

Influence of Nano Additives on Protective Coatings for Oil Pipe Lines of Oman

Muhammad Mumtaz Mirza, Elansezhian Rasu, and Anjali Desilva

Abstract—The paper presents, analyzes and comments on the findings for different type of nano-additives used in painted coatings against the corrosion behavior for steel pipe lines, used in petroleum industry of Oman. The examination for the rate of corrosion in low alloy steel pipelines included a range of coated samples that includes organic paint, metallic paint, Aluminum, Zinc and electroless ones. After the samples were coated, the surface roughness was checked and the coating thickness maintained. For corrosion rate analysis and the evaluation of each coating's life period, a number of test including atmospheric exposure test, dry and wet test and potentiodynamic test were conducted. In order to analyze the surface behavior of coatings, characterization was performed with SEM-scanning electron microscope that later supported with hardness test results. The performance analysis of several coatings investigates that, mixture of nano Al_2O_3 additive with Aluminum paint gives the best result against corrosion and presented good surface performance in comparison with other samples.

Index Terms—Electroless, coatings, corrosion, nano additives, Al_2O_3 .

I. INTRODUCTION

The corrosion of pipelines is one of the major problems faced by the 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 but methods such as passivation and chromate conversion can increase a material's corrosion resistance and therefore reduce such exposure. However, some corrosion mechanisms are less visible and less predictable [2]

EN - Electroless nickel plating is an auto-catalytic reaction

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used to deposit a coating of nickel on a substrate. Unlike electro plating, it is not necessary to pass an electric current through the solution to form a deposit. This plating technique prevents corrosion as well as wear and develops uniform coating thickness [3].

The EN plating of metallic nickel from aqueous solution in the presence of hypophosphite was first noted 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 electrodepositioning Ni-Cr by Odekerken, during the year 1966 [7]. In this study, finely powdered particles such as aluminum oxide and polyvinyl chloride (PVC) resin were distributed within a metallic matrix in an intermediate layer. The first commercial application of their work used the electroless Ni-SiC coatings on the Wankel internal combustion engine in 1981[8].

Fusion-bonded epoxy (FBE) and a three-layer polyolefin (3LPO) (polyethylene or polypropylene (PP)) are currently the most widely used external anti-corrosion coating systems available in the international market [9].

A new technique of protection coating is presented with sufficient results in Electroless Nickel EN-P deposition with Al_2O_3 as nano additive. In this method, coating is done uniformly with equal thickness to the entire surface [10], [11].

II. EXPERIMENTAL SETUP

A. Collection of Samples

The samples considered in this study are low alloy steel taken from the local oil and gas industry of Oman. A total numbers of nine samples were coated as presented in Table I.

TABLE I: COATING TYPES

Coating Type	Qty/size of sample
Aluminum paint with nano ZnO	1(50 ×50 ×7 mm ³)
Zinc Paint with nano ZnO	1(50 ×50 ×7 mm ³)
Organic Paint with nano ZnO	1(50 ×50 ×7 mm ³)
Organic Paint with nano CuO	1(50 ×50 ×7 mm ³)
Aluminum paint with nano CuO	1(50 ×50 ×7 mm ³)
Zinc Paint with nano CuO	1(50 ×50 ×7 mm ³)
Organic Paint with nano Al_2O_3	1(50 ×50 ×7 mm ³)
Zinc Paint with nano Al_2O_3	1(50 ×50 ×7 mm ³)
Aluminum Paint with nano Al_2O_3	1(50 ×50 ×7 mm ³)

B. Sample Preparation

Nine samples were primary polished with wet 400, 600, 800 and 2000 grit SiC paper. For proper adhesion, the surface of each sample was cleaned with distilled water. Later, Acetone was used for further cleaning followed by rinsing with distilled water. Moreover, ultrasonic cleaning was done for three minutes with Methanol again followed by washing with distilled water. For primer base, the samples were coated with primer paint (Red Oxide). Each sample was then painted with 0.5ml paint of organic, zinc and aluminum paint separately. These samples were then used to mix with 0.5 gms of nano additives of ZnO, CuO and Al₂O₃ separately. The size of nano additives has particle size of 50 nm which were used in the coating. Paint and nano additives were mixed and put to stir for 2 hours (see Fig. 1).

