CHAPTER 2

MATERIALS AND METHODS

Volatile corrosion inhibitors (VCI) were evaluated for mild steel and copper in chloride environment. The VCI compounds have been used both in powder form and as impregnated craft paper. Electrochemical and non-electrochemical methods have been used to test their performance. The film characteristics have been identified by FT-IR spectral analysis.

2.1 VOLATILE CORROSION INHIBITORS

2.1.1 Synthetic Compounds

Three Mannich bases, namely, 1-[(cyclohexylamino)methyl]urea, 3-(cyclohexylamino)propanamide and 4-(cyclohexylamino)butan-2-one were synthesized and taken for investigation as VCI.

Mannich reaction is a multi-component condensation of a primary or secondary amine, a nonenolizable aldehyde and an enolizable carbonyl compound which affords aminomethylated products. Many such reactions were reported in the literature (Noller and Baliah 1948, List 2000, Wolfgang et al 2001 and Raman et al 2004). The volatile corrosion inhibitors were synthesized according to Mannich reaction as detailed below.

Equimolar quantities of cyclohexylamine, formaldehyde and urea undergo multi-component condensation at room temperature with constant stirring to form 1-[(cyclohexylamino)methyl]urea (CMU), which was
separated by filtration, dried and recrystalised with ethanol. For the synthesis of 3-(cyclohexylamino)propanamide (CPA) cyclohexylamine, formaldehyde and acetamide were used. Similarly 4-(cyclohexylamino)butan-2-one (CBO) was synthesized by using cyclohexylamine, formaldehyde and acetone. The molecular formula, molecular weight and structure of the compounds are

1) 1-[(cyclohexylamino)methyl]urea (CMU)
   Molecular formula - C₉H₁₇N₃O
   Molecular weight - 171.24
   Vapour pressure - 4.922 × 10⁻⁵ mmHg.

2) 3-(cyclohexylamino)propanamide (CPA)
   Molecular formula - C₉H₁₈N₂O
   Molecular weight - 170.25
   Vapour pressure - 4.538 × 10⁻⁵ mmHg.

3) 4-(cyclohexylamino)butan-2-one (CBO)
   Molecular formula - C₁₀H₁₉NO
   Molecular weight - 169.26
   Vapour pressure - 4.149 × 10⁻⁵ mmHg.
2.1.2 Natural Compounds

**Thyme:** Thymes vulgar L. plant extract, which is commonly called as thyme. This is reported as effective corrosion inhibitor for mild steel in acid medium (Khamis and Al-Andis 2002, Chetouani and Hammouti 2004). It is known from the sources that among the various constituents present in thyme, thymol is in high percentage (Asfaw et al 2000, Hudaib et al 2002, Hudaib and Aburaj 2007) and is known as effective volatile constituent providing inhibitive action against corrosion. So it is decided to investigate thyme as volatile corrosion inhibitor. The presence of thymol in the sample used for the investigation was confirmed by FT-IR spectral analysis. The molecular formula, molecular weight and molecular structure of thymol are

- **Molecular formula**: \( \text{C}_{10}\text{H}_{14}\text{O} \)
- **Molecular weight**: 150.22
- **Vapour pressure**: \( 4.675 \times 10^{-5} \text{mmHg} \)

**Menthol:** The commercially available natural menthol extracted from peppermint was purified and taken as VCI. The molecular formula, molecular weight, vapour pressure and molecular structure are

- **Molecular formula**: \( \text{C}_{10}\text{H}_{20}\text{O} \)
- **Molecular weight**: 156.26
- **Vapour pressure**: \( 4.495 \times 10^{-5} \text{mmHg} \)
2.2 MATERIALS USED FOR CORROSION STUDIES

The following materials have been used for the corrosion studies.

2.2.1 Mild Steel

Commercially available mild steel specimens of the following compositions were used throughout the experiments.

