

Augmentation of Corrosion Inhibition Property of Thiourea by Aliphatic Amines in presence of aggressive Cl^- ions and acidic SO_2 environment

ABSTRACT

With the growth of industrialization and modernization, it has now become essential for any country to construct and develop the basic infrastructure like highways, high speed rails, metro trains, bridges, schools, colleges, hospitals, strong air vehicle network etc. Development of these basic requisites has created a strong demand for production of steel. And we are doing so. We are now 4th largest steel producer in world. But production of steel and its products is only one step towards a sustained growth. We are facing strong challenges in maintaining the quality of steel products. Atmospheric corrosion of almost all parts of these structural elements can cause serious losses to lives, a great loss of money and times as well. 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. Corrosion inhibition property of Thiourea is tested with aliphatic amines i.e. 1,3-Diaminopropane, N,N,N,N-Tetramethylethylenediamine and Ethylamine for mild steel in different aggressive atmospheric conditions of chloride ions and sulphurdioxide by Vapour pressure determination test, Weight loss test, Salt spray test and Sulphur dioxide test at 50°C. It is found that percentage corrosion inhibition efficiency of combinations are in order of Thiourea+N,N,N,N-Tetramethylethylenediamine > Thiourea+Ethylamine > Thiourea+1,3-Diaminopropane. Chloride ions affect the barrier layer of corrosion inhibitor on surface of mild steel coupon and produce porosity on mild steel surface. Mechanism of action of corrosion inhibitors and effect of aggressive corrodent on the surface of mild steel are supported by morphology of mild steel studied by Metallurgical research microscopy and Scanning electron microscopy. Results of scanning electron microscopy provide the evidence of crevice corrosion, formation of barrier layer of vapours of vapour phase corrosion inhibitors and penetration of that barrier layer by chloride ions on mild steel surface. It is found that percentage corrosion inhibition efficiency of Thiourea + N,N,N,N-Tetramethylethylenediamine is very high (80.98%) in weight loss test but become little bit low in NaCl and sulphurdioxide environments by aggressive action of chloride and sulphate ions respectively.

Key Words: Thiourea, Aliphatic amines, Weight loss test, Vapour phase corrosion inhibitor, Salt spray test, Sulphurdioxide test, Metallurgical research microscopy.

1. INTRODUCTION

Atmospheric Corrosion, though not a separate form of corrosion, has received considerable attention because of the staggering associated costs that result [1-7]. 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.

Corvo [8] and Moricelli et al. [9] studied the relationship between chloride ion concentrations with corrosion rate in atmospheric conditions. Ericsson showed that NaCl can cause corrosion at very low concentration because it can induce corrosion by SO₂ on a carbon steel surface [10]. NaCl can enhance 14 times rate of corrosion by SO₂ at 90% relative humidity at 22°C. In another report of Blucher et al., they have investigated adverse effect of CO₂ on corrosion of aluminium [11]. Vuorinen et al. and a list of authors have worked on organic compounds as vapour phase corrosion inhibitors (VPCI). Organic substances have been studied as VPCI for mild steel were morpholine derivatives and diamino hexane derivatives [12], fatty acid thiosemicarbazides [13], cyclohexylamine and dicyclohexylamine [14-15], amine carboxylates [16], diethyl ammonia caprylate [17], ammonium caprylate [18], benzoic hydrazide derivatives [19], polyamines [20], bis-piperidiniummethyl-urea and β-amino alcoholic compounds [21]. Apart from organic substances, natural compounds like wood bark oil [22] and thyme [23-24] have also been used as VPCIs. Cano et al. recently have proposed mechanism of inhibition of dicyclohexamine nitrite and dicyclohexamine isonitrite against corrosion due to vapours of acetic acid and formic acid on carbon steel [25]. Zubielewicz et al studied the electrochemical behavior of mixed anodic inhibitors [26]. Batis et al. evaluated the performance of two primers, first natural rust converter and other on organic primer coating containing VPCI against atmospheric corrosion for reinforcing steel [27]. Lyublinski studied synergistic corrosion management systems by use of corrosion inhibitors [28].

