used for coupons

Coupon	Chemical composition, %						
	C	Mn	Mo	V	Cr	Cu	Ni
s1	0.2250	0.6120	0.0022	0.0033	0.0048	0.0056	0.0037
s2	0.2249	0.6076	0.0023	0.0036	0.0053	0.0059	0.0035
s3	0.2251	0.6104	0.0021	0.0036	0.0052	0.0059	0.0036
s	0.2250	0.6100	0.0022	0.0035	0.0051	0.0058	0.0036

Eighty-four pieces of coupons of the stated dimension were cut from the bar.

Each of the coupons was ground and polished with grade 60 and 120 emery cloth, respectively. The coupons were then etched with nital. Each of the coupons is tagged and weighed, and their masses are record accordingly. Twenty-one of the coupons were then coated with polyurethane and tagged with U, 21 coated with high-density polyethylene tagged with P, 21 coated with medium curing bitumen (MC) tagged with B, and 21 left uncoated tagged with X. Seven coupons, each of the polyurethane-coated, polyethylene coated, bitumen coated and uncoated were suspended in dilute solutions of HCl of pH values 5, 7 and 12 (for acid, neutral and alkaline) respectively. Every week, one coupon is taken from each of the solutions and reweighed without coatings. The weight loss per unit area, corrosion rate, and corrosion inhibition efficiency was also calculated and recorded. The results obtained were represented graphically.

3 Results

In this section, the experiments' results are presented in Fig. 1–6 and Tables 2–7.

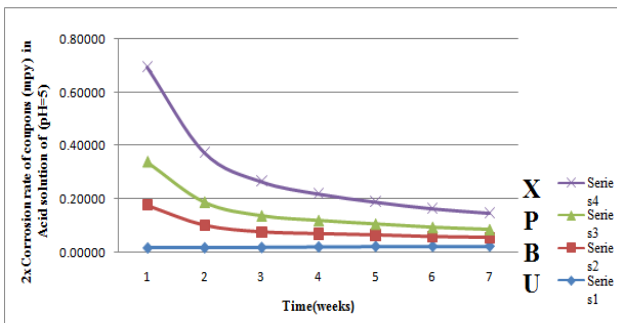


Figure 1 – Corrosion rate of coupons in acid solution

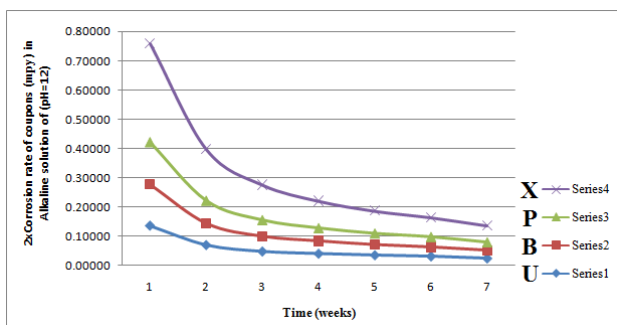


Figure 2 – Corrosion rate of coupons in alkaline solution

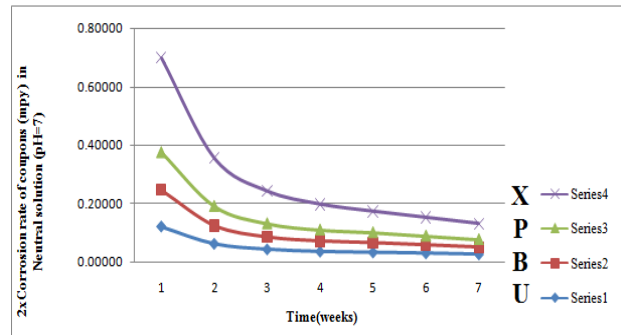


Figure 3 – Corrosion rate of coupons in neutral solution

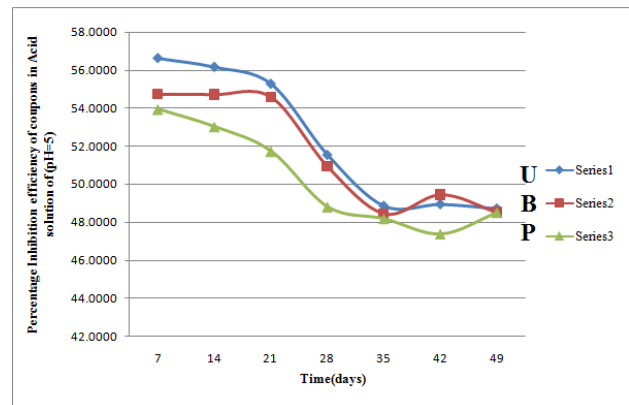


Figure 4 – Percentage corrosion inhibition efficiency of coatings in acid solution

