Augmentation of Corrosion Inhibition Property of Thiourea by Aliphatic Amines in Presence of Aggressive Cl\(^-\) ions and Acidic SO\(_2\) Environment

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**Authors’ contributions**

This work was carried out in collaboration between all authors. Authors VS and HK designed the study and wrote the protocol. Author VS preformed the statistical analysis, managed the literature search and wrote the first draft of the manuscript with assistance from author SKS. All authors read and approved the final manuscript.

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**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
SO NaCl can enhance 14 times rate of corrosion by corrosion by SO at very low concentration because it can induce Ericsson showed that NaCl can cause corrosion with corrosion rate in atmospheric conditions. Corvo [4] and Moricelli et al. [5] studied the relationship between chloride ion concentrations and 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-Tetramethylene diamine > 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 microcopy 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-Tetramethylene diamine 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.

**Keywords:** Thiourea; aliphatic amines; weight loss test; VPCI; salt spray test; SO2 test.

1. INTRODUCTION

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 [1-3].

Corvo [4] and Moricelli et al. [5] 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 [6]. NaCl can enhance 14 times rate of corrosion by SO2 at 90% relative humidity at 22°C. In another report of Bluher et al., they have investigated adverse effect of CO2 on corrosion of aluminium [7]. Vuorinen et al. [8] 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 diaminohexane derivatives, fatty acid thiosemicarbazides [9], cyclohexylamine and dicyclohexylamine [10,11], amine carboxylates [12], diethyl ammonia caprylate [13], ammonium caprylate [14], benzoic hydrazide derivatives [15], polyamines [16], bis-piperidiniummethyl-urea and β-amino alcoholic compounds [17]. Apart from organic substances, natural compounds like wood bark oil [18] and thyme [19,20] have also been used as VPCIs. Cano et al. recently have proposed mechanism of inhibition of dicyclohexamine nitrite and dicyclohexamineisonitrite against corrosion due to vapours of acetic acid and formic acid on carbon steel [21]. Zubielewicz et al. [22] studied the electrochemical behavior of mixed anodic inhibitors. Batis et al. [23] evaluated the performance of two primers, first natural rust converter and other on organic primer coating containing VPCI against atmospheric corrosion for reinforcing steel. Lyublinski studied synergistic corrosion management systems by use of corrosion inhibitors [24]. It has been reported in the literature that the corrosion inhibition efficiency of the mixed vapour phase corrosion inhibitors is significantly increased in comparison to that of individual inhibitors in a corroding system [25]. Influence of combinations of sodium dodecyl sulphate-Zn2+ -HEDP system towards corrosion inhibition of carbon steel was studied by Rajendran et al. [26] and found that this combination gave synergistic effect and provides complete protection in low chloride ion water. Venugopalan et al. [27] studied effects of HEDP, gluconate and zinc on the corrosion inhibition of carbon steel. They developed this ternary inhibitor formulation for carbon steel,
which acts synergistically and gives maximum protection towards corrosion for carbon steel. Similar synergistic effects of HEDP with other combinations have been reported in the literature [28-31].

In continuation to our earlier study [32-39], 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, SO\text{2} test, Metallurgical research microscopy and Scanning electron microscopy.

2. MATERIALS AND METHODS

2.1 Materials

2.1.1 Mild steel

(ASTM-283) coupons of dimensions 3.5 cm × 1.5 cm × 0.025 cm 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.

2.1.2 N,N,N,N-Tetramethylethylenediamine


2.1.3 1,3-Diaminopropane


2.1.4 Ethylamine

Min. assay 99.0%, Grade A.R., Source Qualigens Fine Chemicals Mumbai.

2.1.5 Ammonium chloride


2.1.6 Sodium thiosulphate (anhydrous)


2.1.7 Ehanol

Minimum assay 99.9%, Molecular weight 46.08, Grade A.R., Source Changsu Yangyuan Chemical Ltd. China.

2.1.8 Thiourea

Min. assay 99.0%, Grade A.R., Source nice Chemica Pvt. Ltd. Chochin.

2.1.9 Acetone


2.1.10 Sodium sulphate (anhydrous)


2.1.11 Sodium chloride


Triply distilled water (conductivity < 1 x 10^{-6} ohm^{-1} cm^{-1}) and sulphuric acid were also used to make solutions and washing of metallic specimens.

2.2 Equipments

2.2.1 Weighing balance

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

2.2.2 Humidity chamber


2.2.3 Salt spray chamber

Thermotech. TIC-4000N Temperature Controller, Pumping system Pt-100, AC Frequency 50-60Hz, Max. voltage 300 V, 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.
2.3 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.

\[ P = \frac{W}{At} \sqrt{\frac{2 \pi RT}{M}} \]  

(1)

Where, \( P \) = vapour pressure of tested inhibitor (mmHg), \( A \) = area of orifice of capillary (m²), \( t \) = time of exposure of vapours of tested inhibitor on mild steel coupon (sec.), \( W \) = weight loss of tested inhibitor (kg) in \( t \) time of exposure, \( T \) = temperature (K), \( M \) = molecular mass of the tested inhibitor (kg) and \( R \) = gas constant (8.314 JK⁻¹mol⁻¹).

