# Corrosion Inhibition of Mild Steel by Essential Oils in an HCl Environment

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*Weight loss and polarization methods were used to study the corrosion-inhibiting effect of five essential oils on mild steel in hydrochloric acid (HCl) environments. In both methods, maximum inhibition efficiency was observed at 4% concentration of the inhibitors in the acid of highest strength.*

Inhibitors are known for their specificity of action.[1] A substance, which effectively protects a given metal under certain conditions, may cease to be effective under other conditions or with other metals. The extracts of some common plants and by-products (peels, seeds, fruit shells, leaves, etc.) contain different organic compounds (e.g., amino acids, tannin, alkaloids, and most of their constituents), which are known to have inhibitive action.[2-6] It is therefore expected that the essential oils extracted from plants would exhibit inhibitive action.

Vapor corrosion inhibitors (VCIs) are chemicals that are used to protect metallic items from atmospheric corrosion during manufacture, storage, and transportation. Initially, camphor was used to protect military equipment and machinery parts.[6] In later years, the development of organic compounds as VCIs for metals[7-10] has been important. Our previous work[11-12] revealed that the extracts of bark oils and amine-azole-nitro compounds are quite effective in reducing the corrosion of mild steel in marine and industrial environments. *Jasminum grandiflorum* (JG), *Jasminum auriculatum* (JA), *Oleum palmarosae* (OP), *Ocimum basilicum* (OB), and *Vetiveria zizanioides* (VZ) oils were used in this work.

## Experimental Procedures

### *Materials*

Mild steel of the composition 0.06% C, 0.4% Mn, 0.05% Si, 0.03% P, 0.02% Cr, 0.14% Mo, 0.01% Ni, and 99.29% Fe was obtained from cold-rolled sheet and used for all studies. For weight loss tests, specimens 50 by 10 by 0.25 mm were used. The sources for JG and JA oils are the respective flowers. OP oil was extracted from Palma Rosa grass, OB from flowering tops, and VZ from dried roots of the plant. Essential oils used for the study were procured from Encee Aromatic Co., Mettupalayam Tamil

Nadu, India. One mL of the oil was mixed with 25 mL of absolute alcohol to obtain 4% concentration by volume. For the electrochemical VCI study, a three-electrode type atmospheric corrosion monitor (ACM) was fabricated and used.[9] The working area of this electrode was 50 by 25 mm.

### *Preparation of Vapor Corrosion Inhibitor Impregnated Paper*

VCI-coated Kraft paper was prepared by following the impregnation method.[9] Next, 0.5, 1, 1.5, 2, and 2.5 mL of essential oil were mixed each with 10 mL of ethanol ($C_2H_5OH$). This was sufficient to completely soak 1 ft$^2$ (305 mm$^2$) of Kraft paper. It was taken out and then the excess solvent was allowed to evaporate. The VCI-impregnated paper was enclosed in a polythene envelope and stored in an airtight container, then taken out just before use.

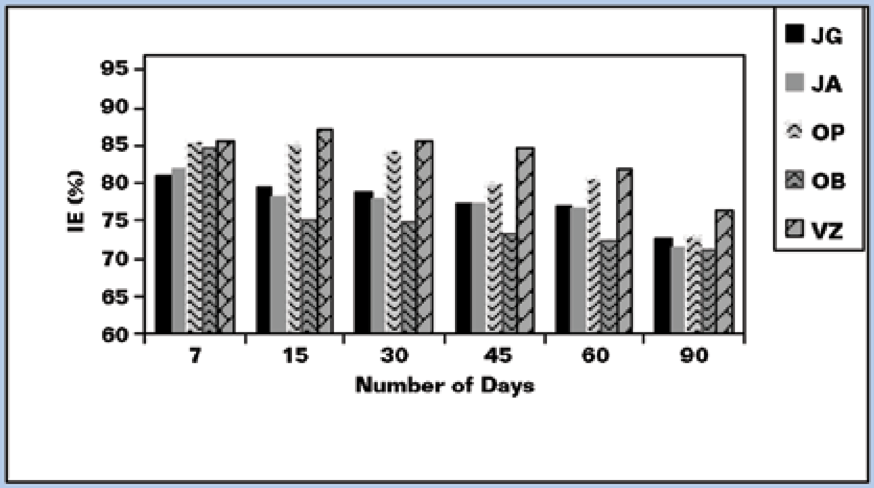
### *Weight Loss Method*

Mild steel specimens were polished, degreased with trichloroethylene, and then weighed. These specimens were wrapped with VCI-impregnated paper with different concentrations of essential oils. Specimens were hung in 1-L capacity jars containing 100 mL of different concentrations of HCl solutions. These jars were then placed in an oven at 40 °C. This arrangement produced a relative humidity (RH) of 100%. The specimens were inspected at the end of the seven-day period and weight losses were measured. From the weight loss (WL) values, the corrosion rate (CR) and inhibition efficiency (IE) were calculated using the formula:

$$\text{CR } (\mu\text{m/y}) = \frac{87.6 \text{ W}}{\text{DAT}} \times 10^7 \qquad (1)$$

where W = weight loss (mg), D = density of the metal (g/cm$^3$), A = area of the metal (cm$^2$), and T = time of exposure in hours and μm/y.

**FIGURE 1**




**Variation of inhibition efficiency of VCI-impregnated Kraft paper on mild steel with time in a laboratory atmosphere.**

### *Polarization Studies*

Electrochemical polarization experiments were carried out for mild steel using an ACM[11] following the procedure described in Besdas, et al.[13] Polarization measurements were taken at a sweep rate of 1 mV/s using an EG 2G PAR model 173† potentiostat. The open circuit potential (OCP) of the electrode with respect to the saturated calomel electrode (SCE) was noted when a steady state was attained (+200 mV). The electrodes were polarized from cathodic to anodic direction. $E_{corr}$, $I_{corr}$, and Tafel slopes ($b_a$ and $b_c$) were evaluated from the control using unimpregnated Kraft paper. All experiments were carried out at room temperature with 4% VCI concentration and in duplicate to confirm the results. Inhibition efficiency (IE) was calculated using the equation:

$$\text{IE } (\%) = \frac{\text{I (without inhibitor)} - \text{I (with inhibitor)}}{\text{I (without inhibitor)}} \times 100 \qquad (2)$$

### *Alternating Current Impedance Measurement*

Alternating current (AC) impedance measurements were taken using 4% concentration VCI-impregnated and unimpregnated papers with the ACM. The experiments were carried out at the corrosion potential for the frequency range of 10 KHz to 100 MHz using a PAR impedance electrochemical analyzer M6310† with M398† software. The values of the charge transfer resistance ($R_{ct}$) and double layer capacitance were obtained from the difference between the measured resistance values at the low- and high-frequency intercepts at the real axis. IE was calculated using the equation:

$$\text{IE } (\%) = \frac{R_{ct} \text{ (with inhibitor)} - R_{ct} \text{ (without inhibitor)}}{R_{ct} \text{ (with inhibitor)}} \times 100 \qquad (3)$$

### *Stevenson Chamber Test*

This test was done, as reported by Rajagopalan, et al. (1979),[14] to evaluate the performance of VCIs in offering long-term protection to metals in the open air and laboratory environments. Mild steel specimens were wrapped with Kraft paper impregnated with 4% VCI concentration and specimens covered with unimpregnated paper as control were kept in the Stevenson chamber. They were exposed to free air for 90 days. The condition of the specimens was examined periodically using a metallurgical microscope.

†Trade name.

**TABLE 1**

**Potentiostatic polarization studies data with 4% VCI**

| | 0.005 M HCl | | | | | 0.01 M HCl | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Name of VCI | $-E_{corr}$ (mV/SCE) | Tafel Slope (mV/dec) $b_a$ | $b_c$ | $I_{corr}$ (μA/cm²) | IE (%) | $-E_{corr}$ (mV/SCE) | Tafel Slope (mV/dec) $b_a$ | $b_c$ | $I_{corr}$ (μA/cm²) | IE (%) |
| Blank | 615 | 85 | 123 | 604.0 | — | 625 | 89 | 129 | 621.4 | — |
| JG | 450 | 83 | 125 | 40.3 | 93.3 | 430 | 87 | 131 | 73.3 | 88.2 |
| JA | 500 | 82 | 124 | 41.6 | 93.1 | 440 | 88 | 130 | 78.1 | 87.4 |
| OP | 465 | 83 | 127 | 29.6 | 95.1 | 415 | 85 | 132 | 63.4 | 89.8 |
| OB | 550 | 84 | 123 | 49.8 | 91.8 | 500 | 89 | 130 | 84.5 | 86.4 |
| VZ | 460 | 82 | 124 | 27.2 | 95.5 | 390 | 86 | 133 | 60.1 | 90.3 |