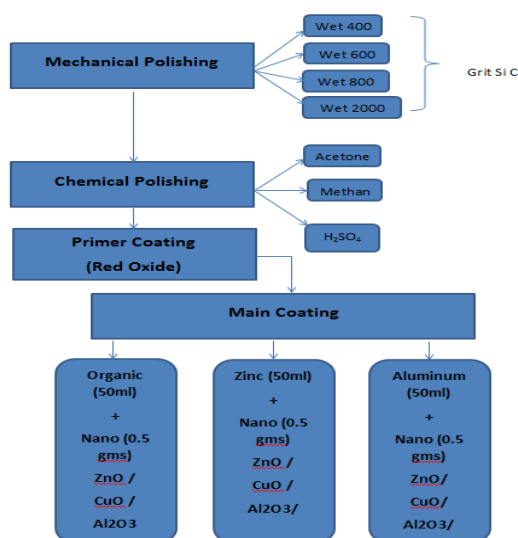


Fig. 1. Sample preparation.

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 ± 1°C

Fig. 2. Chemical composition for EN-P bath.

In preparing EN-P coatings, same procedure of cleaning was followed for low alloy steel samples of size 50×50×7 mm³. The coating bath consists of the chemical composition as shown in Fig. 2. Nano additives of Al₂O₃ (0.2g), and ZnO (0.2g) were mixed with the chemicals prepared for the coating. Process parameters such as pH, temperature and effect of surfactant i.e. Cetyl Trimethyl Ammonium Bromide (CTAB) 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. Sodium lauryl sulfate (SLS-1.2gpl) was used 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. Coated samples are shown in Fig. 3-Fig. 5.

C. Sample Preparation for Atmospheric Exposure Test

Samples were set out in three categories. The first Batch of samples had specimen size of 50×50×7 mm³ as shown in Fig. 3-Fig. 5. Each sample was marked, weighted and recorded. The samples were exposed to the atmosphere for 60 days. The test carried out in ambient condition of Muscat Oman, which was dry with ambient temperature varies from 35 to 46 °C, average relative humidity of 60 to 65 % and average wind speed of 3 m/s.



Fig. 3. Samples after mechanical & chemical polishing.



Fig. 4. Samples after primer coating.

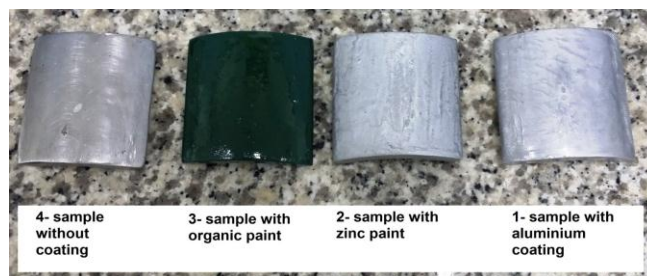


Fig. 5. Samples after coating.

D. Sample Preparation for Dry/Wet Test

Two samples of size 20×20×7 mm³ were also prepared for the dry/wet test as shown in Fig. 6 and Fig. 7. The sample size was configured as per the size allowed by the dry/wet test equipment.

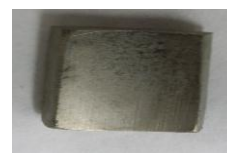


Fig. 6. Sample after mechanical and chemical polishing.



Fig. 7. Sample after coating.

III. EXPERIMENTAL PROCEDURE

A. Surface Roughness Test

In order to evaluate further, initially the samples coating surface roughness were measured. The investigation was carried out by using Mitutoyo surface measurement equipment. Results are shown in Fig. 8 to 10. CuO with Al paint gives the least value of R_z 3.77 μm and maximum surface roughness was for Al_2O_3 with organic paint of R_z 9.92 μm .

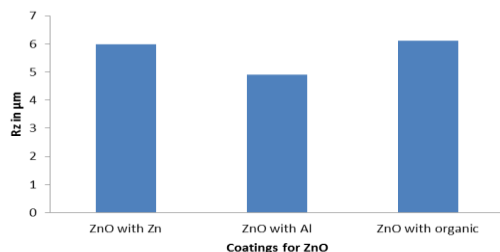


Fig. 8. Surface roughness for ZnO.

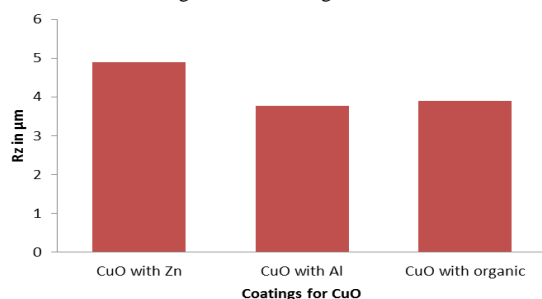


Fig. 9. Surface roughness for CuO.

