Singaporean Journal of Scientific Research(SJSR)
An International Journal (AIJ)
Vol.17.No.1 2025,Pp.28-40
ISSN: 1205-2421
available at :www.sjsronline.com
Paper Received : 04-12-2024 Paper Accepted: 06-01-2025
Paper Reviewed by: 1.Prof. Cheng Yu 2. Dr.Yarab Baig
Editor : Dr. Chen Du Fensidal

INFLUENCE OF NANO ADDITIVES ON PROTECTIVE COATINGS FOR OIL PIPE LINES OF OMAN

Muhammad Mumtaz Mirza
Senior Lecturer, Dept. of Mechanical and Industrial Engineering, Caledonian College of Engineering, Seeb, CPO 111, Sultanate of Oman

Asst.Prof. Elansezhian Rasu
Senior Lecturer, Dept. of Mechanical and Industrial Engineering, Caledonian College of Engineering, Seeb, CPO 111, Sultanate of Oman

Dr Anjali Desilva
School of Engineering & Built Environment
Glasgow Caledonian University, Glasgow, Scotland, UKAbstract

Abstract: This paper investigates experimentally the influence of different types of coatings with nano-additives on the corrosion behavior of steel pipe lines used in petroleum industry of Oman. The investigation was carried out with several types of coated samples to examine the rate of corrosion in pipe lines made of low alloy steel. Different coatings such as organic paint, metallic paint, Aluminum, Zinc and electroless coatings were examined with nano additives to study the corrosion rate. After coating application surface roughness was checked and coating thickness was maintained. To evaluate corrosion rate and life time of each coating, atmospheric exposure test, potentiodynamic test, dry and wet test were conducted. Characterization of the coatings were also performed using SEM-scanning electron microscope along with the hardness test to evaluate the surface morphology, and hardness . Based on coating performance evaluation, nano Al_2O_3 additive with Aluminum paint contributes the best result as compared to the other type of coatings.

1. Introduction

The Corrosion of pipelines is one of the major problems faced by engineers and technicians in the oil field. The annual cost of corrosion worldwide is over three per cent of the world's GDP and is around $2.2 trillion as per the National Association of Corrosion Engineers. Moreover, accidents caused by corroded structures can lead to huge safety concerns, loss of life, and resources [1].

Corrosion is the gradual destruction of materials (usually metals) by chemical reaction with its environment. Many structural alloys corrode merely from exposure to moisture in air, but the process can be strongly affected by exposure to certain substances. Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area more or less uniformly corroding the surface. Because corrosion is a diffusion-controlled process, it occurs on exposed surfaces. As a result, methods to reduce the activity of the exposed surface, such as passivation and chromate conversion, can increase a material's corrosion resistance. However, some corrosion mechanisms are less visible and less predictable. [2]

EN - Electroless nickel plating is an auto-catalytic reaction used to deposit a coating of nickel on a substrate. Unlike electroplating, it is not necessary to pass an electric current through the solution to form a deposit. This plating technique is to prevent corrosion and wear. EN techniques can also be used to manufacture composite coatings by suspending powder in the bath. EN plating has several advantages versus electroplating. Free from flux-density and power supply issues, it provides an even deposit regardless of work piece geometrymand with the proper pre-plate catalyst can deposit on non-conductive surfaces [3].

The EN plating of metallic nickel from aqueous solution in the presence of hypophosphite was first noted as a chemical accident by Wurtz in 1844[4]. In 1911, Roux reported that metal was inevitably precipitated in the powder form; however these works were not in practical applications [5]. In its early stage, progress in the field remained slow until World War II. In 1946, Brenner and Riddell developed a process for plating the inner walls of tubes with nickel-tungsten alloy, derived from the citrate based bath using an insoluble anode, which brought out the unusual reducing properties of hypophosphite [6]. Initially, the co-deposition of particles was carried out for electrodepositing Ni-Cr by Odekerken, during the year of 1966 [7]. In that study, in an intermediate layer, finely powdered particles like aluminum oxide, polyvinyl chloride (PVC) resin were distributed within a metallic matrix. A layer in the coating is composite but other parts of the coating are not. The first commercial application of their work used the electroless Ni-SiC coatings on the wankel internal combustion engine and another commercial composite incorporating polytetrafluoroethylene (Ni-P-PTFE) was co-deposited, during the year of 1981. However, the co-deposition of diamond and PTFE particles was more difficult, than the composites incorporating Al2O3 or SiC. The feasibility to incorporate the fine second phase particles, in submicron to nano size, within a metal/alloy matrix has initiated a new generation of composite coatings [8].