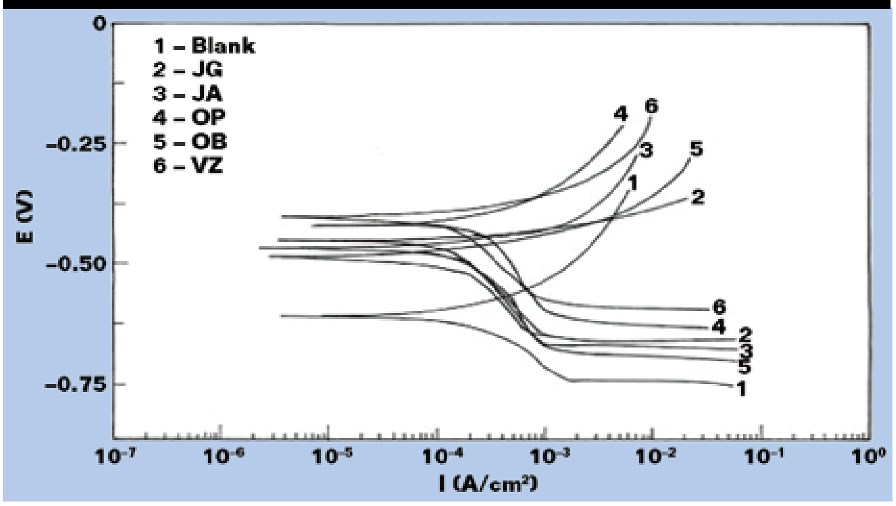
## Results and Discussion

The CR and IE of all VCIs were calculated from the weight loss measurement for the hydrochloric acid (HCl) environment. It was observed that the IE increases with an increase in the concentration of inhibitor and decreases with increases in acid strength. The CR decreases with an increase in concentration of inhibitor and decreases in concentration of acid strength. The inhibitors have shown efficiency in the range of 82 to 96% in 0.005 M HCl concentration and 52 to 89% in 0.1 M HCl concentration. The maximum IE was observed for VZ oil (96%) in 0.005 M HCl concentration and minimum for OB oil (63.8%) in 0.1 M HCl concentration. The CR was also observed to increase with an increase in HCl concentration.

Figure 1 shows the weight loss time curves for mild steel in the presence of VCI in a laboratory atmosphere using the Stevenson chamber method. The reduction of CR in the presence of VCI followed the order: VZ > OP > JG > JA > OB.

The calculated VCI surface coverage values and IE from the weight loss method revealed that IE increased in the presence of the VCI compared to the blank alone. The maximum IE was observed in the range of 90 to 96.5% for 4% VCI concentration of all five oils. The tests also revealed that IE decreases with an increase in HCl concentration. The inhibitive effect of the VCI could be attributed to the presence of some phyto chemical constituents in the oils.[14] Fourier transform infrared spectroscopy (FTIR) studies have shown that the VCI contains the alcoholic O-H, C=C, C-N, and C-O groups. This indicates the presence of linalool, indole, farnesole, geraniol, vetiverol, eugenol, citrol, phytol, and sesquiterpene as part of its phyto chemical composition.[15-19]

**FIGURE 2**




**Potentiostatic polarization curves for the corrosion of mild steel in the presence of 4% VCI in an 0.005 M HCl environment.**

### *Polarization Experiments*

Table 1 presents the corrosion kinetic parameters, such as corrosion potential ($E_{corr}$), corrosion current ($i_{corr}$), and Tafel slopes ($b_a$ and $b_c$) obtained from electrochemical polarization studies for mild steel in the presence of 4% VCI concentration in a 0.005 M HCl environment. Similar data were obtained from the tests in 0.05 M HCl. Figure 2 shows typical polarization curves. VCI-impregnated paper produced less negative $E_{corr}$ values than the control. The values of $i_{corr}$ increased with an increase in the concentration of HCl and decreased in the presence of VCI. The results of weight loss and polarization methods indicated that 4% of VCI will be the most effective inhibitor concentration, offering ~90% protection under 0.005 M HCl concentration.

