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DAPA, EA, TU and BI as Vapour Phase Corrosion Inhibitors for Mild Steel under Atmospheric Conditions

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Abstract

Four new vapour phase corrosion inhibitor (VPCI) i.e. 3,3-diaminodipropylamine (DAPA), ethylamine (EA), thiourea (TU), and benzimidazole (BI) were tested for mild steel in different atmospheric conditions at 50^0C by weight loss, Eschke test, salt spray method, SO_2 test and metallurgical research microscopy technique. All investigated VPCIs exhibited very good corrosion inhibition efficiency for mild steel. DAPA showed the best corrosion inhibition efficiency. The result obtained from weight loss technique, Eschke test, salt spray method, SO_2 test were supported by metallurgical research microscopy technique. Inhibition of corrosion in vapour phase by VPCI takes place because they alkaline the medium to pH value at which the rate of corrosion becomes significantly low.

Keywords: Mild steel, weight loss, atmospheric corrosion, vapour phase corrosion inhibitor.

Introduction

Mild steel is the most common form of steel and because of its low cost it is chief material of construction. Mild steel have good strength, hard and can be bent, worked or can be welded into an endless variety of shapes for uses from vehicles (like cars and ships) to building materials. Because of its unique properties like, very cheap, high strength, hardness and easy availability, it has wide range of applications in nut bolt, chains, hinges, knives, armour, pipes, magnets, military equipments etc.

Metal and their alloys are exposed to aggressive environment under atmospheric condition during the manufacture, processing, storage or transportation and can accelerate the degradation of the metal, alloys and their products. In such cases, the corrosion prevention methods like water-displacing products (oil or grease), water-absorption products (silica gel) and dehumidification are not significant due to high labor, material cost for the application and removal of product and difficulty to calculate specific moisture. The vapour phase corrosion inhibitors (VPCI) play a significant role in minimizing corrosion to metals and their alloy in atmospheric condition by producing vapours with sufficient vapour pressure due to their volatile nature and prevent the metal or alloys from corrosion by adsorption of their vapours onto the metal surface. The effective use of surfactants for corrosion inhibition depends upon the application environment and properties of metals as well as nature of surfactants[1-5].

Use of VPCI is an effective method to prevent atmospheric corrosion[6-9]. The protection of metal is due to the inhibitors volatizing into the atmosphere surrounding the metal parts and modifying the atmosphere[10]. VPCI 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 vapours of the VPCI are condensed and are hydrolyzed by moisture to release protective ions. The choice of a chemical compound as vapour phase corrosion inhibitors depends upon on its vapour pressure and efficiency to prevent corrosion by forming a protective film. The vapour pressure of VPCI must posses some optimum values.

Subramanian et. al studied the most commonly used VPCI, derivatives of ammonium carbonate and ammoniumnitrite on copper, mild steel and zinc in sulphur dioxide (SO_2) environments[11]. Due to their easily availability and their better percentage corrosion inhibition efficiency (PCIE) they have been used in industry for several decades. However, the disadvantages of using these derivatives are their toxic nature to the environment. Thus, replacing them with new environmental friendly inhibitors is desirable. Saurbier et. al suggested toluylalanine as an effective temporary inhibitor of steel in wet atmosphere[12]. Vuorinew reported a series of morpholine-mannich based derivatives as volatile corrosion inhibitors[13]. Polymeric corrosion inhibitors such as polyacrylic and polyamno-benzoquinone etc. are widely used and they have a lower toxicity than their monomers[14-15]. Many kinds of morpholine oligomer (MPO) as VPI for the temporary protection of box shaped hatch covers and rudder blades of large ships at Hudong Shipyard have been studied by Zhang et. Al[16]. Quraishi et. al studied the inhibiting properties of five organic vapour phase inhibitors namely, derivatives of imidazoline maleate, orthophosphate, nitrobenzoate, phthalate, cinnamate on mild steel, brass and copper[17]. They also studied some organic volatile corrosion inhibitors mostly derivative of diaminohexane such as diaminohexane cinnamate, nitrobenzoate, phthalate, orthophosphate and maleate on aluminium, zinc and mild steel[18]. Study of some salts of benzoic hydrazide benzoate (BHB), benzoic hydrazide salicylate (BHS) and benzoic hydrazide nitrobenzoate (BHN) as corrosion inhibitors of mild steel[19-21], brass and copper was studied by weight loss method[22]. Rajagopalan et. al examined derivatives of benzene with β-napthol as a VPCI in a sulphur dioxide and chloride atmosphere[23]. Subrumanian et. al recently studied the corrosion inhibition behaviour of morpholine and its three derivatives salts- morpholine carbonate, borates, and phosphates salts[24]. Of these morpholine and its carbonates salt exhibited 90 and 85% corrosion inhibition efficiency (CIE) respectively while the other salts gave less than 40% corrosion inhibition efficiency.

