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ENHANCEMENT OF CORROSION INHIBITION ACTION OF THIOUREA BY AROMATIC AMINES

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ABSTRACT

Industrialization and modernization has made a strong demand of steel and their maintenance for a strong infrastructure for every country in the race of survival, stabilization, growth and competition. Atmospheric corrosion may cause some dangerous and expensive damage to everything from automobiles, home appliances, water systems to pipelines, bridges and public buildings like other natural hazards such as earthquakes or several weather disturbances. Atmospheric corrosion can aggressively accelerate the rate of degradation of steel during their manufacturing, processing, storage and transportation. In these cases, traditional methods to prevent corrosion are not suitable which provide scope of vapour phase corrosion inhibitors in industries, defense and daily life. Synergistic effect of Thiourea was tested for mild steel in different aggressive atmospheric conditions with aromatic amines (N-Ethylaniline, 1-Benzylimidazole and 5-Aminotetrazole) by Vapour pressure determination test, Weight loss test, Salt spray test, Sulphur dioxide test, Metallurgical research microcopy and Scanning electron microcopy at 50^0C.

Keywords: *Synergistic effect, Salt spray test, Vapour phase corrosion inhibitor, Weight loss test, Sulphurdioxide test, Aromatic amine.*

I. INTRODUCTION

Atmospheric Corrosion, though not a separate form of corrosion, has received considerable attention because of the staggering associated costs that result (Ailor, 1982; Dean and Lee, 1987; Tidblad, 1998; Graedal and Leygraf, 2001; Naixin et. al., 2002; Brown and Masters, 1982; Scully, 1994). With large number of outdoor structures such as buildings, fences, bridges, towers, automobiles, ships and innumerable other applications exposed to the atmospheric environment, there is no wonder that so much attention has been given to the subject. Many variables influenced the corrosion characteristics of an atmosphere. Relative humidity, temperature, sulphur dioxide content, hydrogen sulphide content, chloride content, amount of rain fall, dust and even the position of the exposed metal exhibit marked influence on corrosion behavior, geographic location is also a factor. Atmospheric corrosion depends not only on the moisture content present but also on the dust content and the presence of other impurities in the air, all of which have an effect on the consideration of moisture on the metal surface and the resulting corrosiveness. Air temperature can also be a factor.

In the study of relationship between chloride ion concentrations with corrosion rate in atmospheric conditions, it was showed that NaCl can cause corrosion at very low concentration because it can induce corrosion by SO_2 on a carbon steel surface (Corvo, 1984; Morcillo et. al., 1999). NaCl can enhance 14 times rate of corrosion by SO_2 at 9% relative humidity (Ericsson and Sydberger, 1980). In another report, the adverse effect of CO_2 on corrosion of aluminium was reported (Blucher et. al., 1994). Organic substances have been studied as VPCI for mild steel were morpholine derivatives and diaminohexane derivatives (Vuorinen et. al., 1994), fatty acid thiosemicarbazides (Quraishi et. al., 2002), cyclohexylamine and dicyclohexylamine (Subramanian et. al., 2002, 1999), amine carboxylates (Vuorinen and Skinner, 2002; Skinner, 1999), ammonium caprylate (Quraishi and Jamal, 2005), benzoic hydrazide derivatives (Quraishi et. al., 2005), polyamines (Zhang et. al., 2007), bis-piperidiniummethyl-urea and β–amino alcoholic compounds (Khamis and Andis, 2002). Apart from organic substances, natural compounds like wood bark oil (Poongothai et. al., 2005) and thyme (Premkumar et. al., 2008a, 2008b) have also been used as VPCIs. Recently the mechanism of inhibition of dicyclohexaminenitrite and dicyclohexamineisonitrite against corrosion due to vapours of acetic acid and formic acid on carbon steel has been proposed (Cano et. al., 2005). The electrochemical behavior of mixed anodic inhibitors has been reported (Zubielewicz and Gnot, 2004). The performance of two primers, first natural rust converter and other on organic primer coating containing VPCI against atmospheric corrosion for reinforcing steel was evaluated (Batis et. al., 1998). Synergistic corrosion management systems were also reported by use of corrosion inhibitors (Lyublinski, 2008).