The new technique of protection coating is presented with sufficient results in Electroless Nickel EN-P deposition with Al2O3 as nano additive. In this method, coating is done uniformly with equal thickness to the entire surface. The nickel compound has the advantage to resist against heat which becomes hard while the temperature increases. The addition of nano additives particles to the Electroless nickel gives the advantage like small amount of mass added providing protection to large area.

Materials and Methods

Collection of samples

The low alloy steel samples are considered in this study taken from a local oil and gas industry of Oman. Total numbers of samples were nine that were coated as shown in Table 1:

Coating Type	Qty / size of sample
Aluminum paint with nano ZnO	1(50 x50 x7 mm^3)
Zinc Paint with nano ZnO	1(50 x50 x7 mm^3)
Organic Paint with nano ZnO	1(50 x50 x7 mm^3)
Organic Paint with nano CuO	1(50 x50 x7 mm^3)
Aluminum paint with nano CuO	1(50 x50 x7 mm^3)
Zinc Paint with nano CuO	1(50 x50 x7 mm^3)
Organic Paint with nano Al_2O_3	1(50 x50 x7 mm^3)
Zinc Paint with nano Al_2O_3	1(50 x50 x7 mm^3)
Aluminum Paint with nano Al_2O_3	1(50 x50 x7 mm^3)

Table 1: Coating types

Sample preparation

Samples of low alloy steel were primary polished with wet 400, 600, 800 and 2000 grit SiC paper. For proper adhesion the surface of the samples was cleaned with distilled water. Later, Acetone was used for further cleaning followed with rinsing in the distilled water. Moreover, ultrasonic cleaning was done for three minutes with Methanol followed washing with distilled water. For primer base, the samples were coated with primer paint (Red Oxide) 0.50 ml paint of organic, zinc and aluminum was used to mix separately with nano additives of ZnO, CuO and AL2O3 with 0.5 gms quantity each. Both were mixed and put for stirred for 2 hours (ref figure 1) so that proper missing of paints could be done.

Sample preparation for EN-P coating, same procedure for cleaning was followed for low alloy steel sample size of 50 x50 x7 mm3. The coating bath consists of the chemical composition as shown in figure 2. Nano additives of Al_2O_3 (0.2g), and ZnO (0.2g) mixed with chemical that prepared for the coating. Process parameters such as pH, temperature and effect of surfactant concentrations were varied. The pH level was adjusted by addition of Ammonia. It was noticed that for pH value of 9-10, temperature was maintained at 85°C . SLS (1.2g/l) was produced for better EN-P coating. The electrolyte was heated directly by an electrically heated water bath whose temperature was regulated by PID controller. The coating was prepared for a period of 1hr with total volume of the coating bath restricted to 200ml.