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.07%</td>
</tr>
<tr>
<td>Sulphur</td>
<td>NIL</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>0.008%</td>
</tr>
<tr>
<td>Silicon</td>
<td>NIL</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.34%</td>
</tr>
<tr>
<td>Ferrous iron</td>
<td>Rest</td>
</tr>
</tbody>
</table>

2.2.2 Copper

Commercial grade copper was used throughout the experiments. The purity of the metal was 99.9%.
2.2.3 Pickling Solutions

The specific pickling baths composition used for mild steel and copper are given below (Donovan 1986 and Fontana 2005).

For mild steel

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. HCl</td>
<td>1 litre</td>
</tr>
<tr>
<td>Sb$_2$O$_3$</td>
<td>20 gm</td>
</tr>
<tr>
<td>SnCl$_2$ 2 H$_2$O</td>
<td>50 gm</td>
</tr>
<tr>
<td>Temperature</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Time</td>
<td>until clean</td>
</tr>
</tbody>
</table>

For copper

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. HCl</td>
<td>200 ml</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>800 ml</td>
</tr>
<tr>
<td>Temperature</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Time</td>
<td>Two minutes</td>
</tr>
</tbody>
</table>

2.2.4 Electrolyte Solutions

The following solutions were prepared by using AR grade sodium chloride, hydrochloric acid and double distilled water, which is used as electrolyte solution for the corrosion studies.

- 0.01N Sodium chloride
- 0.01N Hydrochloric acid
2.2.5 Construction of VCI Evaluation Cell

The fabricated to evaluate the volatile corrosion inhibitors in the powdery as well as liquid/oily form is shown in Figure 2.1. It consists of a 1 liter bell jar (10” long × 4” wide) with tight fitting rubber cork carrying a glass rod with hooks having provisions to suspend the coupons. Just below the coupons, a cup was attached to hold VCI sample. At the top of the cup, there is a lid provision to prevent the condensation of the moisture into the cup. At the middle part of the cup, there is a bend type outlet provision for the vapour to escape and fill the space in the jar. This cell design was used for the evaluation of VCI samples through continuous condensation of vapours on the specimens (Subramanian et al 1999).

![Diagram of VCI evaluation cell]

**Figure 2.1** VCI evaluation cell
2.2.6 Preparation of VCI Impregnated Papers

The VCI impregnated papers were prepared by wet impregnation method. A known amount of VCI was taken and dissolved in a measured volume (15 ml/sq.ft) of suitable solvent (ethanol). A craft paper was dipped into the solution till completely wet and taken out when the solvent got evaporated. Then the VCI impregnated paper was stored in tightly closed container from which it was taken just before use.

2.2.7 Construction of Atmospheric Corrosion Monitor

Atmospheric corrosion monitor was constructed by using five metal plates of size 2 × 25mm. The metal plates were insulated from one another by means of PVC separators of thickness 1 mm. The central metal plate is connected to one terminal which acts as the reference electrode (RE). Two alternate plates (except central plate) were connected to get other two terminals, namely, working electrode (WE) and counter electrode (CE). The whole setup was molded in polymeric resin to form atmospheric corrosion monitor as shown in the Figure 2.2.

![Figure 2.2 Atmospheric corrosion monitor](image-url)
The surface of the ACM was prepared by polishing the whole set in a grinder and then by using different grades of emery paper (1/0 to 4/0), degreased with acetone and dried. The area of the working electrode (WE) in the constructed ACM is 1 cm$^2$ (An et al 2003 and Wall et al 2005).

2.3 GRAVIMETRIC CORROSION STUDIES

2.3.1 Evaluation of VCI Powders

Weight loss measurements were made by continuous condensation to choose the best concentration of VCI powders for corrosion protection of mild steel and copper using the VCI evaluation cell.