In continuation to our earlier study [29-36], in the present study, the inhibiting properties of Thiourea (TU) was investigated with aliphatic 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, SO₂ test, Metallurgical research microcopy and Scanning electron microscopy.

2. MATERIAL AND METHODS

2.1. 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.

2.2. Equipments

2.2.1. Weighing balance- Single pan analytical balance, Precision 0.01mg, Model AB 135-S/FACT, Source Mettler Toledo, Japan.

2.2.2. 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.

2.2.3. 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.

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

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

2.2.6. Scanning electron micrograph- JEOL 5900 LV.

2.3. Methods-

2.3.1. 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.

$$P = \frac{W}{AT} \sqrt{\frac{2 \pi RT}{M}} \quad \text{eq.[1]}$$

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 ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$).

2.3.2. Weight loss test³³

2.3.3. Salt spray test³³

2.3.4. Sulphurdioxide test³³

2.3.5. Metallurgical research microscopy (MRM)- This test was employed for the surface study of mild steel coupons to know about nature and type of corrosion. Micrograph of mild steel coupon 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 coupon. 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.

2.3.6. Scanning electron microscopy (SEM)³³

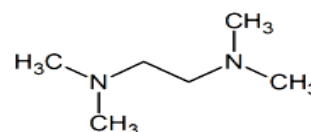
3. RESULTS AND DISCUSSION

Combinations of thiourea with 1, 3- Diaminopropane, N,N,N,N-Tetramethylethylenediamine and Ethylamine are tested 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 1.

Table 1. Molecular formula and structures of vapour phase corrosion inhibitors

Name of VPCI	Molecular formula	Structure
Thiourea	($\text{C}_1\text{H}_4\text{N}_2\text{S}_1$)	$\begin{array}{c} \text{S} \\ \\ \text{H}_2\text{N} - \text{C} - \text{NH}_2 \end{array}$
1, 3-Diaminopropane	($\text{C}_3\text{H}_{10}\text{N}_2$)	$\text{H}_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$

N,N,N,N-Tetramethylethylenediamine (C₆H₁₆N₂)



Ethylamine

(C₂H₇N₁)

CH₃-CH₂-NH₂

**Basis of selection of chemicals as VPCI is presence of lone pair donar atom and vapour pressure at high temperature*

3.1. Vapour pressure determination test- Vapour pressures of combinations of thiourea with different amines are given in table 2.

Table 2. Vapour pressures of combinations of thiourea with aliphatic amines

Combinations of VPCIs	Vapour Pressure (mmHg)
Thiourea + 1, 3-Diaminopropane	156.27 x 10 ⁻²
Thiourea + N,N,N,N-Tetramethylethylenediamine	134.89 x 10 ⁻²
Thiourea + Ethylamine	79.88 x 10 ⁻²

** Vapour pressure of combinations are calculated by Raoult,s Law of vapour pressure after vapour pressure determination test.*

3.2. Weight loss test- Results of this test are given in table 3 which shows that thiourea perform as an efficient VPCI with all combinations for mild steel in atmospheric corrosion. Weight loss and corrosion rate of combinations are very low as compared to that of thiourea due to increase in vapour pressure and vapour density of the combinations. PCIE of the different combinations is in following order: Thiourea+N,N,N,N-Tetramethylethylenediamine > Thiourea+Ethylamine > Thiourea+1,3-Diaminopropane. Thiourea + N,N,N,N-Tetramethylethylenediamine show very high percentage corrosion inhibition efficiency due to presence of strong +I effect of four methyl groups near lone pair donar N atom which 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 as shown in figure 1. In Thiourea + Ethylamine, Ethylamine form compact layer on mild steel surface by chemical adsorption and cover surface uniformly to form barrier layer for atmospheric corrodents. Secondly, presence of four free methyl groups in N,N,N,N-Tetramethylethylenediamine and ethyl group in ethylamine provide barrier for water contents of atmosphere to lower their electrochemical action by their hydrophobic nature.