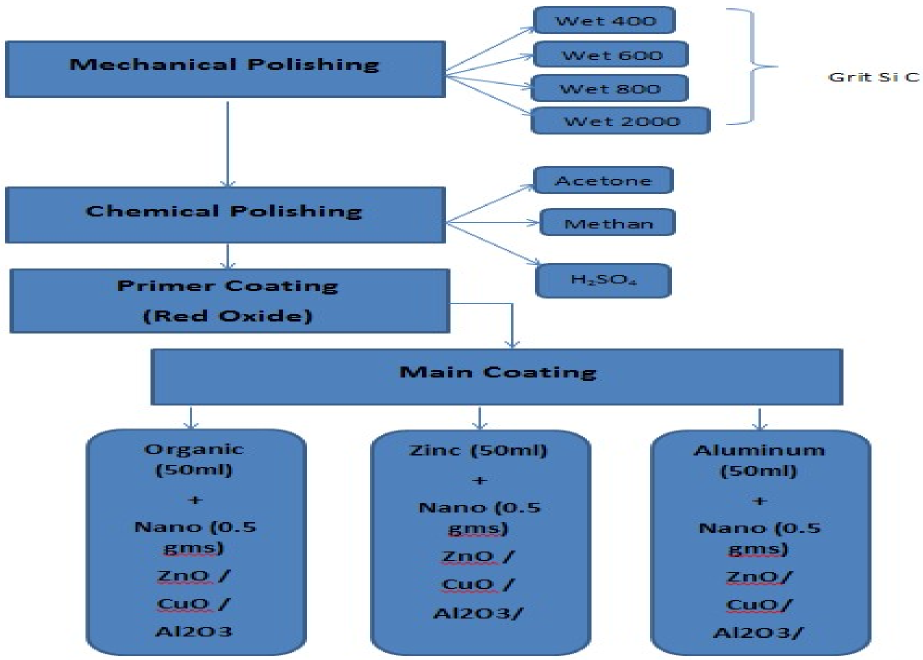

Figure 1: Sample preperation

Particulars	Composition
Nickel Chloride	6 gm/25 ml bath
Sodium hypo-phosphate	8gm/25ml
Sodium Acetate	5 gm/25ml
Ammonium Chloride	10gm/25ml
Bath volume	200 ml
PH	9-10
Temperature	85 ± 1oC

Figure 2: Chemical composition for EN-P bath

Sample preparation for Atmospheric exposure test

Samples were sorted out in three categories. The first Batch of samples was having specimen size of 50 x50 x7 mm^3 as shown in figure 3, 4 and 5.

Figure 3: Samples after Mechanical and Chemical polishing

Figure 4: Samples after primer coating

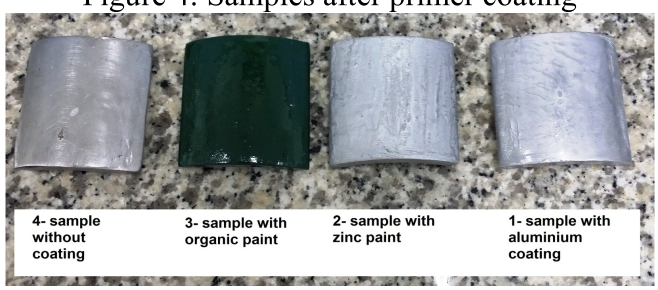

Figure 5: Samples after coating

Sample preparation for dry/wet test

Two samples of size 20 x20 x7 mm^3 were also prepared for the dry/wet test as shown in figure 6 and 7.

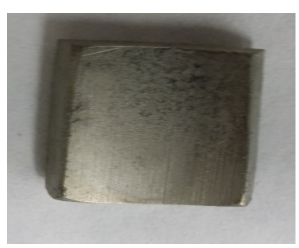

Figure 6: Sample after mechanical and chemical polishing

Figure 7: Sample after coating

Results

Surface Roughness test

For further test on coating surface roughness was required to be measured. The investigation was carried out by using Mitutoyo machine to measure the surface roughness of coated samples as shown in figure 8 to 10.CuO with Al paint gives the least value of Rz 3.77 µm and maximum surface roughness was for Al_2O_3 with organic paint of 9.92 µm.