In the present study, the vapour phase corrosion inhibiting properties of four organic VPCI i.e. 3,3-diaminodipropylamine (DAPA), ethylamine (EA), thiourea (TU) and benzimidazole (BI) were studied on mild steel by weight loss technique at 85% of relative humidity and 50 ^{0}C temperature, salt spray method in a medium of 3.0% sodium chloride, SO_2 test, Eschke test at 85% of relative humidity and research metallurgical microscopy technique for the surface study of corroded metal specimen.

Material and Methods

Experimental: Name, molecular formula and structure of four investigated VPCI studied for Mild steel in atmospheric condition are given in table 1. These VPCIs were selected due to their easily availability, suitable vapour pressure, less toxic nature, high durability, cost effective and eco-friendly nature.

Vapour pressure determination Test: A standard Knudsen method was used to determine the vapour pressure of all the four VPCIs[25]. Definite amount of exactly weighed VPCIs were placed in a single neck round bottom flask fitted with a rubber cork in the neck having a glass capillary of 1.0 mm diameter in the center of rubber cork. Then the flask was kept in air thermostat maintained at the constant temperature of 50 ^{0}C for 10 days. Change in the weight of VPCIs was observed by the single pan analyticl balance (0.01 mg accuracy). Vapour pressure of all the four investigated VPCIs were determined by equation (1) and has been shown in table 2.

$$P = \frac{W}{A\,t}\left[\frac{2\pi\,R\,T}{M}\right]^{1/2} \quad (1)$$

where, P = vapour pressure of the VPCI (mm of Hg), A = area of the orifice (m^2), t = time of exposure (sec.), W = weight loss of substance (kg), T = temperature (K), M = molecular mass of the inhibitor (kg) and R = gas constant (8.314 $JK^{-1}mol^{-1}$).

Table-1
Name, molecular formula and structure of four vapour phase corrosion inhibitors

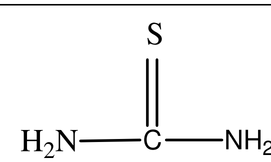
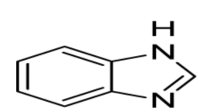
Sr. No.	Name	Molecular formula	Structure
(i)	3,3-diaminodipropylamine (DAPA)	($C_6H_{17}N_3$)	H-N< CH_2-CH_2-CH_2-NH_2 / CH_2-CH_2-CH_2-NH_2
(ii)	Ethylamine (EA)	(C_3H_7N)	CH_3-CH_2-NH_2
(iii)	Thiourea (TU)	(CH_4N_2S)	
(iv)	Benzimidazole (BI)	($C_7H_6N_2$)	

Table- 2
Vapour pressure of all the four investigated VPCIs

S. No.	Inhibitor	Vapour pressure (mm Hg)
1.	DAPA	392.7×10^{-3}
2.	EA	869.7×10^{-3}
3.	TU	10.48×10^{-3}
4.	BI	35.68×10^{-3}

Weight Loss Technique: Mild steel (ASTM-283) used for the investigation was in the form of sheet (0.025 cm thick) and had the following composition: C, 0.17; Si, 0.35; Mn, 0.42; S, 0.05; P, 0.20; Ni, 0.01; Cu, 0.01; Cr, 0.01 and Fe, balance (wt. %). The coupons of mild steel of dimensions 3.5 cm × 1.5 cm × 0.025 cm were used for weight loss studies. All the metal specimens were mechanically polished successively with the help of emery papers of grades 100, 200, 300, 400 and 600 μ and then thoroughly cleaned with plenty of triple distilled water (conductivity less than 1×10^{-6} ohm^{-1} cm^{-1}) and then with acetone. The specimens were dried with hot air blower and stored in desiccators over silica gel. Weight loss experiments were carried out in an electronically controlled air thermostat maintained at a constant temperature of 50^0C with in an accuracy of ± 0.1^0C. Four inhibitors named as DAPA, EA, TU and BI was placed separately in different isolated chambers in the air thermostat.