2.3.2 Weight loss test

Mild steel coupons were mechanically polished successively with the help of emery papers grading 100, 200, 300, 400 and 600 µ 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.

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

(2)

Where, \( W \) = weight loss of mild steel coupon in 10 days of experiment (in mg), \( D \) = density of mild steel (in g/cm³), \( A \) = area of mild steel coupon (in sq. inch), \( T \) = exposure time of vapours of tested inhibitor on mild steel coupon (in hour).

\[ \text{PCIE} = \frac{CR_o - CR}{CR_o} \times 100 \]  

(3)

Where, PCIE = Percentage corrosion inhibition efficiency, \( CR_o \) = corrosion rate in absence of inhibitor and \( CR \) = corrosion rate in presence of inhibitor.

2.3.3 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.

2.3.4 Sulphurdioxide test

SO₂ test was carried out on the mild steel coupons as in weight loss test. SO₂ gas was prepared by dissolving 0.04 g of sodium thiosulphate in 30 mL aqueous solution of 1.0% NH₄Cl and 1.0% Na₂SO₄ solution and 0.5 mL of 1.0N H₂SO₄ was added to the flask. Initially pre-weighted 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 SO₂, was placed in the isolated chambers of air thermostat containing mild steel coupons. After exposing coupons for 10 days, CR and PCIE were calculated.

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)

Morphology of the selected samples was observed by Scanning Electron Microscopy 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.

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 around coupon as shown in Fig. 1. In Thiourea + Ethylamine, Ethylamine form compact layer on surface which provided the information about the size and depth of the pores on the surface of mild steel after the corrosion test.

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

<table>
<thead>
<tr>
<th>Name of VPCI</th>
<th>Molecular formula</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiourea</td>
<td>(C₅H₈N₂S₂)</td>
<td></td>
</tr>
<tr>
<td>1, 3-Diaminopropane</td>
<td>(C₃H₁₂N₂)</td>
<td></td>
</tr>
<tr>
<td>N,N,N,N-Tetramethylethylenediamine</td>
<td>(C₈H₁₈N₂)</td>
<td></td>
</tr>
<tr>
<td>Ethylamine</td>
<td>(C₂H₅N)</td>
<td></td>
</tr>
</tbody>
</table>

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

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

<table>
<thead>
<tr>
<th>Combinations of VPCIs</th>
<th>Vapour pressure (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiourea</td>
<td>10.48 x 10⁻²</td>
</tr>
<tr>
<td>Thiourea + 1, 3-Diaminopropane</td>
<td>156.27 x 10⁻²</td>
</tr>
<tr>
<td>Thiourea + N,N,N,N-Tetramethylethylenediamine</td>
<td>134.89 x 10⁻²</td>
</tr>
<tr>
<td>Thiourea + Ethylamine</td>
<td>79.88 x 10⁻²</td>
</tr>
</tbody>
</table>

* Vapour pressure of combinations are calculated by Raoult’s Law of vapour pressure after vapour pressure determination test.
mild steel surface by chemical adsorption and cover surface uniformly to form barrier layer for atmospheric corrodernts. 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.

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.

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 Fig. 2 and Table 5.

Table 3. Weight loss, corrosion rate and percentage corrosion inhibition efficiency of combinations of vapour phase corrosion inhibitors obtained from weight loss method

<table>
<thead>
<tr>
<th>Combinations of VPCI</th>
<th>Wt. loss (×10⁻¹ mg)</th>
<th>CR (×10⁻⁴ mpy)</th>
<th>PCIE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>148</td>
<td>51</td>
<td>-</td>
</tr>
<tr>
<td>Thiourea</td>
<td>72</td>
<td>25</td>
<td>51.81</td>
</tr>
<tr>
<td>Thiourea+1,3-Diaminopropane</td>
<td>37</td>
<td>12.7</td>
<td>75.1</td>
</tr>
<tr>
<td>Thiourea+N,N,N,N-Tetramethylethylenediamine</td>
<td>28</td>
<td>9.7</td>
<td>80.98</td>
</tr>
<tr>
<td>Thiourea + Ethylamine</td>
<td>32</td>
<td>11</td>
<td>78.43</td>
</tr>
</tbody>
</table>

*Study of mild steel coupons for corrosion rate calculation were carried out after 10 days exposure of atmospheric corrodernts at 50°C. Blank is mild steel coupon untreated with any VPCI before corrosion testing.