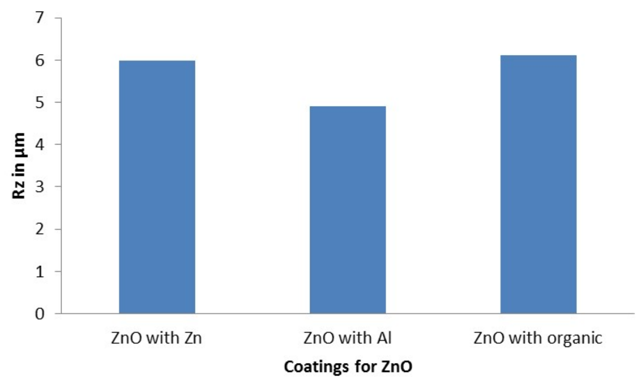

Figure 8: Surface roughness for ZnO

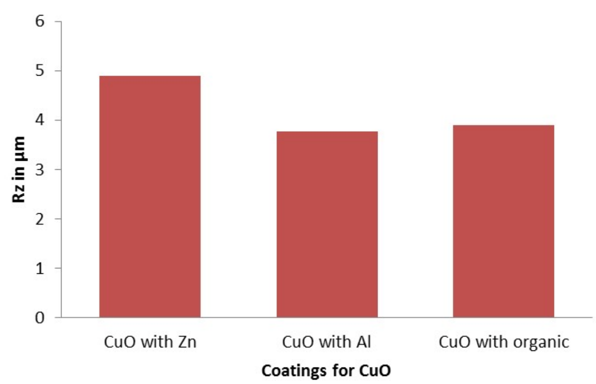

Figure 9: Surface roughness for CuO

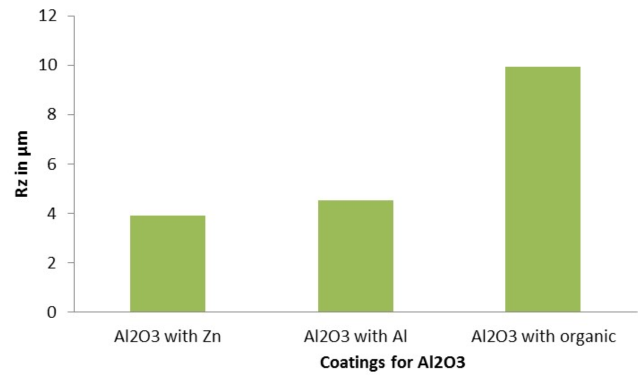

Figure 10: Surface roughness for Al_2O_3

Atmospheric Exposure test

Atmospheric test was the first experiment to be conducted for an exposition period of 60 days i.e. March to June 2015 in the ambient conditions of Muscat Oman, where the temperature varies from 38 to 47 ^{0}C. The different coatings developed like organic paint, aluminum paint, zinc paint, nano additives and electroless Ni-P coatings. Notations used in experimentation are given below in table 2:

ZnO + Organic paint coating	(Z-O)
ZnO + Aluminum paint Coating	(Z-A)
ZnO + Zinc paint Coating	(Z-z)
CuO+ Organic paint coating	(C-O)
Al_2O_3 + Zinc paint coating	(A-Z)
CuO + Aluminum paint coating	(C-A)
CuO + Zinc paint coating	(C-Z)
Al_2O_3+ Organic paint coating	(A-O)
Al_2O_3+ Aluminum paint coating	(A-a)

Table 2:Sample notations

Samples	Period of Exposure (Weeks)											
Coated Samples	1	2	3	4	5	6	7	8	9	10	11	12
(Z-O)									X	X	X	X
(Z-A)										X	X	X
(Z-z)									X	X	X	X
(C-O)										X	X	X
(C-A)										X	X	X
(C-Z)										X	X	X
(A-O)											X	X
(A-a)												X
(A-Z)											X	X

Table 3: Exposure time

Table 3 indicates that Al2O3 with Aluminum paint (A-a) coating provides maximum resistance to corrosion where else ZnO with Zinc coating (Z-z) and ZnO with organic paint (Z-O) gives least corrosion resistance. To calculate the corrosion rate of the samples following formula as shown in eq 1 was used [9]:

Corrosion rate in millimeter per year : mmpy = 87.6 (W/DAT) (1)

Where: mmpy = Corrosion rate in millimeter per year.
W = Weight loss in grams
D = Density in gms / cm^3
A = Area in cm^2
T = Time in hours.