After recording the initial weights of mild steel specimens on a Mettler Toledo, Japan AB 135-S/FACT, single pan analytical balance, (with a precision of 0.01 mg), they were kept in different isolated chambers of air thermostat having fixed amount of VPCI at a constant temperature of 50^0C for 24 hours of exposure time. A uniform thin film of VPCI was adsorbed onto the metal coupons after 24 hours of exposure. Then these coupons were transferred to a digitally controlled humidity chamber maintained at 85% humidity at a constant temperature of 50^0C for 10 days. Blank coupons were also kept in the humidity chamber for the same duration in the same corrosive environment. After exposing the specimens for 10 days, the specimens were taken out from the humidity chamber and washed initially under the running tap water. Loosely adhering corrosion products were removed with the help of rubber cork and the specimen was again washed thoroughly with triple distilled water and dried with hot air blower and then weighed again. Corrosion rate in mils per year (mpy) and percentage corrosion inhibition efficiency (PCIE) were calculated using the equations (2) and (3) respectively[26].

$$\text{Corrosion rate (mpy)} = \frac{534 \times W}{D\ A\ T} \quad (2)$$

where, W = Weight loss (mg), D = Density of carbon steel (g/cm^3), A = Area of specimen (sq. inch), T = Exposure time (hours).

$$\text{\%age corrosion inhibition efficiency} = \frac{CR_{Blank} - CR_{inhibitor}}{CR_{Blank}} \times 100 \quad (3)$$

where, CR_{Blank} = Corrosion rate in blank and $CR_{inhibitor}$ = Corrosion rate in presence of inhibitor.

Salt Spray Method: After exposing the pre weighed mild steel coupons to VPCI in air thermostat for 24 hours, they were transferred to salt spray chamber having 3.0 % sodium chloride solution maintained at constant temperature of 50 ^{0}C for duration of 10 days along with blank specimens. After exposing the specimens for 10 days, the specimens were taken out from the salt spray chamber and washed initially under the running tap water. Loosely adhering corrosion products were removed with the help of rubber cork and the specimen was again washed thoroughly with triple distilled water and dried with hot air blower and then weighed again. Corrosion rate in mils per year (mpy) and PCIE were calculated using the equations (2) and (3), respectively.

Eschke Test: Eschke test was carried out on the pre weighed mechanically polished mild steel coupons as prescribed in the literature[27]. Kraft papers of suitable size were dipped in the VPCI for 30 second and then dried to adsorb uniform layer of the inhibitor on the Kraft papers. Then mild steel coupons were wrapped in VPCI impregnated Kraft papers and then taken in the humidity chamber maintained at 85 % relative humidity maintained at a constant temperature of 50^0C for first 12 hours and 25^0C for next 12 hours, alternately for 10 days. This temperature cycle was maintained in two sets because of formation and condensation of the vapours of VPCI on mild steel surface regularly. After exposing the specimens for 10 days, the specimens were taken out from the humidity chamber and washed initially under the running tap water. Loosely adhering corrosion products were removed with the help of rubber cork and the specimen was again washed thoroughly with triple distilled water and dried with hot air blower and then weighed again. Corrosion rate in mils per year (mpy) and PCIE were calculated using the equations (2) and (3), respectively.

Sulphor dioxide Test: SO_2 test was carried out on the mild steel coupons of same dimension as in weight loss study. SO_2 gas was prepared by dissolving 0.04 g of sodium thiosulphate in 30 mL aqueous solution of 1.0 % NH_4Cl and 1.0 % Na_2SO_4 solution and 0.5 mL of 1.0N H_2SO_4 was added to the flask. Initially pre weighed and mechanically polished mild steel coupons were placed in air thermostat maintained at a constant temperature of 50^0C for duration of 10 days. Definite weight of VPCIs in a petridis and the flask, which is the source of SO_2, were placed in the isolated chambers of air thermostat containing mild steel coupons. After exposing the specimens for 10 days, the specimens were taken out from the air thermostat and washed initially under the running tap water. Loosely adhering corrosion products were removed with the help of rubber cork and the specimen was again washed thoroughly with triple distilled water and dried with hot air blower and then weighed again. Corrosion rate in mils per year (mpy) and PCIE were calculated using the equations (2) and (3), respectively.