In continuation to our earlier study (Kumar et. al. 2013; Kumar and Yadav, 2013a, 2013b, 2014; Kumar and Saini, 2012a, 2012b; Saini and Kumar, 2014a, 2014b), in the present study, the inhibiting properties of Thiourea (TU) was investigated with aromatic amines on mild steel at 85% relative humidity and 50°C by Weight loss test, Salt spray test in a solution of 3.0% NaCl, SO_2 test, Metallurgical research microcopy and Scanning electron microscopy.

II.   MATERIALS AND METHODS
Material
Mild steel (ASTM-283) coupons of dimensions 3.5cm × 1.5cm × 0.025cm and of chemical composition: C–0.17, Si–0.35, Mn–0.42, S–0.05, P–0.20, Ni–0.01, Cu–0.01, Cr–0.01 and Fe-balance (w/w) were used.

Equipments

Weighing balance Single pan analytical balance, Precision 0.01mg, Model AB135-S/FACT, Source Mettler Toledo, Japan.

Humidity chamber Thermotech. TIC-4000N Temperature Controller, Humidity controller with course and fine adjustments, AC Frequency 50-60Hz, Max. voltage 300V, Source Make-Associated Scientific Tech., New Delhi.

Salt spray chamber Thermotech. TIC-4000N Temperature Controller, Pumping system Pt-100, AC Frequency 50-60Hz, Max. voltage 300V, Source Make-Associated Scientific Tech., New Delhi.

Air thermostat Nine adjustable chambered, Electrically controlled, Accuracy ± 0.1°C.

Metallurgical research micrograph Trinocular inverted metallurgical microscope, CXR II Laomed, Mumbai, India, connected with a computer and printer.

Scanning electron micrograph JEOL 5900 LV.

Methods

Vapour pressure determination test A definite amount of exactly weighted VPCI was placed in a single neck round bottom flask fitted with a rubber cork in the neck having a glass capillary of 1.0 mm diameter in the center of rubber cork. Then the flask was kept in electrically controlled air thermostat maintained at the constant temperature of 50°C for 10 days. Change in weight of VPCIs was observed by analytical balance and vapour pressure of investigated VPCI was determined by weight loss of VPCI for time of exposure by equation 1.

$$P = \frac{W}{AT} \sqrt{\frac{2\,\pi\,RT}{M}} \qquad [1]$$

Where, P = vapour pressure of VPCI (mmHg), A = area of orifice (m^2), t = time of exposure (sec.), W = weight loss of VPCI (kg), T = temperature (K), M = molecular mass of the inhibitor (kg) and R = gas constant (8.314 $JK^{-1}mol^{-1}$).

Weight loss test Mild steel coupons were mechanically polished successively with the help of emery papers grading 100, 200, 300, 400 and 600μ and then thoroughly cleaned with plenty of triple distilled water, ethanol and acetone. Then coupons were dried with hot air blower and stored in desiccators over silica gel. Weight loss tests were carried out in an electronically controlled air thermostat maintained at a constant temperature of 50°C. After recording the initial weights of mild steel coupons, they were kept in different isolated chambers of air thermostat having fixed amount of VPCI at a constant temperature of 50°C for 24 hours of exposure time. A uniform thin film of VPCI was adsorbed onto the metal coupon surface after 24 hours of exposure. Then these coupons were transferred to a digitally controlled humidity chamber maintained at 85% humidity at a constant temperature of 50°C for 10 days. Blank coupons untreated with VPCI were also kept in humidity chamber for the same duration in the same corrosive environment. After exposing the coupons for 10 days, coupons were taken out from the humidity chamber and washed initially under running tap water. Loosely adhering corrosion products were removed with the help of rubber cork and coupon was again washed dried and

then weighed again. Corrosion rate in miles per year (mpy) and percentage corrosion inhibition efficiency (PCIE) were calculated by using equations 2 and 3 respectively.

$$\text{Corrosion Rate} = \frac{534 \text{X W}}{\text{DAT}} \qquad [2]$$

Where, W = weight loss (in mg), D = density of mild steel (in g/cm^3), A = area of coupon (in sq. inch), T = exposure time (in hour).

$$\text{Percentage Corrosion Inhibition Efficiency} = \frac{\text{CRo} - \text{CR}}{\text{CRo}} \text{X} 100 \qquad [3]$$

Where, CR_o = corrosion rate in absence of inhibitor and CR = corrosion rate in presence of inhibitor.