Sample	Initial weight (g)	Final weight (g)	Weight loss (g)	Area (cm^2)	Time (hr)	Density (g/cm^3)	Corrosion rate (mmpy)
(Z-O)	121.49	120.69	0.8	64	720	7.874	7.6080
(Z-A)	116.65	115.86	0.79	64	720	7.874	7.5129
(Z-z)	120.28	119.39	0.89	64	720	7.874	8.4639
(C-O)	121.30	120.7	0.6	64	720	7.874	5.7060
(C-A)	120.32	119.76	0.56	64	720	7.874	5.3256
(C-Z)	118.74	118.06	0.68	64	720	7.874	6.4668
(A-O)	116.31	116.11	0.2	64	720	7.874	1.9020
(A-a)	125.27	125.09	0.18	64	720	7.874	1.7118
(A-Z)	119.28	119.08	0.2	64	720	7.874	1.9020

Table 4: Corrosion rate of samples

It is obvious from table 4 that Al_2O_3 with Aluminum paint (A-a) was having least corrosion rate response as compared to other samples.

Potentiodynamic test

The Potentiodynamic test is a type of direct current (DC) Test. During this Test, the potential at a selected (usually anodic) voltage was maintained and measure the current as a function of time. Ag/AgCl in saturated KCl is used as reference electrode. Three tests were conducted for samples without coating, with ZnO and with Al_2O_3.

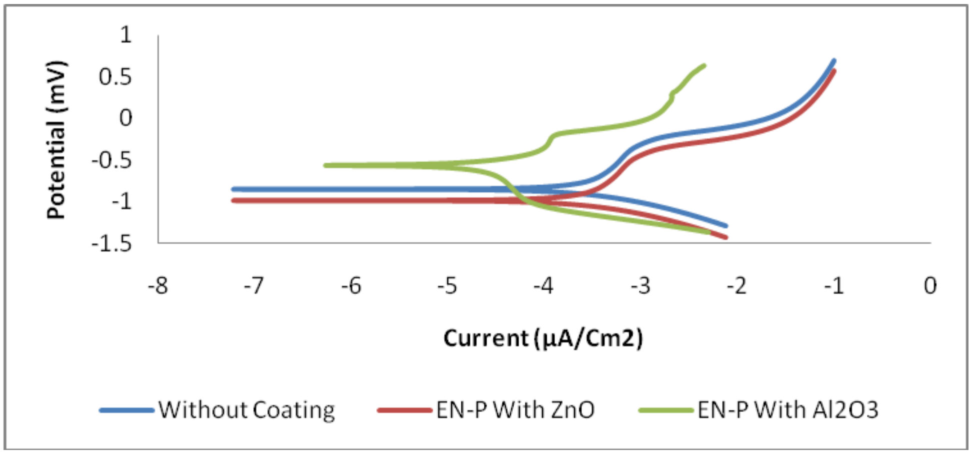

Figure 11: Tafel Graph for coatings

To calculate the corrosion rate using current from metal loss following formula eq 2 was used. [10]:

$$mmpy = 3.27 \times 10^{-3} \times I_{corr} \times W / \rho \qquad (2)$$

where:

W = Equivalent weight in grams for low alloy steel.

ρ = metal density for low alloy steel in g /cm^3

I_{corr} = Current from Tefal graph in µA/cm^2 (ref Figure 11)

Sample	**I_{corr} = Current µA/cm^2**	**E.W gms**	**Density (g/cm^3)**	**Corrosion rate-mmpy**
Without coating	7.25	27.92	7.874	0.0840
EN-P with ZnO	7.20	27.92	7.874	0.0834
EN-P With Al_2O_3	6.20	27.92	7.874	0.0718

Table 5: Corrosion rate in mmpy

The test results showed tafel extrapolation curve for each coated sample. The figure 11 reflects the minimum corrosion current and potential was for the sample coated with EN-P with nano Al2O3 coating and the maximum corrosion rate for the uncoated sample. Same is also proved as shown in table 5.