Metallurgical Research Microscopy Technique: This technique is employed for the surface study of mild steel coupons to know about nature and type of corrosion using metallurgical research microscopy technique (CXR II from Laomed, Mumbai, India). The micrographs of the corroded specimens were taken after exposure of 10 days. Micrographs of the blank mild steel coupons were also taken for the comparative study of metal specimen.

Results and Discussion

Weight Loss Technique: The values of weight loss, corrosion rate and PCIE for all the four VPCIs were shown in **Table 3**. **Figure 1** shows comparative chart of corrosion rate of all the four investigated VPCIs with the CR of blank specimen. The corrosion rate is found to be almost negligible in the coupons of mild steel which were treated with DAPA. PCIE of all the four investigated VPCIs are shown in **Figure 2**. It is clear from Table 3 that, DAPA exhibit highest PCIE i.e. 96.07 for the mild steel under the atmospheric conditions at 50 ^{0}C temperature and BI shows minimum i.e. 48.42. PCIE follows the order as DAPA > EA > TU > BI.

Salt Spray Method: Figure 3 shows weight loss (mg), corrosion rate (mpy) and PCIE of all the four investigated VPCIs at a temperature of 50 ^{0}C by salt spray method. As chloride ions are very aggressive from corrosion point of view, so a high corrosion rate was observed in salt spray method in comparison to weight loss method. All the four investigated VPCIs shows good corrosion inhibition efficiency even in this aggressive environment and at a high temperature of 50 ^{0}C. The PCIE follows the same order as in weight loss method i.e. DAPA > EA > TU > BI.

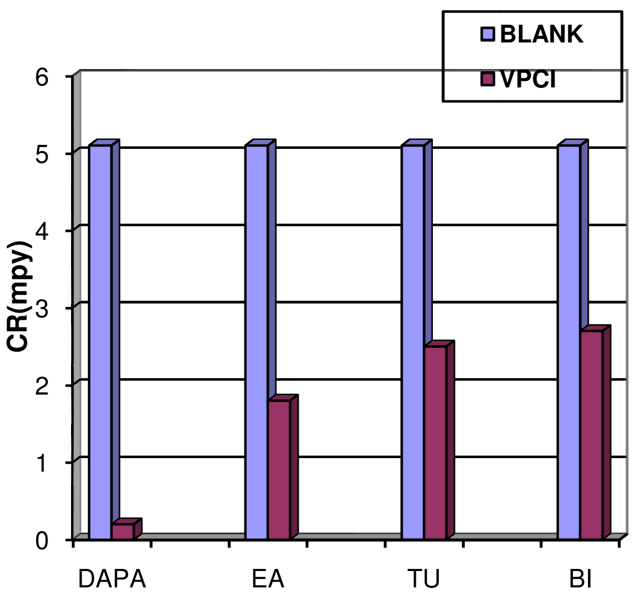


Figure-1
Corrosion rate (mpy) of mild steel coupons treated with four different VPCI with respect to blank coupons

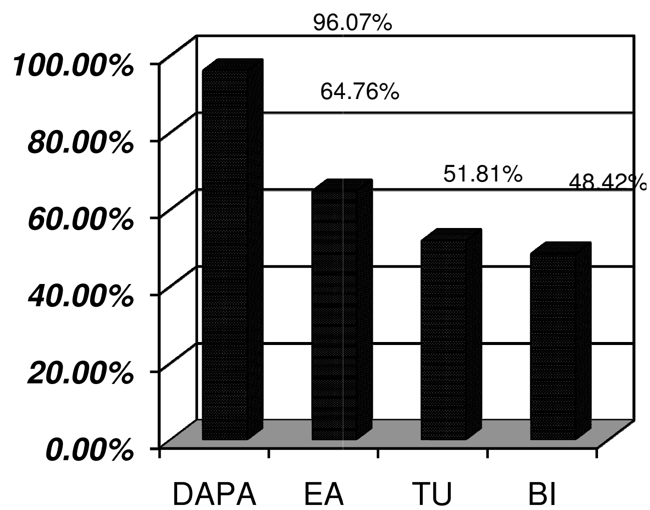


Figure-2
PCIE of all the four investigated VPCIs obtained from weight loss technique