Salt spray test After exposing the pre-weighted mild steel coupons to VPCI in air thermostat for 24 hours, they were transferred to salt spray chamber having 3.0% NaCl solution maintained at 50°C for duration of 10 days along with blank coupons. After exposing coupons for 10 days, coupons were treated in same manner as treated in weight loss test to remove corrosion products and then CR and PCIE were calculated.

Sulphurdioxide test SO$_2$ test was carried out on the mild steel coupons as in weight loss test. SO$_2$ gas was prepared by dissolving 0.04g of sodium thiosulphate in 30mL aqueous solution of 1.0% NH$_4$Cl and 1.0% Na$_2$SO$_4$ solution and 0.5mL of 1.0N H$_2$SO$_4$ was added to the flask. Initially pre-weighed and mechanically polished mild steel coupons were placed in air thermostat maintained at 50°C for duration of 10 days. Definite weight of VPCIs in a petridis and flask, which is the source of SO$_2$, was placed in the isolated chambers of air thermostat containing mild steel coupons. After exposing coupons for 10 days, CR and PCIE were calculated.

Metallurgical research microscopy This test was employed for the surface study of mild steel coupons to know about nature and type of corrosion. Micrographs of the corroded specimen treated with investigated VPCI were subjected to porosity study and morphology of surface which provided the information about the number of pores, size of pores, percentage porosity and the area covered by the pores on the surface of specimen. Percentage porosity (PP) and total objects (TO) shows the roughness of surface. On the other hand maximum perimeter and maximum area object ratio (A/O) provide the information about the size and depth of the pores on the surface of mild steel after the corrosion test.

Scanning electron microscopy Morphology of the selected samples was observed by scanning electron microscopy (SEM) to provide the evidence in support of type of corrosion. In this technique, the sample was studied at different resolutions on the different spots on the mild steel coupons for complete information about the inhibition mechanism.
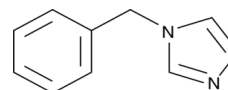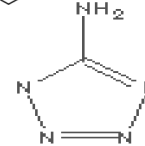
III. RESULTS & DISCUSSION

Thiourea is a suitable vapour phase corrosion inhibitor due the presence of two lone pair donar N atoms and one S atom which provide it specific groups by which it can be easily adhere on the surface of metal and form barrier layer on the surface of metal for the water vapours and for aggressive corrodents of the atmosphere around the mild steel coupons. On the other hand, due to Lewis acid- base concept, presence of three lone pair donar group groups and π electrons in thiourea molecule enhance its basic strength, but upto a limit, due to which it can easily neutralize the acidic environment around metal coupons. But due to very low vapour density, ability of thiourea to alter the aggressiveness of environment is poor and its percentage corrosion inhibition efficiency (PCIE) is less than 60%. To increase PCIE of Thiourea, synergistic effect of thiourea was tested with N-Ethylaniline, 1-Benzylimidazole and 5-Aminotetrazole due to presence of adsorption attacking site like lone pair donar atoms and π electrons system in the structures of these amines as shown in Table I.

Table I. **Molecular Formula and Structures of Vapour Phase Corrosion Inhibitors**

S.N.	Name of VPCI	Molecular Formula	Structure
1.	Thiourea	$(C_1H_4N_2S_1)$	$H_2N - C - NH_2$ with S double bonded to C
2.	N-Ethylaniline	$(C_8H_{11}N_1)$	$NH - C_2H_5$ on benzene ring

3.	1-Benzylimidazole	$(C_{10}H_{10}N_2)$

4.	5-Aminotetrazole	$(C_1H_3N_5)$

Vapour Pressure Determination Test

Vapour pressure of combinations of TU with different amines are given in Table II.

Table II. **Vapour Pressures of Combinations of TU with Amines**

Combinations of VPCIs	Vapour Pressure (mmHg)
Thiourea	10.48×10^{-3}
Thiourea + N-Ethylaniline	79.24×10^{-3}
Thiourea + 1-Benzylimidazole	55.88×10^{-3}
Thiourea + 5-Aminotetrazole	58.99×10^{-3}

Weight Loss Test

Results of this test are given in Table III which clearly showing the synergistic effect of TU with aromatic amines due to increase in specific sites for the adsorption of VPCIs. TU is performed as very efficient VPCI with the combination of BIZ because PCIE of combination is more than that of both in which PCIE exceeds from 51.81% (TU) and 64.90% (BIZ) (35). PCIE of the different combinations with TU is in following order:

<p align="center">TU+BIZ > TU+NEA > TU+ATZ</p>

Table III. Weight loss, Corrosion Rate and Percentage Corrosion Inhibition Efficiency of Thiourea with VPCIs obtained from weight loss method for mild steel at 50ºC after 10 days of exposure

Combinations of VPCI	Weight Loss ($\times 10^{-1}$mg)	CR ($\times 10^{-4}$mpy)	PCIE
Blank	148	51	-
Thiourea	72	24.8	51.81
Thiourea + N-Ethylaniline	38	13.1	75.31
Thiourea + 1-Benzylimidazole	28	9.7	80.98
Thiourea + 5-Aminotetrazole	40	13.8	72.94

TU show high PCIE in the combination with 1-BIZ due to presence of two lone pair donar N atom and presence of two π electrons system. Presence of strong +I effect of ethyl group near lone pair donar N atom in 1-BIZ enhance the Lewis basic strength to form layer of acid base complex on surface of mild steel coupon and to neutralize the acidic environment of atmosphere around coupon. In remaining, TU+ATZ having five lone pair donar atom show less PCIE than TU+NEA because in ATZ lone pair of N atom show delocalization and behave like a system of π electrons not as high degree of lone pair donar attacking site (Figure 1). After adsorption of ATZ on coupon, some basic amine group still remain free to react with acidic corrodent of atmosphere and form salt which penetrate the barrier film of VPCI on coupon.
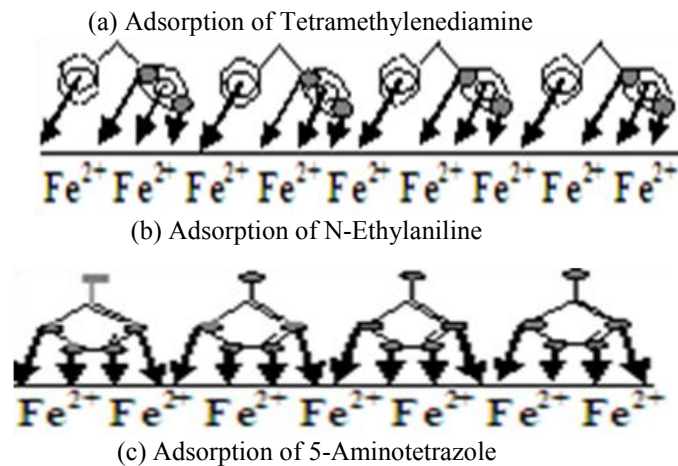
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(a) Adsorption of Tetramethylenediamine

(b) Adsorption of N-Ethylaniline

(c) Adsorption of 5-Aminotetrazole
Figure 1. **Adsorption Mechanism of Combinations of TU on Mild Steel**

Salt Spray Test

Effect of direct spray of chloride ions on the mild steel coupon can be easily explained by the PCIE in this test which are given in Table IV. Due to direct contact of NaCl salt on the surface and its hydrolysis products accelerate the corrosion rate due to which PCIE is little but a low than that of weight loss method. It is shown that PCIE of different combinations of VPCI with TU is in order:

TU+BIZ > TU+NEA > TU+ATZ

Table IV. Weight loss, CR and PCIE of Thiourea with VPCIs obtained from Salt Spray Test for mild steel at 50ºC after 10 days of exposure.

Combinations of VPCI	Weight Loss ($\times 10^{-1}$mg)	CR ($\times 10^{-4}$mpy)	PCIE
Blank	102	35.1	-
Thiourea	49	16.9	51.42
Thiourea + N-Ethylaniline	41	14.1	59.83
Thiourea + 1-Benzylimidazole	37	12.8	63.53
Thiourea + 5-Aminotetrazole	46	15.9	54.70