Dry/wet test

For accelerated corrosion dry/wet test was conducted. The basic idea of the test was to dipped the samples in the filtered sea water and dry it to the atmospheric air. Sea water was used with 7.6 PH value and filtered from impurities. The filtered sea water was poured in to small chambers made from glass. Nine samples were examined as reflected in table 2. Samples were dipped in the filtered sea water for 16 hours and dried in the atmospheric air for 8 hours for 14 days. Results are shown in table 6.

Table 6: Corrosion rate of samples

The result concluded that the sample coated with nano additives of Al_2O_3 has promising corrosion resistance result of 0.34 mmpy. Moreover, the highest rate of corrosion in terms of the sample coated is with (Z-O) paint of 5.62 mmpy.

Characterization

Surface morphology

Surface morphology of the samples was studied to analyze the microstructure of the coatings through SEM (Scanning Electron Microscope). The images of the six samples after corrosion happening are shown in figure 12. Aluminum, zinc and organic coatings indicate the corrosion in different areas. It is also observed that organic coating was affected more than zinc and aluminum coating. The image of Electroless nickel depicts that the nickel was deposed on the surface of the sample. Image of EN-P with addition of Al_2O_3 demonstrate the deposition of Nickel with small particles of Nano Al_2O_3 that contributes better resistance than sample coated with EN-P only. Moreover, the sample without coating illustrates the surface area totally corroded.

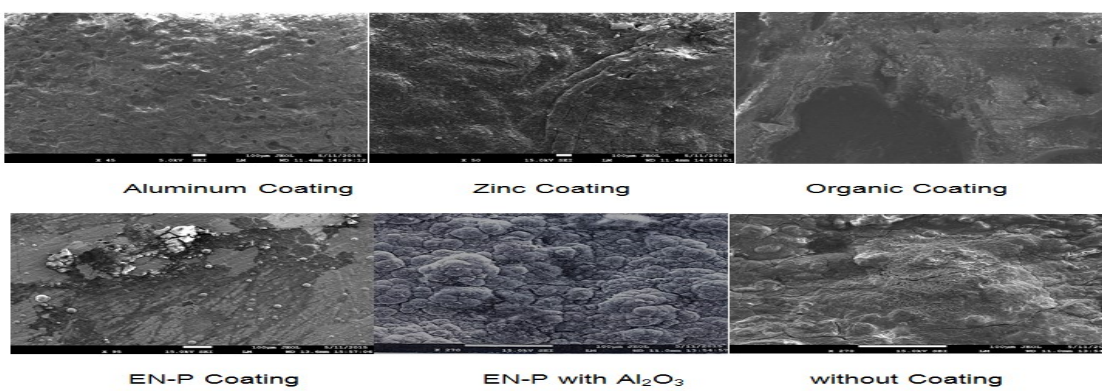

Figure 12: Images of samples through SEM

Hardness testing

Hardness test for coatings was done through Vickers hardness test. The weight used was 5 kg for 10 seconds for all samples. Ref figure 13 and 14 showing result:

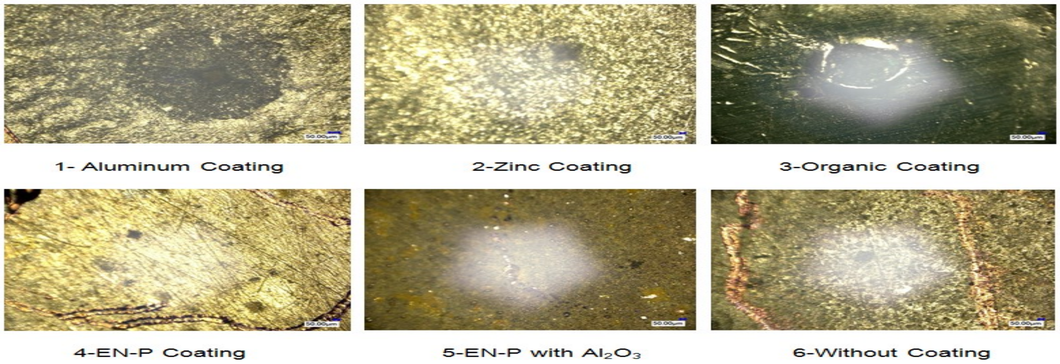

Figure 13: Samples after indentation

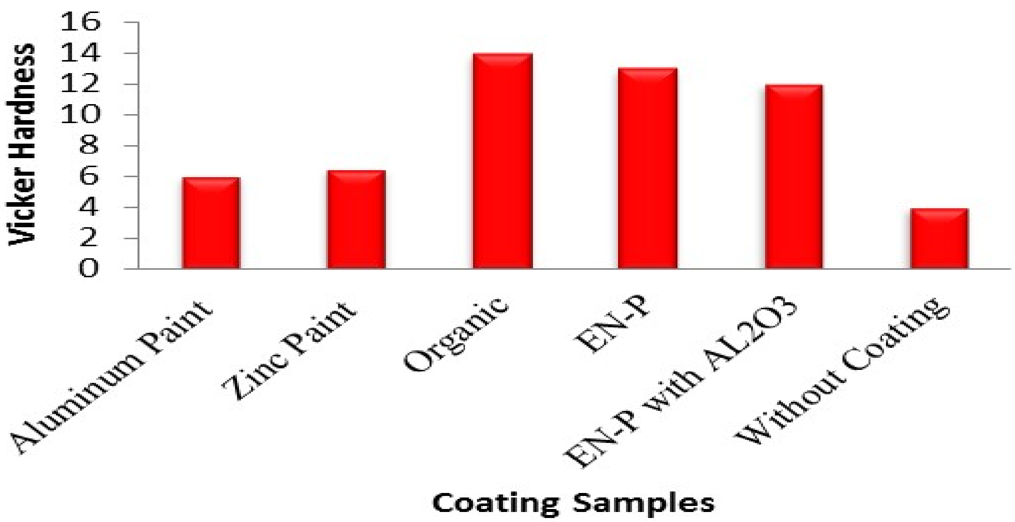

Figure 14: Samples hardness

The micro radial cracks were examined on sample EN-P with Al2O3 had less crack generation as compared to other samples. It proved that sample would have fewer tendencies to be peeled off as compared to other indented samples. It also shows that adhesion process between the deposit and substrate is good.

Discussion

Electroless nickel phosphorous (EN-P) is an autocatalytic electrochemical oxidation and reduction process. The oxidation of a substance is portrayed by loss of electrons and diminishment is recognized by gain of electrons. It is preferred coating processes because of its simple construction and no electricity is involved in the process. The novel properties of EN-P are enhanced micro hardness, great imperviousness to wear and corrosion resistance etc [10] .

It is also observed that when nano additives are added in the coating they spread and dissolve uniformly on the layers of coatings. The volume to surface area of nano additives since the particle sizes will be from 40 to 50 nm. These nano particles do not allow the oxidation to takes place on the protective barrier of coatings. As all the nano particles chosen for investigation are from oxide group i.e. nano Al_2O_3, this oxide forms a passive layer on the coating preventing corrosion. Moreover, the dissolved nano particles reduces the direct exposure of coating area to the environment resulting lesser reaction on the surface and hence less weight loss.