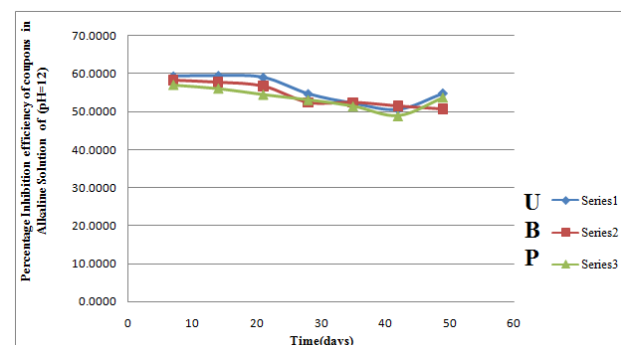


Figure 5 – Percentage corrosion inhibition efficiency of coatings in alkaline solution

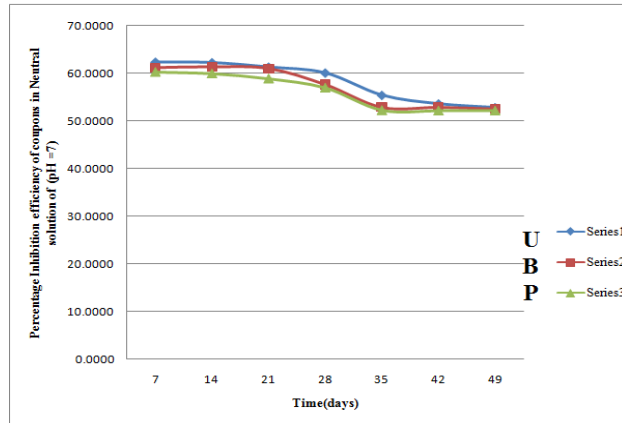


Figure 6 – Percentage corrosion inhibition efficiency of coatings

Table 2 – Alloy steel coupons in a dilute acid solution of HCl (pH = 5)

TAG	U1	U2	U3	U4	U5	U6	U7	B1	B2	B3	B4	B5	B6	B7
Time, days	7	14	21	28	35	42	49	7	14	21	28	35	42	49
W _o , g	58.200	57.980	58.110	58.020	58.060	57.980	58.140	58.080	58.150	58.010	57.910	58.400	58.060	58.090
W, g	57.635	57.380	57.479	57.309	57.286	57.191	57.329	57.490	57.530	57.369	57.190	57.620	57.279	57.276
ΔW, g	0.565	0.600	0.631	0.711	0.774	0.789	0.811	0.590	0.620	0.641	0.720	0.780	0.781	0.814
ΔW/A, g/cm ²	0.016	0.017	0.018	0.020	0.022	0.022	0.023	0.017	0.017	0.018	0.020	0.022	0.022	0.023
CR	0.154	0.082	0.057	0.049	0.042	0.036	0.032	0.161	0.085	0.058	0.049	0.043	0.036	0.032
IE, %	56.639	56.172	55.280	51.534	48.843	48.932	48.703	54.720	54.711	54.571	50.920	48.447	49.450	48.514

Table 3 – Alloy steel coupons in a dilute acid solution of HCl (pH = 5)