From low PCIE in this test, it is concluded that the presence of the corrodent combination provide the synergistic effect to accelerate the corrosion rate for the metal. Chloride ions in aqueous condition provide the mechanism of penetration of barrier protection film on the metallic surface and initiate the pitting corrosion. Presence of CO_2 accelerates the rate of corrosion due to formation of carbonic acid and salt of carbonates. This mechanism of the effect of chloride ions and CO_2 is explained in the Figure 2 which also provides the overview of the survey of literature. Mechanism and type of corrosion on mild steel in presence of chloride ion is supported by results of metallurgical research microscopy and SEM as given in Table V and Figure 3 respectively.
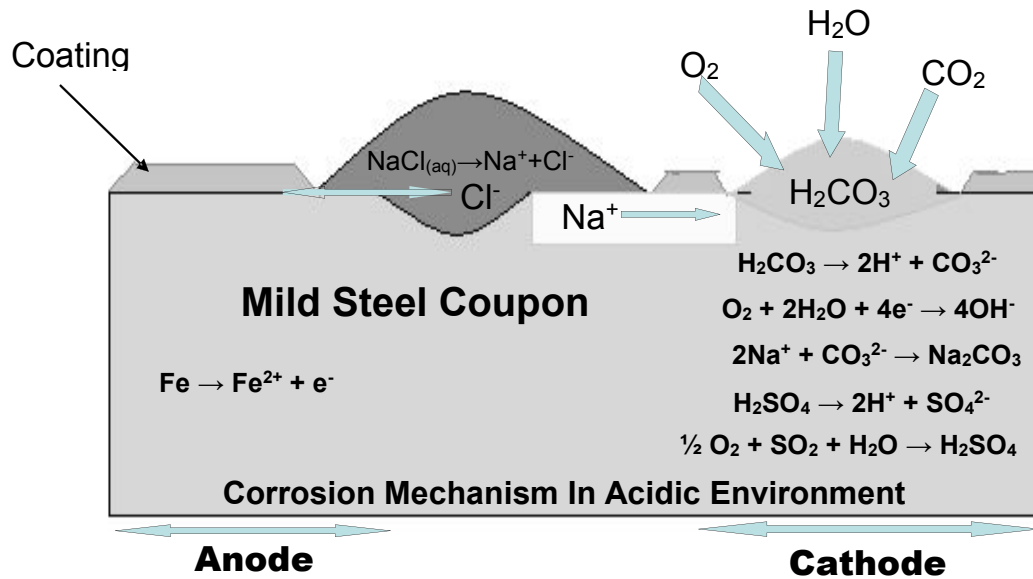
Figure 2. Mechanism of Corrosion showing the effect of NaCl, H_2O and CO_2 on Mild Steel Surface.

Table V. **Results of Metallurgical Research Microscopy of Coupon in NaCl Environment**

Morphological Parameters	Result	Micrograph
Total Objects (TO)	5278	
Percentage Porosity (PP)	11.89	
Maximum Perimetre (MP)	4392.1623 μ	
Maximum Area (MA)	26513.4058 $μ^2$	

In salt spray test, percentage porosity (11.89%) and numbers of pores (5278) are very high due to direct spray of salt on surface of coupon. In this test, perimeter of pore (4392.1623μ) and A/O ratio are very high due to large size and high depth of pores respectively. Morphological results and porosity of metallurgical research microcopy provide the evidence of penetration of adsorbed barrier layer of VPCI on mild steel coupon by the synergistic corroding effect of chloride ion with different corrodents of atmosphere and crevice type of corrosion which is further confirmed by the SEM images of coupon at high resolution (x2700) as shown in Figure 3.
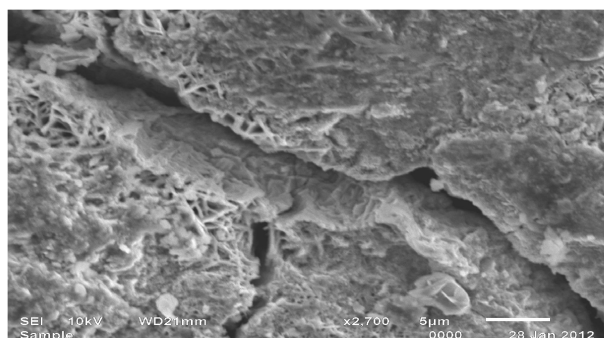

Figure 3. SEM of Mild Steel Coupon treated in Salt Spray Test

Sulphurdioxide Test

Results of this test are clearly showing the synergistic effect of TU in which PCIE of TU in the combination are good as compared with the individual performance as shown in Table VI.

Table VI. Weight loss, CR and PCIE of Thiourea with VPCIs obtained from Sulphurdioxide Test for mild steel at 50ºC after 10 days of exposure.