The specimens of size 5 $\times$ 1 $\times$ 0.2 cm were polished with different grades of emery sheets (1/0, 2/0, 3/0 and 4/0), degreased with acetone and weighed. They were suspended from the glass hooks in the VCI evaluation cell. The experiments were carried out in the absence and in the presence of various concentration of the inhibitors. The cell set-up was placed in a thermostatic water bath at 40°C for 14 days to allow continuous condensation of vapour on the metal specimen. 100 ml of 0.01N NaCl/0.01N HCl were taken in the cell to give 100% relative humidity. At the end of 14$^{th}$ day, the visual observations were made and the specimens were pickled in pickling solution, washed and dried. The loss in weight was calculated to determine the corrosion rate.

2.3.2 Evaluation of VCI Impregnated Papers

The usage of VCI impregnated papers is relatively more than that used in other forms. The paper should not produce obnoxious vaporous in such concentration as to cause annoyance or health hazard to the persons handling them.
Weight loss measurements were made by continuous condensation test, to choose the best concentration of VCI impregnated paper for corrosion protection of the metals.

The mild steel and copper specimens of size $5 \times 1 \times 0.2\text{cm}$ were polished with different grades of emery sheets (1/0, 2/0, 3/0 and 4/0), degreased with acetone and weighed. They were wrapped with various concentrations of VCI impregnated and unimpregnated papers separately and kept hung in one-litre bell jars containing 100 ml of 0.01N NaCl/0.01N HCl. The size of the wrapping kraft paper used was same in all the experiments and it was just sufficient to cover the specimen freely. The jar assemblies were placed in a thermostat maintained at a temperature of $40^\circ\text{C}$. This arrangement made it possible to have continuous condensation of water vapour at 100%RH on the paper wrapped metal specimens. At the end of 14th day, the specimens were pickled in pickling solution washed and dried. The loss in weights was calculated to determine the corrosion rate.

### 2.3.3 Calculation of Corrosion Rate and Inhibition Efficiency

The corrosion rate for VCI powder and impregnated craft paper were calculated using the equation (2.1) (Quraishi and Sardar 2002).

$$\text{Corrosion rate (CR) (}\mu\text{my}^{-1}) = \frac{87.6 \times 10^3 \times W}{A \times t \times D}$$  \hspace{1cm} (2.1)$$

where $W$ is weight loss in mg, $A$ is the area of the coupon in cm$^2$, $t$ is time of exposure in hours and $D$ is density of metal in g/cm$^3$.

The inhibition efficiency was calculated from the initial and final weight of the specimen at particular concentration, weight loss without
inhibitor and with inhibitor were determined. The inhibition efficiency and surface coverage were calculated using the equations (2.2) – (2.3) (Talati and Modi 1976, Al-Shamma et al 1987).

\[
\text{Inhibition efficiency (IE \%) } = \frac{W_o - W_i}{W_o} \times 100 \tag{2.2}
\]

\[
\text{Surface coverage } (\theta) = \frac{W_o - W_i}{W_o} \tag{2.3}
\]

where \( W_o \) and \( W_i \) are the corrosion rates of the specimen in the absence and presence of inhibitor respectively.

2.4 ELECTROCHEMICAL STUDIES

Electrochemical studies such as Tafel polarization, linear polarization and AC impedance measurements were carried out using three electrode type atmospheric corrosion monitor. The experiments were carried out by thin layer technique using CH electrochemical analyzer (Model CHI 608B). The experimental set-up used for the electrochemical studies is shown in Figure 2.3.

![Figure 2.3 Set-up for electrochemical measurements using ACM](image)
2.4.1 Tafel Polarization

Polarization measurements were carried out potentiodynamically by thin layer technique for mild steel and copper using atmospheric corrosion monitor. One ml of the electrolyte (0.01N NaCl/0.01N HCl) was applied on the well-polished three electrode type ACM, over which various concentrations of VCI impregnated paper was pressed. The potentiodynamic polarization measurements were carried out at a sweep rate of 2 mV/s using CH electrochemical analyzer (Model CHI 608B) The OCP was first noted when the electrode attained a steady value. The potential range was fixed at ±200 mV from the OCP and then the polarization measurements were carried out from cathodic to anodic direction. The plot of E vs log I was made from which corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$), anodic and cathodic Tafel slopes ($b_a$ & $b_c$), and linear polarization resistance (LPR) values were calculated. The same experiment was also carried out for the blank using VCI unimpregnated paper and it is termed as control. 0.01N NaCl and 0.01N HCl were used as the experimental electrolytes. The inhibition efficiency of these systems was calculated using the Equation 2.4 (Amar et al 2006).