Table-3
Weight loss, corrosion rate, PCIE for all the four VPCIs at a temperature of 50^{0}C and 85% relative humidity for 10 days by weight loss method

S.No.	VPCI	Weight loss (10^{-1} mg)	CR (mpy)	PCIE
1.	Blank	148	5.1	-
2.	DAPA	7	0.2	96.07
3.	EA	52	1.8	64.76
4.	TU	72	2.5	51.81
5.	BI	78	2.7	48.42

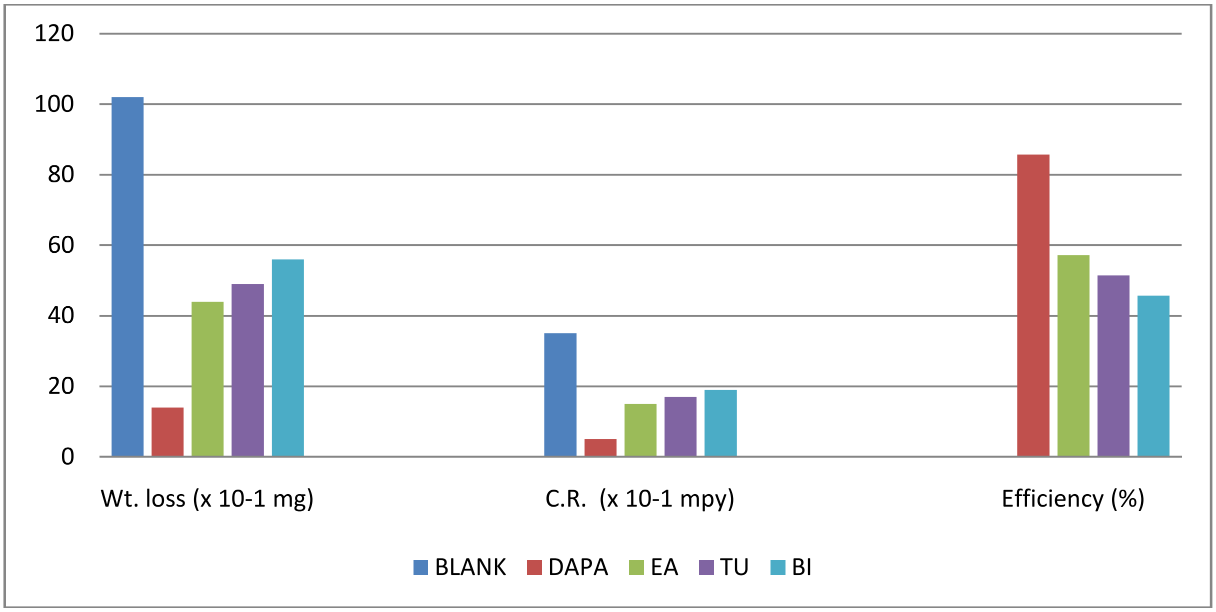


Figure-3
Weight loss (mg), CR (mpy), PCIE of all the four VPCIs obtained from Salt spray method

