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Effect of menthol coated craft paper on corrosion of copper in HCl environment

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Abstract. Natural menthol was coated on craft paper by impregnation and studied as volatile corrosion inhibitor for copper in hydrochloric acid environment. The effect of menthol on copper corrosion was studied by gravimetric and electrochemical methods such as potentiodynamic polarization and electrochemical impedance measurements. The results indicate that menthol adsorbs on the metal surface, which protects copper against further corrosion. The adsorption behaviour of menthol on copper surface was found to obey Temkin's adsorption isotherm.

Keywords. Volatile corrosion inhibitor; copper; adsorption isotherm; Tafel polarization; electrochemical impedance spectroscopy.

1. Introduction

Corrosion is defined as destruction or deterioration and consequent loss of metals or alloys by chemical or electrochemical reaction with the environment. Corrosion causes heavy economic losses. World wide studies have shown that the overall cost of corrosion amounts to atleast 4–5% of the gross national product (GNP) and that 20–25% of this cost could be avoided by using appropriate corrosion control technology (Natesan *et al* 2006). Temporary corrosion protection methods have been developed to prevent corrosion of metals and metallic equipments during transport and storage. Among the various methods available for temporary protection of metals and alloys from corrosion, the use of volatile corrosion inhibitors (VCI) is a most effective and convenient method. Initially, camphor (Vernon and Stroud 1952) was used to protect military equipment. Numerous investigations are going on in the development of organic compounds as volatile corrosion inhibitor for ferrous and non-ferrous metals. The organic substances studied as volatile corrosion inhibitors were morpholine and its derivatives (Vuorinen *et al* 1994; Subramanian *et al* 1998), diamino hexane derivatives (Quraishi and Jamal 2002), octylamine (Subramanian *et al* 2002), cyclohexylamine and dicyclohexylamine (Subramanian *et al* 1999), amine carboxylates (Vuorinen and Skinner 2002), ammonium caprylate (Skinner *et al* 1999), benzoic hydrazide derivatives (Quraishi and Jamal 2005; Quraishi *et al* 2005), *bis*-piperidiniummethyl-urea (Zhang *et al* 2007), β-amino alcoholic compounds (Gao and Liang 2007a) etc.

In the present study, natural menthol having a molecular structure shown in figure 1 was used as volatile corrosion inhibitor for copper in HCl environment. Inhibition of copper corrosion by menthol was studied by weight loss and electrochemical studies.

2. Experimental

2.1 *Materials and apparatus*

Copper strips of 99·9% purity were used for the gravimetric and electrochemical measurements. For the gravimetric test, specimens of copper were made with dimensions of 5 × 1 × 0·1 cm and a hole was drilled in each for suspending purpose. The menthol impregnated papers were prepared by wet impregnation method. A known amount

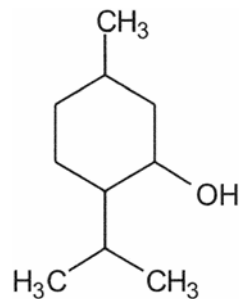

Figure 1. Molecular structure of menthol.

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(250–1250 mg) of menthol was taken and dissolved in 15 ml ethanol. One square feet of craft paper was dipped into the solution till completely wet and taken out when the solvent got evaporated. Then the impregnated paper was stored in tightly closed container. It was used for gravimetric and electrochemical studies. Gravimetric experiments were carried out in a 1 l bottle with tight fitting rubber cork. The specimens were suspended in the bottle and placed in an electrically heated thermostat at $40 \pm 1^{\circ}$C. Atmospheric corrosion monitor (ACM) was constructed by using five metal plates of size, 2 mm thick and 25 mm long. The metal plates were insulated from one another by means of PVC separators of thickness, 1 mm. The central metal plate was connected to one terminal which acts as the reference electrode (RE). Two alternate plates (except central plate) were connected to get other two terminals, viz. working electrode (WE) and counter electrode (CE). The whole setup was encapsulated in a polymer resin and it was used as a three-electrode type ACM. For polishing of copper specimens and ACM, 1/0, 2/0, 3/0 and 4/0 emery sheets were used. For the degreasing purpose trichloroethylene was used as a solvent. Tafel polarization and electrochemical impedance spectroscopy measurements were performed using CH electrochemical analyser (Model CHI 608B).

