Azole, amine, benzoate and nitrate compound mixture as VPI for metals in NaCl and SO$_2$ environments

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A variety of tests were performed to evaluate the feasibility of vapour phase corrosion inhibitor’s (VPI’s) application for maintenance and protection of transporting metal articles from corrosion damage. Three types of VPI were evaluated for their inhibition characteristics for mild steel (MS) and copper. Minimum dosage of one g/L is required for protections of both metals. Influence of SO$_2$ and chloride contamination on inhibitor performance was also investigated. The corrosion behaviour of MS and Cu in sodium chloride (0.005 M NaCl) environment in presence of VPI impregnated and unimpregnated paper has been studied by using weight loss, potentiodynamic polarization and A.C impedance spectroscopic methods. It has been found that 1g L$^{-1}$ of VPI impregnated on Kraft paper provides nearly 98% inhibition efficiency for mild steel and copper in 0.005 M NaCl environment.

Keywords: Vapour phase corrosion inhibitors (VPI), Mild steel (MS), Copper, Inhibition efficiency, Sodium chloride

IPC Code(s): C23F11/00, D21H21/38

Materials used in army, navy, aircraft and electronic equipments as well as finished products have to be transported and stored for many months or even years. Unless their surfaces are protected during manufacture, the articles will corrode owing to the effects of humidity and polluted atmosphere during storage period and transportation. The materials used for such protection are called temporary corrosion preventives. They provide protection only when the equipment is idle$^1$. Originally, VPIs were developed for protection of ferrous metals in tropical climates. The use of VPI has increased substantially during the last 20 years$^2$-10. Research activities have also increased and various chemicals have been investigated for possible applications. Among these certain benzoates, amines and morpholine derivatives were tested for application in multi-metal protection$^{11}$.

In modern practice, inhibitors are rarely used in the form of single compound, formulation of two or more inhibitors is usually employed$^{12}$-14. The use of mixtures of inhibitors has been found to be advantageous. They show synergistic effects in retarding the corrosion of metal in its surrounding environment$^{15}$. In the present work, the influence of benzotriazole, ammonium benzoate, diethanol amine and sodium nitrite on corrosion inhibition of mild steel (MS) and copper in NaCl and SO$_2$ environments were studied using weight loss, polarization and A.C impedance spectroscopic methods.

Experimental Procedure

Preparation of metal specimens

Mild steel and copper were selected due to their wide usage and easy availability. The rectangular copper and steel sheets (as experimental specimens) were cut into pieces of 5 × 1 cm and polished with 1/0, 2/0, 3/0 and 4/0 emery papers$^{16}$. The specimens were degreased with trichloro ethylene, weighed and stored in a desiccator. The specimens in duplicate were used and average weight loss was taken for calculating inhibition efficiency.

VPI preparation

BAE was prepared by mixing equal amount (0.1, 0.2, 0.5 and 1 g/L) of benzotriazoles, ammonium benzoate with one mL of diethanolamine. BAN was prepared by mixing equal amount (0.1, 0.2, 0.5 and 1 g/L) of benzotriazoles, ammonium benzoate and sodium nitrite. BEAN was prepared by mixing equal amount of (1 g/L) benzotriazoles, ammonium benzoates and sodium nitrates with one mL diethanolamine.
Preparation of VPI impregnated Kraft paper

A known amount of VPI compound was taken and dissolved in a measured volume (25 mL) of ethanol. One square feet of pre-weighed Kraft paper was dipped into the solution until completely wet and taken out; the solvent was allowed to evaporate. Then the weight of VPI impregnated Kraft paper was taken and from the increase in weight of Kraft paper, the amount of substance absorbed per square foot was calculated. The VPI impregnated paper was stored in a desiccator.