TAG	P1	P2	P3	P4	P5	P6	P7	X1	X2	X3	X4	X5	X6	X7
Time, days	7	14	21	28	35	42	49	7	14	21	28	35	42	49
W _o , g	58.100	58.110	58.000	57.980	58.200	58.000	58.100	58.120	59.000	57.780	58.020	58.100	58.030	58.040
W, g	57.500	57.467	57.319	57.229	57.416	57.187	57.286	56.817	57.631	56.369	56.553	56.587	56.485	56.459
ΔW, g	0.600	0.643	0.681	0.751	0.784	0.813	0.814	1.303	1.369	1.411	1.467	1.513	1.545	1.581
ΔW/A, g/cm ²	0.017	0.018	0.019	0.021	0.022	0.023	0.023	0.037	0.039	0.040	0.041	0.043	0.043	0.044
CR	0.164	0.088	0.062	0.051	0.043	0.037	0.032	0.356	0.187	0.128	0.100	0.083	0.070	0.062
IE, %	53.952	53.031	51.736	48.807	48.182	47.379	48.514	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 4 – Alloy steel coupons in an alkaline solution of pH of 12

TAG	U1	U2	U3	U4	U5	U6	U7	B1	B2	B3	B4	B5	B6	B7
Time, days	7	14	21	28	35	42	49	7	14	21	28	35	42	49
W _o , g	57.980	58.200	58.000	58.100	58.200	57.980	58.110	58.110	58.000	57.980	58.200	58.000	58.100	57.980
W, g	57.479	57.680	57.460	57.490	57.532	57.265	57.455	57.595	57.457	57.409	57.559	57.335	57.397	57.264
ΔW, g	0.501	0.520	0.540	0.610	0.668	0.715	0.655	0.515	0.543	0.571	0.641	0.665	0.703	0.716
ΔW/A, g/cm ²	0.014	0.015	0.015	0.017	0.019	0.020	0.018	0.014	0.015	0.016	0.018	0.019	0.020	0.020
CR	0.137	0.071	0.049	0.042	0.036	0.033	0.026	0.141	0.074	0.052	0.044	0.036	0.032	0.028
IE, %	59.400	59.533	59.060	54.748	52.286	50.690	54.921	58.266	57.743	56.710	52.448	52.500	51.517	50.723

Table 5 – Alloy steel coupons in an alkaline solution of pH of 12

TAG	P1	P2	P3	P4	P5	P6	P7	X1	X2	X3	X4	X5	X6	X7
Time, days	7	14	21	28	35	42	49	7	14	21	28	35	42	49
W _o , g	58.020	58.060	57.980	58.140	58.110	58.000	57.980	58.200	57.980	58.200	58.000	58.100	58.200	58.100
W, g	57.490	57.496	57.380	57.508	57.430	57.259	57.308	56.966	56.695	56.881	56.652	56.700	56.750	56.647
ΔW, g	0.530	0.564	0.600	0.632	0.680	0.741	0.672	1.234	1.285	1.319	1.348	1.400	1.450	1.453
ΔW/A, g/cm ²	0.015	0.016	0.017	0.018	0.019	0.021	0.019	0.035	0.036	0.037	0.038	0.039	0.041	0.041
CR	0.145	0.077	0.055	0.043	0.037	0.034	0.026	0.337	0.175	0.120	0.092	0.076	0.066	0.057
IE, %	57.050	56.109	54.511	53.116	51.429	48.897	53.751	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 6 – Alloy steel coupons in a neutral solution of pH of 7

TAG	U1	U2	U3	U4	U5	U6	U7	B1	B2	B3	B4	B5	B6	B7
Time, days	7	14	21	28	35	42	49	7	14	21	28	35	42	49
W _o , g	58.000	58.100	58.200	57.980	58.110	58.200	58.000	58.200	57.980	58.110	58.020	58.060	57.980	58.240
W, g	57.555	57.647	57.730	57.468	57.520	57.558	57.347	57.740	57.515	57.635	57.476	57.437	57.329	57.584
ΔW, g	0.445	0.453	0.470	0.512	0.590	0.642	0.653	0.460	0.465	0.475	0.544	0.623	0.651	0.656
ΔW/A, g/cm ²	0.013	0.013	0.013	0.014	0.017	0.018	0.018	0.013	0.013	0.013	0.015	0.018	0.018	0.018
CR	0.121	0.062	0.043	0.035	0.032	0.029	0.025	0.126	0.063	0.043	0.037	0.034	0.030	0.026
IE, %	62.352	62.250	61.317	60.062	55.337	53.512	52.715	61.083	61.250	60.905	57.566	52.839	52.860	52.498