2.2 *Procedures*

2.2a *Gravimetric measurements*: The gravimetric test was conducted under continuous condensation to evaluate the inhibition effect of menthol impregnated craft paper. The test specimens' mill scales were removed by using the pickling solution as given in ASTM G1 specification. After pre treatments such as polishing and degreasing the specimens were weighed. The final geometrical area of each specimen was 10 cm^2. After initial weighing the test specimens were covered with unimpregnated and impregnated craft paper of menthol concentration, 250 to 1000 mg per square feet. The covered specimens were held by hooks in a one litre bottle containing 100 ml of 0·01 N HCl solution. The bottles were placed in a electrically heated thermostat at 40 ± 1°C. The test process includes continuous condensation of samples in a corrosion testing bottle of 100% relative humidity (RH). The period of gravimetric measurements was 14 days. After 14 days, the samples were removed for visual inspection and mass loss determination. The loose product of corroded sample was removed by hard rubber and rinsed in distilled water. Corrosion rates, inhibition efficiency and surface coverage were calculated by means of the following equations:

$$\text{Corrosion rate (CR)}\ (\mu\text{my}^{-1}) = \frac{87{\cdot}6 \times 10^3 \times W}{A \times t \times D},$$

$$\text{Inhibition efficiency (IE \%)} = \frac{CR_1 - CR_2}{CR_1} \times 100,$$

$$\text{Surface coverage}\ (\theta) = \frac{CR_1 - CR_2}{CR_1},$$

where W is weight loss in mg, A the area of the coupon in cm^2, t the time of exposure in hours, D the density of metal in g/cm^3 and CR_1 and CR_2 are the corrosion rates of the specimen without and with an inhibitor, respectively. The experiments were carried out in triplicate, i.e. the gravimetric corrosion rate was listed as an average value of the three specimens studied under identical conditions.

2.2b *Potentiodynamic polarization measurements*: A three-electrode type atmospheric corrosion monitor (Subramanian *et al* 2000; Bastidas *et al* 2005) with working electrode area of 1 cm^2 was used for potentiodynamic polarization studies. About 1ml of 0·01 N HCl was applied over the well polished atmospheric corrosion monitor, VCI impregnated craft paper was pressed over it. Open circuit potential (OCP) was noted, when a steady state is attained. The potential was varied from OCP within the range of –200 mV to +200 mV at the rate of 2 mV/s. Corrosion kinetic parameters such as E_{corr}, Tafel slopes and I_{corr} were evaluated from E vs log I plot. A similar experiment was carried out using unimpregnated craft paper as control. All the experimental results were replicated three times to ensure their reproducibility and statistical significance. The inhibition efficiency and surface coverage were calculated using the following equations:

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

$$\text{Surface coverage}\ (\theta) = \frac{I_{corr} - I_{corr(i)}}{I_{corr}},$$

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

2.2c *Electrochemical impedance measurements*: Electrochemical impedance measurements were carried out for VCI impregnated and unimpregnated papers. One ml of 0·01 N HCl was applied on a 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–100 mHz. 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 gives the charge transfer resistance (R_{ct}) value. All the experimental results were replicated three times to ensure their reproducibility and statistical significance. The inhibition efficiency was calculated using the following formula:

Table 1. Gravimetric corrosion results of menthol impregnated and unimpregnated craft papers as VCI for copper in 100% RH using 0·01 N HCl at 40 ± 1°C for 14 days.