Humidity chamber test

A simple apparatus which provides supersaturated conditions was used. Visual observation and weight loss measurements were made during humidity test, to choose the best concentration of VPI impregnated paper for protection of MS and Cu. The experiments were carried out in presence and in absence of inhibitors at various concentrations. In these experiments, one litre bottle (25 × 10 cm, length × breadth) with a tight fitting rubber cork was taken. The bottom of the cork carried glass rods with four hooks to suspend the specimens. Just below the specimens a cup with lid was made to place VPI. The lid was used to prevent condensation of moisture into VPI. At middle part of the cup, a bent type outlet provision was made for the vapours to escape and fill the space inside the jar. The metal specimens were wrapped with VPI impregnated Kraft paper and suspended in the bell jar. The cell design is shown in Fig. 1. The specimens were removed from the bell jar after 30 days exposure, the rust products were cleaned by using respective pickling solution, washed, dried and reweighed. The weight loss was calculated using the initial and final weights of the metal specimens and the corrosion rate (C.R) was determined in millimeter per year (mm/y) by using the following equation,

\[
C.R = \frac{8.76 \times W}{DAT}
\]

where W-weight loss (mg), D-density of metal (g cm\(^{-3}\)), T-corrosion period (h), A-specimen area (cm\(^2\)).

Stevenson chamber test

This test was carried out, as reported by Rajagopalan et al., to evaluate the performance of VPI in affording long-term protection to metals. Metal specimens were wrapped with the VPI impregnated Kraft paper and kept in a Stevenson chamber. Free access of air was allowed to the chamber and the exposure was continued for 90 days in laboratory atmosphere. The condition of the specimens and their weight were monitored periodically (7, 15, 30, 45, 60 and 90 days).

SO\(_2\) environment test

This test was used to evaluate the efficiency of VPI at highly polluted SO\(_2\) atmosphere. In the present work VPIs were evaluated on 5 mg/L SO\(_2\) environmental conditions. Hence, the laboratory test containing SO\(_2\) atmosphere was designed to simulate the condition of the industrial atmosphere. The rate of corrosion of MS and Cu were determined for 7 days at 100% RH at 40°C.

Electrochemical methods

Atmospheric corrosion monitors (ACM)

For electrochemical studies a three electrodes type atmospheric corrosion monitor (ACM) was fabricated with corresponding metals. A typical ACM is shown in Fig. 2. Each cell contains 12 metal plates of 2 × 2 cm size. They were insulated from one another by means of PVC separators. The whole unit was tightly masked by epoxy resin which forms a mono layer of two-electrode type atmospheric corrosion monitor. The five alternate plates were connected to each other and formed one terminal. The other five intermittent plates were connected and formed the other terminal. These terminals were used for making connections. The working area of the electrodes was 1.5 × 2.5 cm\(^2\).

![Fig. 1—Cell design for humidity chamber test](image1)

![Fig. 2—Atmospheric corrosion monitor (ACM)](image2)
Potentiodynamic polarization studies

Potentiodynamic polarization studies were carried out for MS and Cu by using ACM on to which a thin layer of NaCl solution had been deposited. One mL of NaCl solutions was applied to a well-polished three-electrode type ACM, over which VPI impregnated paper was placed. The polarization measurements were carried out at a sweep rate of 1 mV/s using potentiostat (EG and GPAR model-173). The open circuit potential (OCP) of the electrode was noted with respect to saturated calomel electrode, after a steady state was attained within 5 to 10 min. The potential was fixed at ±200 mV from the OCP and then the polarization measurements were carried out. The plot of E versus log I was drawn and from this the corrosion kinetic parameters such as corrosion potential \(E\text{corr}\), corrosion current \(I\text{corr}\) and Tafel slopes were evaluated.

A similar experiment was carried out for the control using unimpregnated Kraft paper and C.R was calculated using the following equation
\[
C.R = \frac{0.13 \times I_{\text{corr}} \times E.Wt.}{D}
\]
where, \(I_{\text{corr}}\) corrosion current \((\mu A\ cm^{-2})\), E.Wt.-equivalent weight, D-density of the metal

A.C. impedance studies

A.C. impedance measurements were carried at the corrosion potential by applying 10 mV of A.C. signal to the ACM cell for the frequency range from 10 KHz to 100 MHz using PAR impedance electrochemical analyzer (Model M6310) attached with software (M398). The values of charge transfer resistance \(R_{ct}\) and double layer capacitance \(C_{dl}\) were obtained by auto curve fitting method provided with the software. The impedance was measured in NaCl in the absence and presence of 1g L \(^{-1}\) of VPI compounds. The inhibition efficiency (IE) of these VPIs were calculated from the following equation,
\[
\text{I.E.(%)} = \frac{R_{ct} - R_{ct}^*}{R_{ct}} \times 100
\]
where, \(R_{ct}\) and \(R_{ct}^*\) are charger transfer resistance with and without inhibitor respectively.