Table 4. Weight loss, corrosion rate and percentage corrosion inhibition efficiency of combinations of vapour phase corrosion inhibitors obtained from salt spray test

<table>
<thead>
<tr>
<th>Combinations of VPCI</th>
<th>Wt. loss (×10⁻¹ mg)</th>
<th>CR (×10⁻⁴ mpy)</th>
<th>PCIE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>102</td>
<td>35.1</td>
<td>-</td>
</tr>
<tr>
<td>Thiourea</td>
<td>49</td>
<td>16.8</td>
<td>51.85</td>
</tr>
<tr>
<td>Thiourea+1,3-Diaminopropane</td>
<td>42</td>
<td>14.4</td>
<td>58.57</td>
</tr>
<tr>
<td>Thiourea+N,N,N,N-Tetramethylethylenediamine</td>
<td>39</td>
<td>13.5</td>
<td>61.54</td>
</tr>
<tr>
<td>Thiourea + Ethylamine</td>
<td>40</td>
<td>13.8</td>
<td>60.68</td>
</tr>
</tbody>
</table>

*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.

Table 5. Results of metallurgical research microscopy of coupon in NaCl environment

<table>
<thead>
<tr>
<th>Morphological parameters</th>
<th>Blank coupon</th>
<th>Coupon treated with VPCI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Objects (TO)</td>
<td>13380</td>
<td>7036</td>
</tr>
<tr>
<td>Percentage Porosity (PP)</td>
<td>69.94</td>
<td>10.27</td>
</tr>
<tr>
<td>Maximum Perimeter (MP)</td>
<td>52323.4375μ</td>
<td>3067.0276μ</td>
</tr>
<tr>
<td>Maximum Area (MA)</td>
<td>1096879.5014μ²</td>
<td>19465.6391μ²</td>
</tr>
</tbody>
</table>

* Minimum perimeter of pore on mild steel coupon studied by MRM is 10.5263μ
In salt spray test, percentage porosity (69.94%), numbers of pores (13380) and the porous area (1096879.5014µ²) on the mild steel surface are high due to corrosive action of direct exposure of chloride ions on the surface of mild steel coupon. In this test, perimeter of pore (52323.4375µ) and A/O ratio are high due to large size and high depth of pores respectively. On the other hand low percentage porosity (10.27%), less numbers of pores (7036) and low porous surface area of mild steel coupon treated with VPCI provide the effectiveness of VPCI against the corrosive environment of Cl⁻. 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 images of blank coupon and mild steel coupon treated with VPCI at high resolution as shown in Fig. 3. Results of SEM clearly indicate the crevice type of corrosion in NaCl environment on mild steel coupon.

### 3.4 Sulphurdioxide Test

Results of effect of acidic nature of sulphurdioxide on mild steel coupon are given in Table 6.

<table>
<thead>
<tr>
<th>Combinations of VPCI</th>
<th>Wt. loss (×10⁻⁷mg)</th>
<th>CR (×10⁻⁴mpy)</th>
<th>PCIE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>152</td>
<td>52.4</td>
<td>-</td>
</tr>
<tr>
<td>Thiourea</td>
<td>66</td>
<td>22.7</td>
<td>56.67</td>
</tr>
<tr>
<td>Thiourea+1,3-Diaminopropane</td>
<td>51</td>
<td>17.6</td>
<td>66.41</td>
</tr>
<tr>
<td>Thiourea+N,N,N,N-Tetramethylethylenediamine</td>
<td>45</td>
<td>15.5</td>
<td>70.42</td>
</tr>
<tr>
<td>Thiourea + Ethylamine</td>
<td>42</td>
<td>14.5</td>
<td>72.33</td>
</tr>
</tbody>
</table>

* Study of mild steel coupons for corrosion rate calculation were carried out after 10 days exposure of SO₂ gas
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 perform excellent corrosion inhibition property against the aggressive environments of $\text{SO}_2$ and $\text{NaCl}$ at high relative humidity and high temperature. It is clear that 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. Rate of adsorption of combinations on mild steel coupon is increased due to presence of more lone pair donor sites in the molecule of N,N,N,N-Tetramethylethylenediamine and 1,3-Diaminopropame molecules. High basic strength of vapour phase corrosion inhibitor can easily neutralize the acidic character of environment around mild steel coupon and retard the corrosion rate. Basic strength of molecule is enhanced by $\pm I$ effect in N,N,N,N-Tetramethylethylenediamine and Ethylamine. It is found that Thiourea + N,N,N,N-Tetramethylethylenediamine show very high PCIE (80.98%) in weight loss test. Mechanism of action of corrosion inhibitors and the effect of aggressive corrodents on the surface of mild steel coupon are supported by morphology of mild steel studied by MRM and SEM. Results of MRM and SEM provide evidences of crevice type of corrosion, formation of barrier layer of vapours of VPCI and penetration of that layer by $\text{Cl}^-$ ions on mild steel surface.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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