Amount of menthol impregnated on craft paper (mg/sq ft)	Weight loss (mg)	Corrosion rate ($\mu m\ y^{-1}$)	Surface coverage (θ)	Inhibition efficiency (%)
Control	26·30	76·53	–	–
250	16·90	49·18	0·36	35·74
500	12·50	36·38	0·52	52·47
750	8·90	25·90	0·66	66·16
1000	5·70	16·59	0·78	78·33
1250	6·10	17·75	0·77	76·81

Table 2. Electrochemical polarization parameters of menthol impregnated and unimpregnated craft papers as VCI for copper in 0·01 N HCl by thin layer technique.

Amount of menthol impregnated on craft paper (mg/sq ft)	E_{corr} (mV)	Tafel slopes (mV/decade)		I_{corr} ($\mu A/cm^2$)	LPR (Kohm cm^2)	Surface coverage (θ)	*IE* (%)
		b_a	$-b_c$				
Control	–50	69	129	11·41	1·72	–	–
250	–19	83	120	7·50	2·84	0·34	34·29
500	–52	75	122	5·48	3·67	0·52	51·94
750	–56	74	121	4·13	4·83	0·64	63·84
1000	–57	77	113	3·21	6·19	0·72	71·83
1250	–56	79	123	3·37	6·19	0·70	70·48

$$\text{Inhibition efficiency (IE\%)} = \frac{R_{ct(i)} - R_{ct}}{R_{ct}} \times 100,$$

where R_{ct} is charge transfer resistance for unimpregnated paper and $R_{ct(i)}$ the charge transfer resistance for impregnated paper.

3. Results and discussion

3.1 *Gravimetric measurements*

The observation of continuous condensation test with unimpregnated and various concentrations of menthol impregnated craft papers for copper in 0·01 N HCl at 100% RH for 14 days are given in table 1. It can be seen from the values in the table that the corrosion rate and inhibition efficiency increased with increase in concentration of menthol in the craft paper only up to 1000 mg/sq ft. The maximum inhibition efficiency of 78·33% was observed at a menthol concentration of 1000 mg/sq ft. At higher concentration the inhibition efficiency decreased due to the formation of soluble metal inhibitor complex in HCl environment.

3.2 *Potentiodynamic polarization measurements*

Potentiodynamic polarization behaviour of copper in 0·01 HCl environment in presence of various concentrations of menthol impregnated and unimpregnated papers were studied at a sweep rate of 2 mV/s. The polarization curves are shown in figure 2. The corrosion kinetic parameters were obtained from the anodic and cathodic polarization curves by Tafel extrapolation method and the results are given in table 2. It can be seen from the polarization values in the table that the E_{corr} and Tafel slopes were not much affected due to the presence of various concentrations of menthol. It infers that the inhibition of copper corrosion by menthol is a mixed type. It is also seen from the data that the linear polarization values get increased with increase in concentrations of menthol. The linear polarization resistance exhibited by the copper specimen covered with unimpregnated craft paper and menthol impregnated craft paper of concentration, 1000 mg/sq. ft, were 1·72 and 6·19 Kohm cm^2, respectively. The increase in linear polarization resistance is due to the adsorption of menthol and thereby formation of a protective layer on copper surface. It is further observed from the results that there is no significant change in the Tafel slopes; it infers that the menthol acts as a mixed type inhibitor. The corrosion current values decreased with increase in concentration of menthol only up to 1000 mg/sq ft and then there is a slight increase. The maximum inhibition efficiency of 71·83% was exhibited by menthol of concentration, 1000 mg/sq. ft.

3.3 *Electrochemical impedance measurements*

Impedance diagrams for copper in 0·01 N HCl covered with menthol impregnated and unimpregnated papers are

Table 3. AC impedance parameters of menthol impregnated and unimpregnated craft papers as VCI for copper in 0·01 N HCl by thin layer technique.