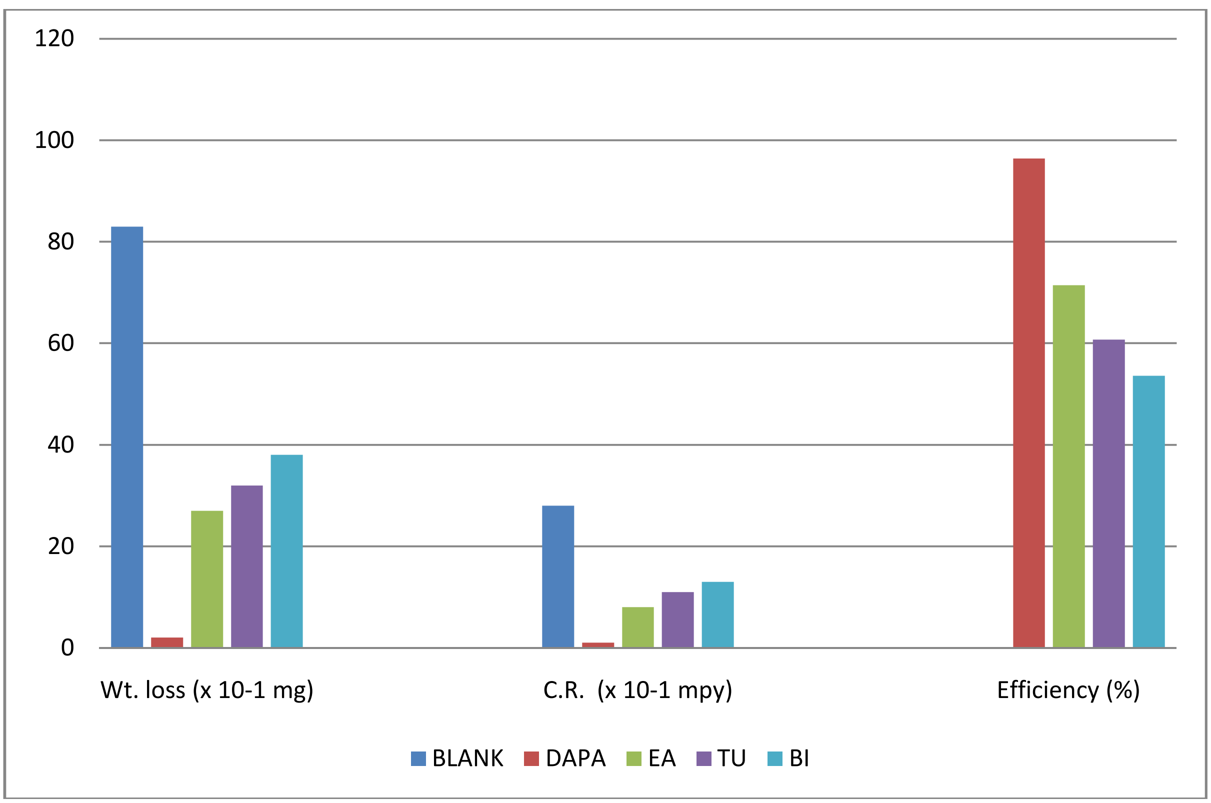


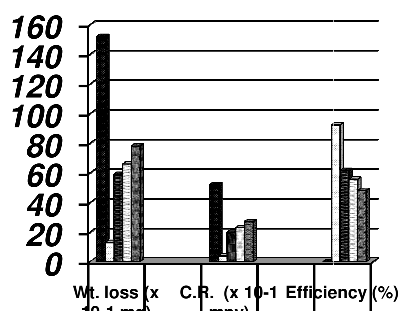
Figure-4
Weight loss, CR and PCIE of all the four VPCIs for mild steel by Eschke Test

Eschke Test: Figure 4 shows weight loss, CR and PCIE data of all the four VPCIs at 50 ^{0}C after 10 days of exposure by Eschke test. It is clear from the Fig.4 that DAPA shows almost 100 % corrosion inhibition efficiency for mild steel. The PCIE follows the same order as in weight loss method and salt spray method i.e. DAPA > EA > TU > BI. Results of visual examinations of the mild steel coupons by Salt spray, Eschke test and SO_2 test were shown in table 4.

Table- 4
Results of visual examination of surface of mild steel coupons in presence and absence of VPCIs after corrosion experiments performed at 50^{0}C for 10 days

VPCI	Salt Spray Method	Eschke Test	SO_2 Test
Blank	Pits were visible	Uniform corrosion seen	Pitting corrosion
DAPA	Smooth surface No corrosion product	Smooth surface No corrosion product	Smooth surface No corrosion product
EA	Slightly corroded	Almost clean surface	Almost clean surface
TU	Few corrosion product	Slightly corroded	Corrosion product seen
BI	Uniform corrosion seen	Corrosion product seen	3-4 spots of corrosion

SO_2 Test: Figure 5 shows data of weight loss, CR and PCIE of all the four VPCIs obtained from SO_2 test. Due to the acidic nature of sulphur dioxide gas, observed CR was very high in comparison to weight loss, salt spray and Eschke test. All the four VPCIs shows good corrosion inhibition efficiency. The PCIE follows the same order as in weight loss method, Eschke test and salt spray method i.e. DAPA> EA > TU > BI. Results of visual examinations of the mild steel coupons by salt spray, Eschke test and SO_2 test were shown in table 4.