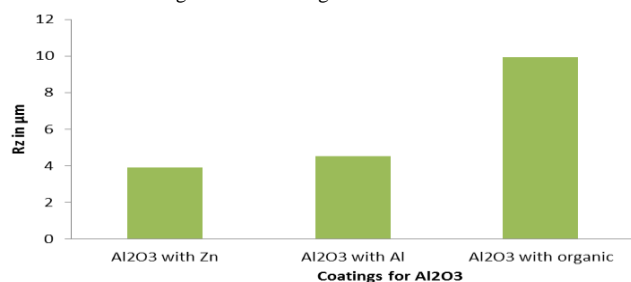


Fig. 10. Surface roughness for Al_2O_3 .

B. Atmospheric Exposure Test

Atmospheric test was the first experiment to be conducted for an exposition period of 60 days with ambient conditions as stated above. Nine different coatings were developed i.e. organic paint, aluminum paint, zinc paint with nano additives. Notations used in experimentation are given below in Table II.

TABLE II: SAMPLE NOTATIONS

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 III: EXPOSURE TIME

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 III indicates that Al_2O_3 with Aluminum paint (A-a) coating provides maximum resistance to corrosion where as ZnO with Zinc coating (Z-z) and ZnO with organic paint (Z-O) gives the least. To calculate the corrosion rate of the samples following formula was used [12]:

Corrosion rate in millimeter per year

$$mmpy = 87.6 (W/DAT) \quad (1)$$

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.

TABLE IV: CORROSION RATE OF SAMPLES

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

It is indicative from Table IV that Al_2O_3 with Aluminum paint (A-a) was having the lowest corrosion rate response when compared with the rest.

C. 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 measured the current as a function of time. Ag/AgCl in saturated KCl is used as a reference electrode. Three tests were conducted for samples without coating, EN-P with ZnO and with Al_2O_3 .

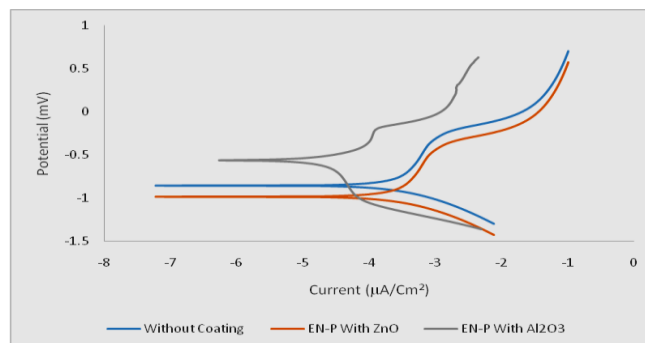


Fig. 11. Tafel graph for coatings.

To calculate the corrosion rate using the current from metal loss, the following formula is used as shown in Equation (2) [13]:

$$mm/y = 3.27 \times 10^{-3} \times I_{\text{corr}} \times W / \rho \quad (2)$$

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 Tafel graph in $\mu A/cm^2$ (see Fig. 11).

TABLE V: CORROSION RATE IN MMPY

Sample	I_{corr} = Current $\mu A/cm^2$	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

The test result showed Tafel extrapolation curve for each coated sample. Current calculated for each sample was then used in calculating the corrosion rate using Eq. (2). Calculations are shown in Table V. EN-P with Al_2O_3 stated minimum corrosion rate of 0.0718 and without coating indicates maximum corrosion rate of 0.0840 mmpy.

D. Dry/Wet Test

For accelerated corrosion, dry/wet test was conducted. The basic idea of the test was to have the samples dipped in the filtered sea water and dry it to the atmospheric air. Filtered from impurities, the sea water was used with pH value of 7.6. The filtered sea water was poured in to small glass made chambers and nine samples were examined as indicated in Table II. Samples were dipped in the filtered sea water for 16 hours and dried in the atmospheric air for 8 hours. Test was conducted for 14 days, results are shown in Table VI.

TABLE VI: CORROSION RATE OF SAMPLES

Sample	Initial weight (g)	Final weight (g)	Weight loss (g)	Area(cm^2)	Time (hr)	Density (g/cm^3)	Corrosion rate (mmpy)
(Z-O)	123	120.7	2.31	13.6	336	7.874	5.62
(Z-A)	117	115.9	1.14	13.6	336	7.874	2.78
(Z-z)	121	119.4	1.61	13.6	336	7.874	3.92
(C-O)	121	120.7	0.3	13.6	336	7.874	0.73
(C-A)	122	119.8	2.24	13.6	336	7.874	5.45
(C-Z)	119	118.1	0.94	13.6	336	7.874	2.29
(A-O)	116.5	116.1	0.39	13.6	336	7.874	0.95
(A-a)	125.23	125.1	0.14	13.6	336	7.874	0.34
(A-Z)	119.29	119.1	0.21	13.6	336	7.874	0.51

The results indicated that the sample coated with nano additives of Al_2O_3 possessed strong corrosion resistance with value of 0.34 mmpy. Moreover, the highest rate of corrosion was with (Z-O) paint of 5.62 mmpy.