Conclusion

Corrosion is a natural occurring phenomena, therefore cannot be eliminated from the metals. It can be isolated from the reaction by applying coating to cover from the exposure or can be coated with strong volunteer component as coated layer from the base metal wanted to be protected. Different coating behaviors on the external surface of low alloy steel pipe line used in Oman oil and gas industry are studied. To confirm the corrosion rate for different coating behavior, test were conducted like atmospheric exposure test, dry/wet test and potentiodynamic test. Similarly, SEM and hardness test were also performed to confirm characterization. The following results are drawn:

a. Atmospheric exposure test was conducted for the said materials. The highest corrosion rate was investigated for Z-z for 8.46 mmpy and lowest corrosion rate was observed for A-a i.e. 1.7118 mmpy. Therefore the coating paint group is resulted with highly resistance to the corrosion occurs i.e. aluminum paint followed by organic paint and then Zinc paint.
b. The samples coated with EN-P Electroless nickel- Phosphorus. Two types of coatings were used by EN- P, one without nano additives particles and other with the addition of nano additives of Al_2O_3. Dry/wet test was conducted. The sample coated with EN-P with nano additives of Al_2O_3 (A-a) has promising corrosion resistance result of 0.34 mmpy. Moreover, the highest rate of corrosion in terms of the sample coated with Z-O has 5.62 mmpy.
c. Potentiodynamic test was also concluded for the said samples. The minimum corrosion current and potential was for the sample coated with EN-P with nano Al_2O_3 coating and the maximum corrosion rate for the uncoated sample.
d. For accelerated corrosion dry/wet test was conducted. The result establish that the sample coated with nano additives of Al_2O_3 has promising corrosion resistance result of 0.34 mmpy. Moreover, the highest rate of corrosion is in terms of the sample coated is with the Z -O of 5.62 mmpy.
e. Surface morphology of the samples was studied through SEM to analyze the microstructure of the coatings. The image of Electroless nickel depicts that the nickel was deposed on the surface of the sample. Image of EN-P with addition of Al_2O_3 shows the deposition of Nickel with small particles of Nano Al_2O_3 that contributes better resistance than sample coated with EN-P only. Moreover, the sample without coating shows the surface area totally corroded.
f. The alloy also shows excellent resistance to stress corrosion cracking and corrosion fatigue when examined through Vicker hardness test. The micro radial cracks observed for Al2O3 with Aluminum paint were fewer.

This work may be further continued in future by trying out other types of surfactants.

References

1. NACE,(2011), Corrosion costs and preventive

strategies in the United States, PUBLICATION NO. FHWA- RD-01-156.

2. Dr. Jim Breakell,(2005), Selecting a strategy for dealing with accelerated low water corrosion ,CIRIA, London UK.
3. Jamal Amera.(2014) Influence of multiple electroless nickel coatings on beech wood: preparation and characterization. Composite Interfaces.; 21 (3): 191-201.
4. Fernando B Mainier, (2013), Quality of Electroless Ni-P (Nickel-Phosphorus) Coatings Applied in Oil Production Equipment with Salinity, Journal of Materials Science and Chemical Engineering, 2013, 1, 1-8.
5. S Roux (2010), Influence of a biopolymer admixture on corrosion behaviour of steel rebars in concrete, Materials and Corrosion, Volume 61, Issue 12, pages 1026–1033.
6. Riddle, Y. and McComas.C, (2005), Advances in Electroless Nickel-Boron Coatings: Improvements to Lubricity and Wear Resistance on Surfaces of Automotive Components, SAE Technical Paper 2005-01-0615, 2005, doi:10.4271/2005-01-0615.
7. Odekerken Jules Marie (1966), Method of electrodepositing a corrosion resistant nickel-chromium coating and products thereof , US3282810 A.
8. Dhinakaran, R., Elansezhian, R. and Lalitha, A. (2013). Effect of Nanoadditives with Surfactant on the Surface. 1st ed. [ebook] Pondicherry 605014, India: Hindawi Publishing Corporation Advances in Tribology.
9. Corrosion rate formula by General Magna Plate corporation, http://frictioncalculator.com/corrosion-rate-formula,[on line accessed].
10. M. F. Arenas and R. G. Reddy, Corrosion of steel in ionic liquids, Journal of Mining and Metallurgy, 39 (1&2) B (2003) 81 – 91.