Prevention of metallic corrosion by some salts of benzoic hydrazide under vapour phase conditions

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Three volatile corrosion inhibitors (VCIs) namely, benzoic hydrazide benzoate (BHB), benzoic hydrazide salicylate (BHS), and benzoic hydrazide nitrobenzoate (BHN), were synthesized and evaluated as corrosion inhibitors of mild steel, brass and copper by weight loss method. Eschke test method, sodium chloride inoculation test method and sulphur dioxide (SO2) test method were also carried out to investigate the corrosion inhibiting effect of the compounds. All the investigated VCIs exhibited good inhibition efficiency (IE) for all the metals. Benzoate salt showed best result among all the studied compounds for all the metals.

Keywords: Brass, copper, benzoic hydrazide, mild steel, volatile corrosion inhibitor.

IPC Code: C07C 243/00; C23F 11/10

Corrosion is defined as the destruction or deterioration of metals. Corrosion causes heavy economic losses. In India, the annual economic losses have been estimated as high as Rs.2500 crore. Corrosion commonly occurs at metal surfaces in the presence of oxygen and moisture and involves two electrochemical reactions. Oxidation takes place at anodic site and reduction occurs at cathodic site. In acidic medium hydrogen evolution reaction predominates, while in neutral medium reduction of oxygen takes place. Corrosion inhibitors reduce or prevent these reactions, they are adsorbed onto the metal surface and act by forming a barrier to oxygen and moisture, by complexing with metal ions or by removing corrodants from the environment, some of the inhibitors facilitate formation of passivating film on the metal surface.

Use of volatile corrosion inhibitor (VCI) is an effective method to prevent atmospheric corrosion. The VCIs are used to protect metallic articles and equipments in enclosed atmosphere. The protection of metal is due to the inhibitors volatizing into the atmosphere surrounding the metal parts and modifying the atmosphere. VCI functions by forming a bond on the metal surface and by forming a barrier layer to aggressive ions. On contact with the metal surface, the vapour of the VCI condenses and is hydrolysed by moisture to release protective ions. The choice of a chemical compound as VCI depends on its vapour pressure as well as its efficacy in preventing corrosion by forming a protective film. The vapour pressure (VP) of the compounds used as VCI must possess some optimum values. It must not have too high or too low a VP. Substitution of an organic compound with an inorganic functional group may give a desirable property.

Recent work on vapour phase corrosion inhibitors has been extended here by exploring the inhibiting properties of three organic vapour phase inhibitors (VCIs) namely, benzoic hydrazide benzoate (BHB), benzoic hydrazide salicylate (BHS), and benzoic hydrazide nitrobenzoate (BHN), on mild steel, brass and copper.

Experimental Procedure

Inhibitors

Benzoic hydrazide was synthesized according to the reported procedure and the salts were prepared by dissolving equimolar quantities of benzoic hydrazide and organic acids in ethanol. The reaction mixture was stirred for 1 h at 40 °C. The precipitated compounds were filtered and crystallized from ethanol. All compounds were purified by crystal-
lization and their purity was confirmed by thin layer chromatography. Name and structural formulas of the compounds are given in Table 1.

**Conical flask method**

Corrosion experiments were carried out according to the reported procedure using various ferrous and non-ferrous metals viz. mild steel, brass and copper. The specimens of size 2.5×2.0×0.025 cm were used for weight loss measurement studies. Weight loss experiments were carried out in the presence and absence of inhibitors at a fix concentration of 500 ppm, using tight fitting rubber cork 250 mL conical flasks containing 25 mL of water-glycerin mixture to produce 90% relative humidity. The concentration of the inhibitors used for the study was taken according to the volume of the conical flask. The metal specimens were suspended in these bottles by nylon tags and just below these specimens weighed VCI samples were kept in a glass container which had no contact with the liquid kept inside the conical flask. A battery of conical flasks were kept in an air thermostat set at temperature 40±1 °C and 90% relative humidity during the day and were removed at night to allow condensation of moisture on metal specimen. The experiment was conducted for 20 days. The coupons were suspended in inhibited acid bath to remove corrosion products and then weighed. Each experiment was run in duplicate and the average values of weight loss were taken for the study.

**Eschke test**

Eschke test was carried out as per reported procedure using various specimens. Polished strips of size 5.0×2.0×0.025 cm were wrapped in single layer of inhibitor impregnated Kraft papers and suspended in climatic cabinet maintained at 90% relative humidity. 1 g/ft² of various inhibitors were used for the experiment. The temperature cycle was set at 40±1 °C for 12 h and at room temperature for another 12 h for condensation of the moisture. The duration of the test was 20 days. A similar experiment was done with metals covered with untreated Kraft paper (control).