IV. CHARACTERIZATION

A. Surface Morphology

Surface morphology of the samples was studied to analyze the surface of the coatings through SEM (Scanning Electron

Microscope). Images of the six samples are shown in Fig. 12. Aluminum, zinc and organic coatings indicate the corrosion in different areas. It is also observed that organic coating was affected more than the zinc and the aluminum. The image of Electroless nickel depicts that the nickel was deposited on the surface of the sample. Image of EN-P with addition of Al_2O_3 demonstrates 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 surface area of the sample without any coating can be seen as completely corroded.

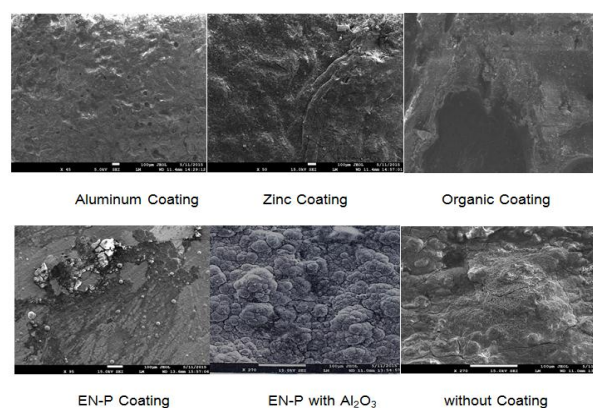


Fig. 12. Images of samples through SEM.

B. Hardness Testing

Hardness testing for coatings was done through Vickers hardness test. The weight used was 5 kg for 10 seconds for all the samples (see Fig. 13 & Fig. 14).

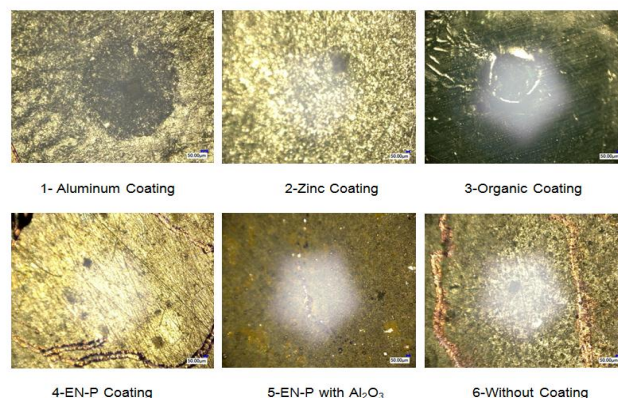


Fig. 13. Samples after indentation.

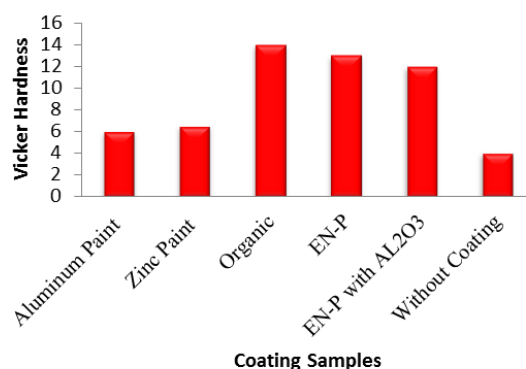


Fig. 14. Samples hardness.

The micro radial cracks were examined on sample EN-P with Al_2O_3 and a lesser crack generation was observed as

compared with the other samples. It also observed that the sample would not be peeled off as easily compared to the rest of the batch. It also illustrated that the adhesion process between the deposit and substrate was rather good [14].

V. CONCLUSION

Corrosion is a natural occurring phenomena and although cannot be eliminated from the metals. It can be isolated from the reaction by applying coating to cover the metal from exposure or can be coated with strong volunteer component as coated layer from the base metal to be protected [15]. Different coating behaviors on the external surface of low alloy steel pipe line used in Oman oil and gas industry are examined. To confirm the corrosion rate for different coating behaviors, test were conducted like atmospheric exposure test, dry/wet test and potentiodynamic test. Similarly, SEM and hardness test were also performed to confirm the characterization. The following results are drawn:

1) Atmospheric exposure test was conducted for the said materials in specific ambient conditions. 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.

2) 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.

3) 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 whereas the maximum was for the uncoated sample.

4) For accelerated corrosion a dry/wet test was conducted. The result established 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 the Z-O of 5.62 mmpy.

5) 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 deposited 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. Use of CTAB surfactant improves the wettability of coating on the substrate coating.

6) The alloy also shows excellent resistance to stress corrosion cracking (SCC) and corrosion fatigue when examined through Vicker hardness test. The micro radial cracks observed for Al_2O_3 with Aluminum paint were fewer.

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

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