$$\text{Inhibition efficiency (IE \%) = } \frac{I_{corr(i)} - I_{corr}}{I_{corr}} \times 100 \tag{2.4}$$

where $I_{corr}$ is corrosion current density for unimpregnated craft paper and $I_{corr(i)}$ is corrosion current density for VCI impregnated craft paper.

2.4.2 AC Impedance

Impedance measurements were carried out for VCI impregnated and unimpregnated papers. One ml of 0.01N NaCl / 0.01N HCl was applied on the well-polished three electrode type ACM over which various concentrations of VCI impregnated paper was pressed and allowed to attain a
steady potential value. The experiments were carried out in the frequency range of 10 kHz to 100 mHz using CH electrochemical analyzer (Model CHI 608B). The real and imaginary parts of the impedance were plotted in Nyquist plots. The solution resistance \( R_s \) and total resistance \( R_t \) were obtained from the low frequency and high frequency intercepts on \( Z' \) axis of Nyquist plot respectively. The difference between \( R_t \) and \( R_s \) values give the charge transfer resistance \( (R_{ct}) \) value. The \( C_{dl} \) values were obtained from of the equation (2.5).

\[
C_{dl} = \frac{1}{2\pi f_{max} \times R_{ct}} \quad (2.5)
\]

where

- \( C_{dl} \) - double layer capacitance
- \( R_{ct} \) - Charge transfer resistance
- \( f_{max} \) - frequency at \( Z'' \) value maximum

The inhibition efficiencies were obtained from the equation (2.6).

\[
\text{Inhibition efficiency (IE\%) = } \frac{R_{ct(i)} - R_{ct}}{R_{ct}} \times 100 \quad (2.6)
\]

where

- \( R_{ct} \) - Charge transfer resistance for unimpregnated paper
- \( R_{ct(i)} \) - Charge transfer resistance for impregnated paper
2.5 DETERMINATION OF VAPOUR PRESSURE OF VCI

A standard Knudsen method was used to determine the vapor pressure of the inhibitors. A weighed compound was placed in a glass container with an orifice of 1.0 mm diameter. The glass container was then placed in an oven set at 313 K for 20 days. Mass loss was measured by an electronic balance. The vapour pressure of VCI was calculated using the equation (2.7) (Quraishi and Jamal 2005).

\[ P = \frac{W}{At} \times \left( \frac{2\pi RT}{M} \right)^{\frac{1}{2}} \]  

(2.7)

where, \( p \) is the vapor pressure of the inhibitor in mmHg, \( A \) is the area of the orifice in m\(^2\), \( t \) is time of exposure in seconds, \( W \) is the weight of the evaporated substance in kg, \( T \) is temperature in K, \( M \) is the molecular mass of the compound in kg, and \( R \) is the gas constant (8.314 J/K-mol).

2.6 FT-IR REFLECTION SPECTRAL ANALYSIS

The mild steel and copper specimens of size 10mm × 10mm × 2mm were polished with different grades of emery sheets (1/0, 2/0, 3/0 and 4/0), washed and degreased with acetone and dried. The specimens were placed in an air tight vessel containing VCI compounds for surface adsorption. After 24 hour film forming period, the VCI treated mild steel and copper samples were transported for FT-IR spectral analysis. The FT-IR spectral analysis were carried out in the frequency range 4000 - 375 cm\(^{-1}\) using FT-IR Raman microscope (Make: Thermo Electron Corporation, USA. And Model Nexus 670).