Table 7 – Alloy steel coupons in a neutral solution of pH of 7

TAG	P1	P2	P3	P4	P5	P6	P7	X1	X2	X3	X4	X5	X6	X7
Time, days	7	14	21	28	35	42	49	7	14	21	28	35	42	49
W _o , g	57.980	58.200	58.000	58.100	58.120	58.100	58.200	57.980	58.020	58.060	57.980	58.140	58.110	58.440
W, g	57.510	57.719	57.500	57.548	57.489	57.439	57.539	56.798	56.820	56.845	56.698	56.819	56.729	57.059
ΔW, g	0.470	0.481	0.500	0.552	0.631	0.661	0.661	1.182	1.200	1.215	1.282	1.321	1.381	1.381
ΔW/A, g/cm ²	0.013	0.014	0.014	0.016	0.018	0.019	0.019	0.033	0.034	0.034	0.036	0.037	0.039	0.039
CR	7	14	21	28	35	42	49	7	14	21	28	35	42	49
IE, %	57.980	58.200	58.000	58.100	58.120	58.100	58.200	57.980	58.020	58.060	57.980	58.140	58.110	58.440

4 Discussion

Figures 1, 2, and 3 show that the corrosion rate of coupons in the acid environment is higher than those in an alkaline medium. It is also seen that the corrosion rate of the coupons in a neutral environment is appreciably low. From the graphical presentations, it is seen that the corrosion rate of polyurethane-coated coupons has a relatively low corrosion rate in all the test media and at all exposure time. It is also significant that the corrosion rate of the coupons falls over time and more rapidly within the first and the second week of exposure. Fig. 4 shows that the inhibition efficiency of polyurethane-coated coupons is always higher and in all mediums. However, it is observed that there is a fall in inhibition efficiency, which may be attributed to the degradation of the coatings over time in the test media. The decrease in corrosion rate may be due to the corrosion product's presence, which tends to form a passive film on the surface of the metal and hence mitigate corrosion. The fall in the coated coupons'

corrosion rate over time indicates the degradation of the coatings in the exposure media. This data may be used to predict the useful life or durability of the coatings in each of the media. In Fig. 4, there is a sudden increase in inhibition efficiency at the end of the fifth week, decreasing at the sixth week. This may be related to the fall in acid concentration over exposure time. From Table 2, it is seen that the weight of the coupons increases with time for both the coated and uncoated coupons in the acid environment, which is applicable in all the exposure media used for this study.

The results obtained from this study also show polyurethane is more efficient than medium curing bitumen and polyethylene in mitigation of corrosion of alloy steel in acid, alkaline and neutral environment. It is also seen from figures 4, 5, and 6 that bitumen is comparatively better than polyethylene in fighting corrosion.

This study's overall result may be used as a guide in selecting the most suitable protective coating against

corrosion of alloy steel in acid, alkaline, and neutral media. However, there may be variations in the results if the experiment is performed at various temperatures, applicable in real-life situations. On this basis, it is recommended to carry out a similar study in which the experiment is conducted at different temperatures. In this study, polyurethane coating has an average thickness of 100 microns; bitumen coating has an average thickness of 0.3 mm, and polyethylene coatings have an average thickness of 3 mm.

Naturally, an increase in coating thickness will impose more difficulty in the penetration of corrosive substances. Hence, the variation of coating thickness may also vary the results obtained in this study.

5 Conclusions

Looking at Figures 1–6, it can be said that polyurethane coating is more efficient than bitumen coating in the entire test environment. Comparatively, polyethylene has the least corrosion inhibition efficiency. However, polyethylene may be recommended in the absence of polyurethane for corrosion protection of alloy steel in acid, alkaline, and neutral environments at ambient temperature. It is also concluded that alloy steel corrosion is more severe in the acid environment than in alkaline medium and least in a neutral environment at ambient temperature. Another conclusion drawn from this work results is that the weight loss of the coupons increases with time. From Figure 6, it is concluded that the corrosion inhibition efficiencies of bitumen and polyethylene are almost the same after 28 days of exposure.

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