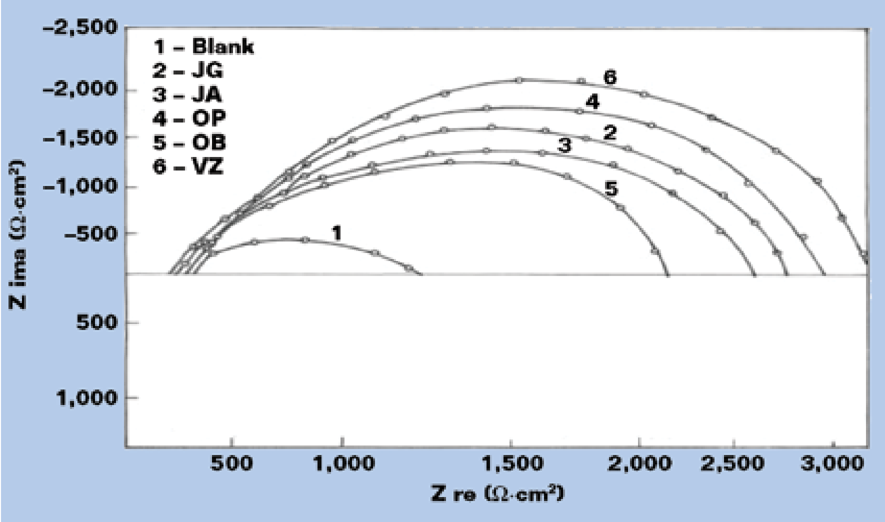
The $b_c$ and $b_a$ values of VCI did not differ very much from that of the control.

This observation illustrates that the inhibition of corrosion of mild steel by VCI may be due to mixed control (both anodic and cathodic).The higher values of cathodic Tafel slopes than the anodic slopes reveals that the corrosion inhibition is predominantly under cathodic control.

### *Alternating Current Impedance Measurement*

The Nyquist impedance plots for mild steel that were covered with VCI-impregnated and unimpregnated papers had almost a semicircular appearance (Figure 3). This observation indicates that the corrosion of mild steel was controlled by a charge transfer process. The charge transfer resistance ($R_{ct}$) and double layer capacitance ($C_{ct}$) values were evaluated from the Nyquist plot for mild steel in the presence of the best inhibiting concentration of VCI-impregnated paper and for unimpregnated paper in 0.005 M and 0.1 M HCl environments. Table 2 summarizes the values obtained. The higher $R_{ct}$ values of VCI-impregnated papers compared to the unimpregnated paper confirmed the inhibition by VCI.

**FIGURE 3**




**AC impedance diagram for mild steel in 0.005 M HCl in the presence of 4% VCI.**

### *Mechanism of Corrosion Inhibition*

Generally, the adsorption of organic molecules involves the O, N, and S atoms. This process may block the active sites and hence decrease the CR.[20] The essential oils contain these groups and could be adsorbed on the metal surface and decrease the surface area available for a cathodic and/or anodic reaction to take place. Because of the complex chemical composition of the VCI, it is quite difficult to assign the inhibitive effect to a particular constituent.

## Conclusions

The following conclusions can be drawn from this investigation:

- The rate of corrosion of mild steel in an HCl environment is a function of concentration of VCI.
- The IE increases with increased VCI concentration up to 4% and then decreases.
- The five essential oils function as VCIs.
- Stevenson chamber tests showed that in an industrial atmosphere, VCI-impregnated paper could offer a corrosion inhibition efficiency up to 90% for mild steel.
- Electrochemical polarization studies suggest that these VCIs can act as a mixed-type inhibitor for mild steel.
- AC impedance studies showed that protection from atmospheric corrosion for mild steel occurred by the charge transfer process.

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**TABLE 2**

**IE based on AC impedance measurements with 4% VCI impregnated Kraft paper**

| Name of VCI | 0.005 M HCl $R_{ct}$ (Ω·cm²) | $C_{dl}$ μF × $10^{-5}$ | IE (%) | 0.1 M HCl $R_{ct}$ (Ω·cm²) | $C_{dl}$ μF × $10^{-4}$ | IE (%) |
|---|---|---|---|---|---|---|
| Blank | 920 | 9.79 | — | 200 | 6.83 | — |
| JG | 2,520 | 3.54 | 63.5 | 455 | 2.96 | 56.0 |
| JA | 2,145 | 4.15 | 57.1 | 410 | 3.29[4] | 51.2 |
| OP | 2,752 | 3.24 | 66.6 | 520 | 2.60 | 61.5 |
| OB | 1,940 | 4.60 | 52.6 | 370 | 3.69 | 45.9 |
| VZ | 3,150 | 2.89 | 70.8 | 580 | 2.34 | 65.5 |

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