Table 3. Weight loss, corrosion rate and percentage corrosion inhibition efficiency of thiourea and its combinations obtained from weight loss method for mild steel

Combinations of VPCI	Wt. loss (x10 ⁻¹ mg) CR (x10 ⁻⁴ mpy) PCIE
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Blank	148	51	-
Thiourea+1,3-Diaminopropane	37	12.7	75.1
Thiourea+N,N,N,N-Tetramethylethylenediamine	28	9.7	80.98
Thiourea + Ethylamine	32	11	78.43

* Study of mild steel coupons for corrosion rate calculation were carried out after 10 days exposure of atmospheric corrosents at 50°C.

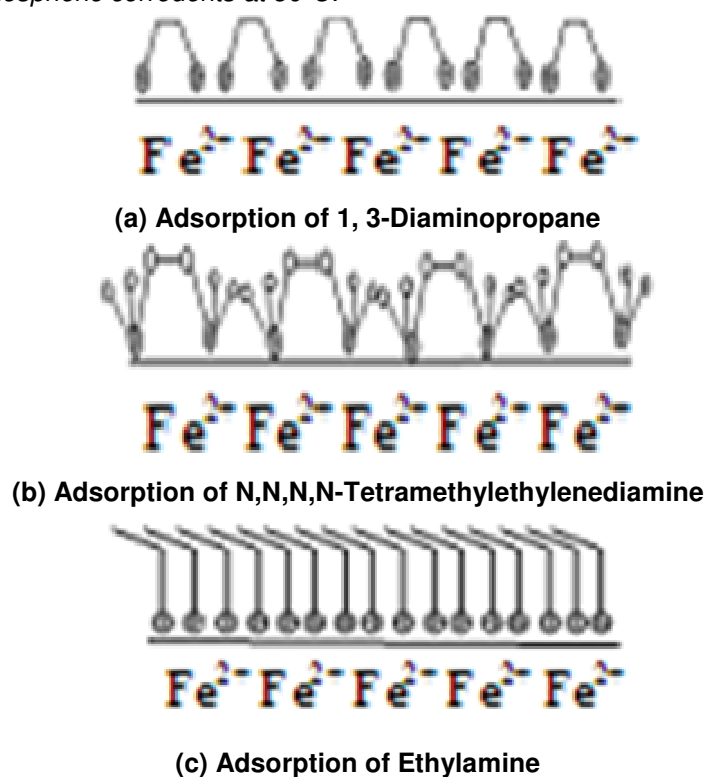


Figure 1. Adsorption mechanism of combinations of thiourea on mild steel

3.3. Salt spray test- Direct contact of NaCl salt on the surface of mild steel coupon and its hydrolysis products accelerate the corrosion rate due to which percentage corrosion inhibition efficiency is little bit a low than that of weight loss test as shown in table 4.

Table 4. Weight loss, corrosion rate and percentage corrosion inhibition efficiency of thiourea and its combinations obtained from salt spray test for mild steel

Combinations of VPCI	Wt. loss ($\times 10^{-1}$ mg)	CR ($\times 10^{-4}$ mpy)	PCIE
Blank	102	35.1	-
Thiourea+1,3-Diaminopropane	42	14.4	58.57
Thiourea+N,N,N,N-Tetramethylethylenediamine	39	13.5	61.54

Thiourea + Ethylamine	40	13.8	60.68
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** Study of mild steel coupons for corrosion rate calculation were carried out after 10 days exposure of 3% NaCl solution in salt spray chamber at 50°C.*

To determine the effect of salt hydrolysis product and type of corrosion on mild steel in presence of chloride ion is studied by morphology of mild steel coupon with the help of metallurgical research microscopy which are given in figure 2 and table 5.