Amount of thyme impregnated on craft paper (mg/sq ft)	R_{ct} (Kohm cm^2)	C_{dl} (μF/cm^2)	Inhibition efficiency (%)
Control	1·85	15·66	–
250	3·08	11·35	39·96
500	4·12	8·50	55·06
750	5·57	6·29	66·76
1000	6·21	5·64	70·19
1250	5·87	5·96	68·48

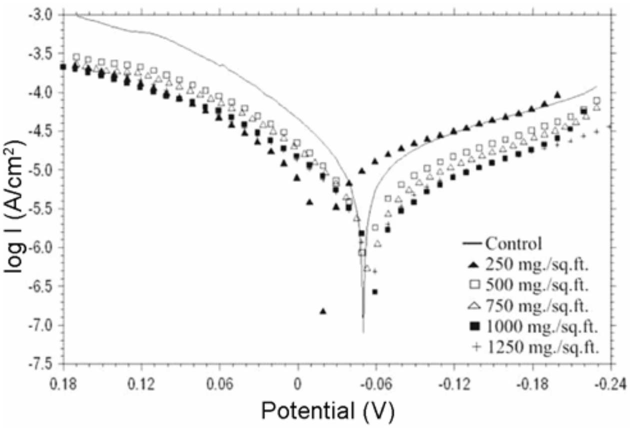

Figure 2. Potentiodynamic polarization curves of menthol for copper in 0·01 N HCl by thin layer technique.

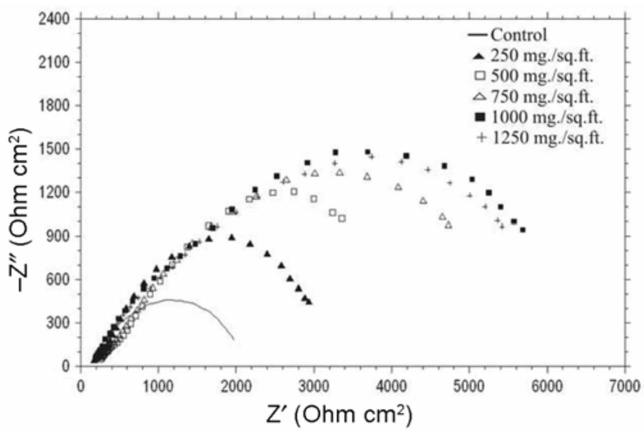

Figure 3. Electrochemical impedance curves of menthol for copper in 0·01 N HCl by thin layer technique.

depicted in figure 3. It is observed from the figure that the curves are of depressed semi circular type. It indicates that the mechanism of corrosion process in the presence and absence of menthol was a charge transfer process. The electrochemical impedance parameters were evaluated from the Nyquist plots and the observations are presented in table 3. It can be seen from the data that the charge transfer resistance of copper in 0·01 N HCl with different concentrations of menthol are several times higher than those in the absence of menthol, indicating that corrosion resistance increases in the presence of menthol. The charge transfer resistance and inhibition efficiency for the highly protected specimen with menthol concentration, 1000 mg/sq ft, were 6·21 Kohm cm^2 and 70·19%, respectively.

3.4 *Adsorption isotherm*

Adsorption isotherm plays a vital role in the determination of the mechanism of organo-electrochemical reactions. Generally, it has been accepted that organic molecules inhibit corrosion by adsorption at the metal/solution interface. The adsorption process depends on the electronic characteristics of molecules, chemical composition of the solution, the nature of the metal surface, temperature of the reaction and on the electrochemical potential at the metal/solution interface (Gao and Liang 2007b). The frequently used isotherms are Langmuir, Frumkin, Parsons, Temkin, Flory-huggins and Bockris-sinkles. All these isotherms are of the general form

$$f(\theta, x)\exp(-2a\theta) = kc,$$

where $f(\theta, x)$ is configuration factor, a the interaction factor, k the equilibrium constant, c the concentration and θ the surface coverage.

Figure 4 shows the plot of surface coverage (θ) vs log concentration for copper in 0·01 N HCl. The data appear to fit in a straight line, indicating the applicability of Temkin's adsorption isotherm model to describe the adsorption process of menthol on copper surface in HCl environment.