Results and Discussion

Humidity test

The values of corrosion loss and the inhibition efficiency obtained by weight loss method in the absence and presence of various concentrations of VPI for mild steel and copper in 0.005 M NaCl environment for a period of 30 days are summarized in Table 1. It can be seen that all the VPI used have shown good inhibition efficiency. From the table, it was observed that as the concentration of VPI increases, the percentage of rust formed on the surface was decreased. One g/L inhibitor concentration provides more than 90% protection for both metals.

<table>
<thead>
<tr>
<th>Name of VPI</th>
<th>Conc. of VPI (g L(^{-1}))</th>
<th>Weight loss (mg)</th>
<th>Inhibition efficiency (%)</th>
<th>Visual observation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MS</td>
<td>Cu</td>
<td>MS</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>1.038</td>
<td>0.15</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BAE</td>
<td>0.1</td>
<td>0.227</td>
<td>0.0124</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.175</td>
<td>0.0097</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.064</td>
<td>0.0042</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.0105</td>
<td>0.0075</td>
<td>99</td>
</tr>
<tr>
<td>BAN</td>
<td>0.1</td>
<td>0.261</td>
<td>0.0157</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.216</td>
<td>0.0104</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.156</td>
<td>0.0067</td>
<td>85</td>
</tr>
<tr>
<td>BEAN</td>
<td>1</td>
<td>0.047</td>
<td>0.0018</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.0031</td>
<td>0.0012</td>
<td>99</td>
</tr>
</tbody>
</table>
The results given in Table 1 show that the duration of protection is directly proportional to the amount of VPI compound present in the Kraft papers. The reason for having used combination of surface-active components is that a metal surface has many active sites where corrosion can begin. A surface active component of the inhibitor will be strongly chemisorbed or adsorbed at the active sites. Thus, it would form much tighter and more uniform thick layer over the metal surface. Inhibitor BAN also provides protection in vapour phase for metal surface, but not sufficiently covered with the product due to the presence of the easily volatile parts in the formulation. Among the three VPIs used, BEAN provides better efficiency and BAN has shown least efficiency.

SO2 environment test

Table 2 reveals the inhibition efficiency of the inhibitors in SO2 environment in 100% RH at 40°C in continuous condensation method up to 7 days of exposure. The high inhibition efficiency values prove the better performance of the VPI even in highly polluted industrial atmosphere. This may be due to the formation of passive film of VPI over the metal surface.

Polarization measurements

The results of potentiodynamic polarization behaviour of mild steel and copper in 0.005 M NaCl solution are summarized in Table 3. As the inhibitor concentration increases the inhibition efficiency also increases. It can be seen from the data that all concentrations of VPI impregnated paper result in less negative electrode potential \(E_{\text{corr}}\) value (i.e.) shifted to more positive direction than the control sample for both metals. It is also observed from the table that the corrosion current \(I_{\text{corr}}\) for control is more than that of VPI. It shows that both the metals were protected from corrosion in the presence of these inhibitors. The polarization curves are shown in Fig. 3(a, b, c and d). It is found that the anodic and cathodic curves are diffusion control and are affected nearly to equal extent with respect to the blank under inhibited condition. Hence, all the compounds are found to control corrosion by acting as mixed inhibitors. Values of corrosion current \(I_{\text{corr}}\) decreased with increase of VPI concentration. Based on this it is assumed that the VPI molecules in the vapour forms thin layer on metal surface. These inhibitors have much greater affinity for metal surface than for water. Therefore, all the three inhibitors have the following

### Table 2

<table>
<thead>
<tr>
<th>Name of VPI</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS</td>
<td>Cu</td>
</tr>
<tr>
<td>BAE</td>
<td>98.4 97.1</td>
</tr>
<tr>
<td>BAN</td>
<td>90.0 90.8</td>
</tr>
<tr>
<td>BEAN</td>
<td>99.2 97.3</td>
</tr>
</tbody>
</table>

Fig. 3(a) —Potentiodynamic polarization curves of BAE in 0.005 M NaCl environment for MS