**Sulfur dioxide (SO₂) test**

Clean and dry specimens of size 5.0×2.0×0.025 cm were placed inside one-liter glass container. Weighed VCI compound was kept inside the container. A small beaker containing 0.04 g of sodium thiosulphate was placed inside the container. 50 mL capacity beaker containing 30 mL aqueous solution of salt (1% NH₄Cl + 1% Na₂SO₄) was placed inside the container. 0.5 mL of 1 N sulphuric acid was directly added to the beaker containing sodium thiosulphate and the glass container was immediately sealed. The glass container was placed in an oven set at 40±1 °C for 16 h and at 10 °C for another 8 h. A similar experiment was done with the one-liter glass container in absence of VCI compound (control).

**Salt inoculation test**

0.1 g of sodium chloride was placed in 200 mL carbon tetrachloride and the whole solution were stirred by a magnetic stirrer. The metal specimen of size 5.0×2.0×0.025 cm was introduced in the stirred solution for 3-4 s and taken out when approximately 10-12 particles of salt were deposited at random on each side of metal surface. One side of the metal surface was cleaned off the salt particles and the whole metal surface was wrapped in single layer of inhibitor impregnated Kraft papers and suspended in climatic cabinet maintained at 90% relative humidity. 1 g/ft² of various inhibitors were used for the experiment. The temperature cycle was set at 40±1 °C for 12 h and at room temperature for another 12 h for condensation of the moisture. The duration of the test was 20 days. A similar experiment was done with metals covered with untreated Kraft paper (control).

**Vapour pressure determination**

Knudsen method was used to determine the vapour pressure of the inhibitors. Weighed compound was placed in a glass container having an orifice of 1.0 mm diameter. The glass container was then placed in an oven set at 40±1 °C for 20 days. Loss in mass was measured by an electronic balance and the values were put into the formula given as,

<table>
<thead>
<tr>
<th>Table 1—Name and molecular structures of the compounds used</th>
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<td>O H H N H HOOC</td>
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<td>O H H N H HOOC</td>
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<td>O H H N H HOOC</td>
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</tbody>
</table>

Knudsen method was used to determine the vapour pressure of the inhibitors. Weighed compound was placed in a glass container having an orifice of 1.0 mm diameter. The glass container was then placed in an oven set at 40±1 °C for 20 days. Loss in mass was measured by an electronic balance and the values were put into the formula given as,
\[ p = \frac{W}{At} \times \left[ \frac{2\pi RT}{M} \right]^{1/2} \]

where, \( p = \) vapour pressure of the inhibitor in mm Hg, \( A = \) area of the orifice in \( m^2 \), \( t = \) time of exposure in second, \( W = \) weight of evaporated substance in kilogram, \( T = \) temperature in Kelvin, \( M = \) molecular mass of the compound in kilogram and \( R = \) gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)). Values of the vapour pressure obtained are given in Table 2.

**Results and Discussion**

**Conical flask method**

The values of percentage inhibition efficiency (\( %\ IE \)) and corrosion rate (\( CR \)) obtained by weight loss method in absence and presence of various VCIs for different metals at 40±1 °C are summarized in Table 3. The \( %\ IE \) was calculated using the following equation,

\[ %\ IE = \left[ \frac{(CR^o - CR)}{CR^o} \right] \times 100 \]

where \( CR^o \) and \( CR \) are the corrosion rates in the absence and presence of inhibitors, respectively. The corrosion rate was calculated using the following formula\(^9\),

\[ CR = \frac{K \times W}{A \times T \times D} \]

where \( K = \) a constant (3.45×10\(^4\) mpy, mills per year), \( W \) is weight loss in g, \( A \) is area of the coupon in cm\(^2\), \( T \) is time of exposure in hour and \( D \) is density of metal in g/cm\(^3\).

All VCIs have shown good \( %\ IE \), which may be attributed to the formation of a physical barrier between metal and corrosive environment by the interaction of metal and inhibitor molecules. However, the difference in their inhibiting action may be due to their different molecular structures.

**Eschke test**

The values of \( %\ IE \) and \( CR \) obtained by Eschke test are summarized in Table 3. The summary of the visual observations of the test for BHB is represented in Table 4. The graphical representation of \( CR \) for all the metals, in the absence (control) and presence of BHB, is shown in Fig. 1.