Figure 2. Micrograph of mild steel coupon treated in salt spray test

Table 5. Results of metallurgical research microscopy of mild steel coupon in NaCl environmentt

Morphological parameters	Result
Total Objects (TO)	7036
Percentage Porosity (PP)	10.27
Maximum Perimetre (MP)	3067.0276μ
Maximum Area (MA)	19465.6391μ ²

In salt spray test, percentage porosity (10.27%) and numbers of pores (7036) are very high due to direct spray of salt on surface of coupon. In this test, perimeter of pore (3067.0276μ) and A/O ratio are very high due to large size and high depth of pores respectively. Morphological results and porosity of metallurgical research microscopy provide the evidence of presence of porosity and barrier layer of VPCI on mild steel coupon which is further confirmed by the SEM image of mild steel coupon at high resolution (x4300) as shown in figure 3 which clearly indicate the crevice type of corrosion in NaCl environment on mild steel coupon.

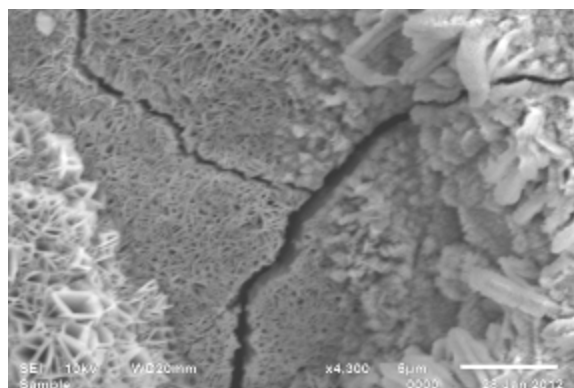


Figure 3. SEM of mild steel coupon treated in NaCl environment

3.4. Sulphurdioxide test- Results of effect of acidic nature of sulphurdioxide on mild steel coupon is given in table 6.

Table 6. Weight loss, corrosion rate and percentage corrosion inhibition efficiency of thiourea and its combinations obtained from sulphurdioxide test for mild steel

Combinations of VPCI	Wt. loss ($\times 10^{-1}$ mg)	CR ($\times 10^{-4}$ mpy)	PCIE
Blank	152	52.4	-
Thiourea+1,3-Diaminopropane	51	17.6	66.41
Thiourea+N,N,N,N-Tetramethylethylenediamine	45	15.5	70.42
Thiourea + Ethylamine	42	14.5	72.33

** Study of mild steel coupons for corrosion rate calculation were carried out after 10 days exposure of SO₂ gas at 50°C.*

By results of combinations of thiourea with different aliphatic amines in weight loss test, salt spray test and SO₂ test, it is clear that in combinations, vapour pressure rises to a level of best performance by which vapours can easily neutralized the acidity of environments due to their basic strength, saturated the atmosphere around the mild steel coupon by its vapours, 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.

4. CONCLUSIONS

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 and morphology of mild steel coupon show that all combinations of thiourea with aliphatic amines perform excellent corrosion inhibition property against the aggressive environments of SO₂ and NaCl at high relative humidity and high temperature. From the experimental study it is concluded that

1. Due to rise in vapour pressure of thiourea 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 corrosive environments.
2. Presence of two lone pair donor N atoms in N,N,N,N-Tetramethylethylenediamine and 1,3-Diaminopropane 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 corrosion rate.
3. Presence of alkyl group near the lone pair donor atom in N,N,N,N-Tetramethylethylenediamine and Ethylamine enhance the basic strength due to +I effect and protect the mild steel easily by neutralization of acidic environment.
4. Presence of aggressive chloride ions penetrate the barrier layer and decrease the percentage corrosion inhibition efficiency of vapour phase corrosion inhibitors.
5. Direct contact of sulphate ions and presence of free basic functional group in VPCI molecule also reduce the percentage corrosion inhibition efficiency of vapour phase corrosion inhibitors.
6. Results of metallurgical research microscopy and SEM of mild steel coupon in salt spray test provide evidence of destruction of barrier layer and crevice type of corrosion in NaCl environment.

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