### Table 3

<table>
<thead>
<tr>
<th>Name of VPI</th>
<th>Conc. of VPI (g L⁻¹)</th>
<th>Mild steel</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(-E_{\text{corr}})</td>
<td>(I_{\text{corr}})</td>
<td>I.E (%)</td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>686</td>
<td>354</td>
</tr>
<tr>
<td>BAE</td>
<td>0.1</td>
<td>624</td>
<td>133</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>639</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>653</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>666</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>513</td>
<td>128</td>
</tr>
<tr>
<td>BAN</td>
<td>0.2</td>
<td>529</td>
<td>109</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>596</td>
<td>70.0</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>671</td>
<td>9.9</td>
</tr>
<tr>
<td>BEAN</td>
<td>1</td>
<td>528</td>
<td>5.0</td>
</tr>
</tbody>
</table>
multifunctional properties: (a) volatility, (b) water displacement (dehumidification) and (c) corrosion inhibition. These properties are critically important for protection of metal during storage and transportation in highly corrosive environments.

A.C. impedance studies

Figure 4 (a and b) shows the impedance behaviour of mild steel and copper in 0.005 M NaCl in 1 g/L of VPI impregnated and unimpregnated paper. The values obtained from the figure are shown in Table 4. The $R_{ct}$ values increased in the presence of VPI, indicating that they are corrosion inhibitive in nature. The higher $R_{ct}$ values again confirm the good performance of the compounds in NaCl environment. The decrease in the $C_{dl}$ values in the presence of inhibitors shows that they are adsorbed on the metal surface, resulting in a decrease in the double layer capacitance value. The results of impedance studies are more or less in good agreement with those
Table 4 — A.C impedance parameter for MS and Cu in presence of 1 g/ L VPI impregnated papers in 0.005 M NaCl environment

<table>
<thead>
<tr>
<th>Name of VPI</th>
<th>Double layer capacitance (C dl) μF</th>
<th>Charge transfer resistant (R ct) (Ohms cm²)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MS</td>
<td>Cu</td>
<td>MS</td>
</tr>
<tr>
<td>Control</td>
<td>$1.59 \times 10^{-5}$</td>
<td>$18.25 \times 10^{-4}$</td>
<td>35</td>
</tr>
<tr>
<td>BAE</td>
<td>$0.22 \times 10^{-5}$</td>
<td>$8.39 \times 10^{-4}$</td>
<td>233</td>
</tr>
<tr>
<td>BAN</td>
<td>$0.41 \times 10^{-5}$</td>
<td>$9.12 \times 10^{-4}$</td>
<td>115</td>
</tr>
<tr>
<td>BEAN</td>
<td>$0.18 \times 10^{-5}$</td>
<td>$7.20 \times 10^{-4}$</td>
<td>295</td>
</tr>
</tbody>
</table>

obtained in weight loss and polarization techniques\(^{22}\). Figure 4(b) shows a depressed semicircle indicating a combination of a charge transfer and diffusion control process on metal surface.

**Stevenson chamber test**

The Stevenson chamber was kept in laboratory near the exhaust and the exposure was continued in the rainy season for the period of 90 days. The metal specimens wrapped with VPI impregnated Kraft paper retained brightness even after three months of exposure, whereas metal specimens wrapped with unimpregnated Kraft paper underwent severe corrosion. Only trace of corrosion product could be seen at the surfaces of the control specimen of copper. Figure 5(a and b) provides the most explicit visual results for mild steel and copper. It is important to mention that these inhibitors have dual functional properties as they provide dehumidification along with inhibition. The order of these three inhibitors with respect to their I.E. values for both Cu and MS are

BEAN > BAE > BAN

The condition of the specimen with these VPI compounds was better even after 90 days. They were totally rust free retaining their original luster as was introduced in the chamber.

**Conclusions**

The results of this study indicate that the inhibitors BAE, BAN and BEAN can be used as VPI in NaCl and SO\(_2\) environments. One g/L concentration of these VPI offered above 90% inhibition efficiency for both mild steel and copper metals. The I.E obtained from various corrosion tests gives more or less the same result for these VPIs compounds for MS and Cu, and 1 g/L VPI impregnated papers (BAE, BAN and BEAN) gave excellent corrosion protection under the chloride and SO\(_2\) environmental conditions. The composition BEAN has shown higher inhibition efficiency than other compositions (BAE and BAN). The inhibition efficiency of all inhibitors can be explained by the adsorption of VPI molecules on metal surface. Stevenson chamber test results showed that all these VPIs could offer better inhibition efficiency for both metals upto three months. Further, it is clear that these VPIs function through mixed type inhibition.

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References