Combinations of VPCI	Weight Loss ($×10^{-1}$mg)	CR ($×10^{-4}$mpy)	PCIE

Blank	152	52.4	-
Thiourea	66	22.8	55.76
Thiourea + N-Ethylaniline	52	17.9	65.84
Thiourea + 1-Benzylimidazole	33	11.4	78.24
Thiourea + 5-Aminotetrazole	58	20	61.83

Effect of acidic environment and synergistic corroding effect of sulphate ion with different environment corroding components can be easily shown by the low PCIE of combinations of TU in Sulphurdioxide environment. Presence of free basic functional group (in NEA) reduce the inhibition action of VPCI by reacting with acid to form salt which accelerate the destruction of barrier layer of VPCI on mild steel coupon. On the other basic strength of VPCI enhance the corrosion inhibition property of VPCI by neutralizing the acidic environment. From the Table VI, it is shown that PCIE of different combinations of VPCI with TU is in order:

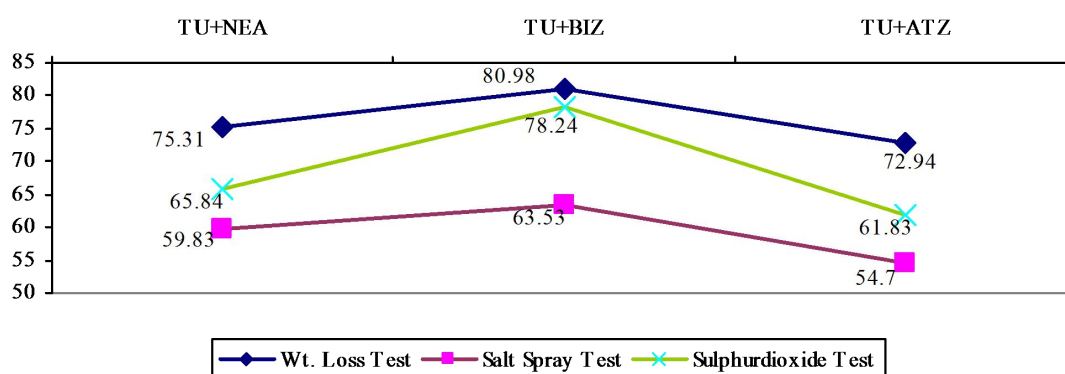<p align="center">TU+1-BIZ > TU+NEA > TU+5-ATZ</p>

Figure 4. Comparison of PCIE of different tested combinations in all tests performed.

By results of combinations of TU with different VPCIs in weight loss method, salt spray method and SO$_2$ test, it is clear that TU perform as very good VPCI with combination of amines for mild steel under atmospheric corrosion. From Figure 4, it is shown that in combination of TU with 1-BIZ, vapour pressure rises to a level of best performance by which vapours saturate the atmosphere around the metals, easily adsorbed on surface of mild steel to form protective covering for the corrodents, retard the rate of corrosion and protect the mild steel from corrosion. Mechanism of adsorption and surface area covered of mild steel by VPCI also affect the inhibition property of combinations.

IV. CONCLUSION

As a result of experimental work carried out on the performance of investigated vapour phase corrosion inhibitors, a deep analysis of corrosion parameters obtained by corrosion testing experiments, morphology of mild steel coupon show that TU perform excellent corrosion inhibition properties against the aggressive environments of SO$_2$ and NaCl at high relative humidity and high temperature. From the experimental study it is concluded that

a)   Due to rise in vapour pressure of TU with combinations of amines, rate of adsorption of combinations on mild steel coupon is increased by which combination form barrier layer on mild steel easily and protect mild steel from corrodents of environments.

b)   Presence of two lone pair donar atoms in 1-BIZ molecules increase the basic strength of combinations by which it can easily neutralize the acidic character of environment around mild steel coupon and retard the CR.

c)   Presence of alkyl group near the lone pair donar atom in BIZ enhance the basic strength due to +I effect and protect the mild steel easily by neutralize of acidic environment.

d)   Presence of π-electrons in NEA, BIZ and ATZ provides the adsorption system to form barrier on mild steel coupon for atmospheric corrodents.

e)   Presence of aggressive chloride ions penetrate the barrier layer and decrease the PCIE of VPCIs.

f)   Direct contact of sulphate ions and presence of free basic functional group in VPCI molecule also reduce the PCIE of VPCIs.

g) Metallurgical research microscopy results and SEM images of coupon in salt spray test provide evidence of destruction of barrier layer and crevice type of corrosion in NaCl environment respectively.

V. ACKNOWLEDGEMENT

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