**SO\(_2\) test**

The values of \( %\ IE \) and \( CR \) obtained by SO\(_2\) test for 24 h are summarized in Table 3. The result obtained in the presence of SO\(_2\) for BHB is shown in Fig. 2. It is seen that values of \( CR \) were reduced considerably in the case of inhibited specimens. The summary of the visual observations of the test for BHB is represented in Table 4. Corrosion of all the metals was reduced considerably in the presence of BHB.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Vapour pressures of VCIs</th>
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<tbody>
<tr>
<td>Compounds</td>
<td>Vapour pressure (mmHg)</td>
</tr>
<tr>
<td>BHB</td>
<td>0.85×10(^{-7})</td>
</tr>
<tr>
<td>BHS</td>
<td>2.79×10(^{-7})</td>
</tr>
<tr>
<td>BHN</td>
<td>2.71×10(^{-7})</td>
</tr>
</tbody>
</table>

![Fig. 1](image1.png)

**Fig. 1**—Results of Eschke test. CR for mild steel, brass and copper in absence and presence of BHB at 40±1°C and 90% relative humidity for 20 days test duration.

![Fig. 2](image2.png)

**Fig. 2**—CR of different metals in absence and presence of BHB in SO\(_2\) environment for 24 h of test duration.
Salt inoculation test

The values of %IE and CR obtained by salt inoculation test are summarized in Table 3. The results obtained when the metal specimens are inoculated with sodium chloride in absence (control) and presence of BHB are shown in Fig. 3. The summary of the visual observations of the test is shown in Table 4. It is also observed visually that in the case of inhibited samples the extent of corrosion around the salt nuclei is restricted and further spreading of the rust was arrested to a considerable extent.

Mechanism of corrosion inhibition

Inhibition of metallic corrosion in presence of benzoic hydrazide salts involves vaporization of the inhibitors in a non-dissociated molecular form, followed by hydrolysis of the salts into carboxylate anions (RCOO⁻) and organic cations (RCONHNH₃⁺). Anions are adsorbed on the anodic site of the metal and inhibit anodic reaction while organic cations are adsorbed on cathodic side thereby preventing cathodic reaction¹⁴. The corrosion inhibiting action of the volatile corrosion inhibitors is attributed to the presence of lone pair of electrons present on the N and O atoms of the inhibitor molecules, which facilitate adsorption of these inhibitors onto the metal surface. The presence of extensively delocalised
π-electrons on benzene ring further facilitates adsorption process. In the present investigation, benzoate salt exhibited highest IE (i.e., >96%) for all the metals studied. Lesser IE of salicylate salt may be attributed to the orientation of the substituent group (–OH) at ortho position, which prevents flat orientation on the metal surface causing less adsorption thereby less inhibition. The lesser IE of nitrobenzoate salt may be attributed to the –I effect of –NO₂ group which reduces its adsorption at the active sites of the metal surface.

**Conclusion**

All the tested organic inhibitors showed good inhibition efficiency (IE) for mild steel, brass and copper. The benzoate salt exhibited highest IE for all the metals. The order of the IE for various inhibitors for all the metals follows the order BHB > BHS > BHN.

**Acknowledgement**

Two of the authors (DJ) and (VB) thankfully acknowledge CSIR, New Delhi, India for the award of Research Associateship and Senior Research Fellowship, respectively.

**Table 4**—Visual observations of the metal surface in the presence and absence of BHB from various test methods

<table>
<thead>
<tr>
<th>System</th>
<th>Visual observation</th>
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<tbody>
<tr>
<td><strong>Mild steel</strong></td>
<td></td>
</tr>
<tr>
<td>(Control)</td>
<td></td>
</tr>
<tr>
<td>BHB</td>
<td>Moderate to heavy rusting.</td>
</tr>
<tr>
<td></td>
<td>Severe rusted all-over the surface.</td>
</tr>
<tr>
<td><strong>Brass</strong></td>
<td></td>
</tr>
<tr>
<td>(Control)</td>
<td></td>
</tr>
<tr>
<td>BHB</td>
<td>Moderate to heavy tarnishing.</td>
</tr>
<tr>
<td></td>
<td>Slight tarnishing.</td>
</tr>
<tr>
<td><strong>Copper</strong></td>
<td></td>
</tr>
<tr>
<td>(Control)</td>
<td></td>
</tr>
<tr>
<td>BHB</td>
<td>Moderate to heavy tarnishing.</td>
</tr>
<tr>
<td></td>
<td>Slight tarnishing.</td>
</tr>
</tbody>
</table>

**References**