3.5 *Mechanism of inhibition*

The corrosion inhibiting action of menthol is attributed to the presence of lone pair of electrons present on the O atoms of the inhibitors molecule, which facilitates adsorption of the inhibitor onto the metal surface. Schematic representation of menthol adsorbed on the metal surface is shown in figure 5.

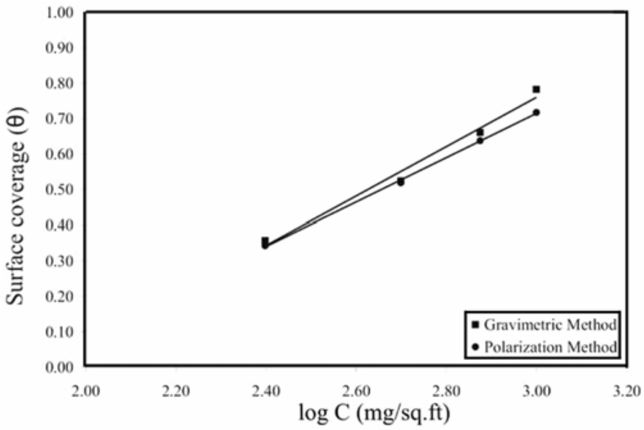

Figure 4. Temkin's adsorption isotherm plot of menthol for copper in HCl environment.

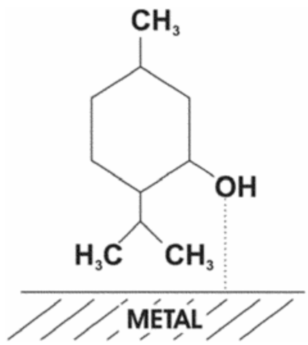

Figure 5. Schematic representation of menthol adsorbed on copper.

4. Conclusions

(I) Menthol has been found to be an effective volatile corrosion inhibitor for copper in hydrochloric acid environment. The maximum inhibition efficiency was achieved at menthol concentration, 1000 mg/sq. ft.

(II) Tafel polarization studies infer that the menthol is acting as mixed type inhibitor. Adsorption of menthol on copper surface in hydrochloric acid environment is found to obey Temkin's adsorption isotherm.

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References

Bastidas D M, Cano E and Mora E M 2005 *ACMM* **52** 71

Gao G and Liang C 2007a *J. Electrochem. Soc.* **154** 144

Gao G and Liang C 2007b *Corrosion Sci.* **49** 3479

Natesan M, Palraj S, Venkatachari G and Palaniswamy N 2006 *Corrosion* **62** 883

Quraishi M A and Jamal D 2002 *Corrosion* **58** 387

Quraishi M A and Jamal D 2005 *J. Metall. & Mater. Sci.* **47** 45

Quraishi M A, Bhardwaj V and Jamal D 2005 *Indian J. Chem. Technol.* **12** 93

Skinner W, Du Preez F and Vuorinen E 1999 *Br. Corros. J.* **34** 151

Subramanian A, Gopalakrishnan R, Boopathy C, Balakrishnan K, Vasudevan T, Natesan M and Rangaswamy N S 1998 *Bull. Electrochem.* **14** 289

Subramanian A, Rajendran P, Natesan M, Balakrishnan K and Vasudevan T 1999 *ACMM* **46** 346

Subramanian A, Natesan M, Muralidharan V S, Balakrishnan K and Vasudevan T 2000 *Corrosion* **56** 144

Subramanian A, Rathinakumar R, Natesan M and Vasudevan T 2002 *ACMM* **49** 354

Vernon E G and Stroud H J 1952 *J. Appl. Chem.* **2** 178

Vuorinen E and Skinner W 2002 *Br. Corros. J.* **7** 153

Vuorinen P, Ngobent G H, Van der Kalashorst, Skinner W, De Wet E and Ernst W S 1994 *Br. Corros. J.* **29** 120

Zhang D Q, Gao L X and Zhou G D 2007 *Mater. & Corros.* **58** 594