	Wt. loss (x 10-1 mg)	C.R. (x 10-1 mpy)	Efficiency (%)
BLANK	152	52	0
DAPA	13	4	92.3
EA	59	20	61.53
TU	66	23	55.76
BI	78	27	48.07

Figure- 5
Weight loss, CR and PCIE of all the four VPCIs obtained from SO_2 test

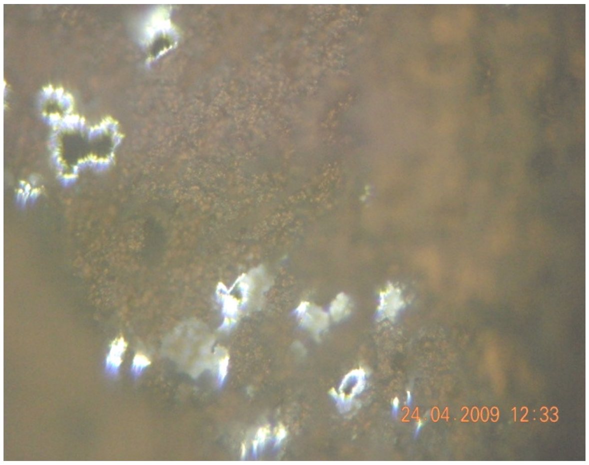
Metallurgical Microscopy Technique: Figure 6 shows metallurgical micrograph of mild steel coupons treated with different VPCIs by weight loss method after exposure of 10 days at 50^{0}C. Pits are clearly visible in the micrograph of blank sample showing pitting types of corrosion in absence of inhibitor. The surface of mild steel coupon treated with DAPA is very smooth and clear which confirms the high PCIE shown by DAPA against the atmospheric corrosion. There is uniform type of corrosion on mild steel coupons treated with TU and BI.

Mechanism of inhibition: Inhibition of metallic corrosion by the VPCI may involves the vapourization of the VPCIs in non dissociated molecular form, followed by the adsorption of these vapour on the metal surface either due to the presence of lone pairs of electrons on N atoms of inhibitors or formation of barrier film by aliphatic chain on metal surface in case of DAPA. The VPCIs investigated in present study inhibited corrosion of metals in different ways i.e., by saturating the space with their vapours and reducing the relative humidity below critical value, by alkalizing the medium to pH value at which the rate of corrosion become significantly low, by reducing the corrosion current density to a minimum value by rendering the metal surface hydrophobic which prevented the reaction of metal with environment.

The presence of more number of lone pairs in the inhibitor molecule enhances their corrosion inhibition efficiency. But, the presence of unsaturation near the lone pair of hetero atom retards their action of inhibition due the resonance stabilization.

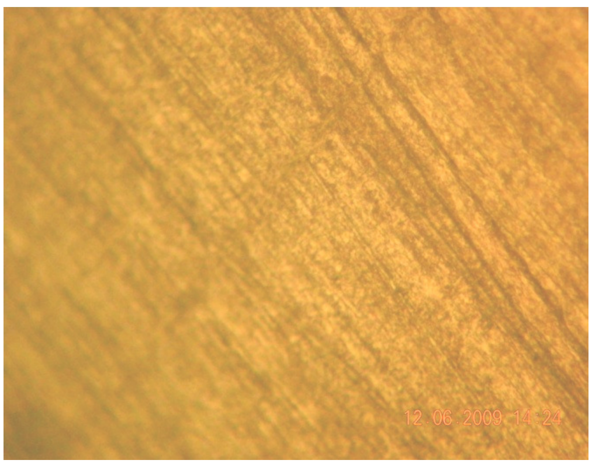
Conclusion

From the results of weight loss, salt spray, Eschke test and sulphur dioxide test, the following conclusion can be drawn: All the four investigated VPCIs show good corrosion inhibition efficiency toward mild steel in different corrosive environment like very high relative humidity, 3.0 % sodium chloride, acidic conditions (sulphur dioxide gas) and high temperature i.e. 50^{0}C. Out of four investigated VPCIs, DAPA shows best corrosion inhibition efficiency in different corrosive environment. VPCI saturate the space with their vapours and reducing the relative humidity below critical value and also alkalize the medium to a higher pH value at which the rate of corrosion become significantly low. Percentage corrosion inhibition efficiency was found to be in the order DAPA > EA > TU > BI. Results obtained from weight loss technique, Eschke test, SO_2 test, salt spray method were further supported by metallurgical microscopy technique

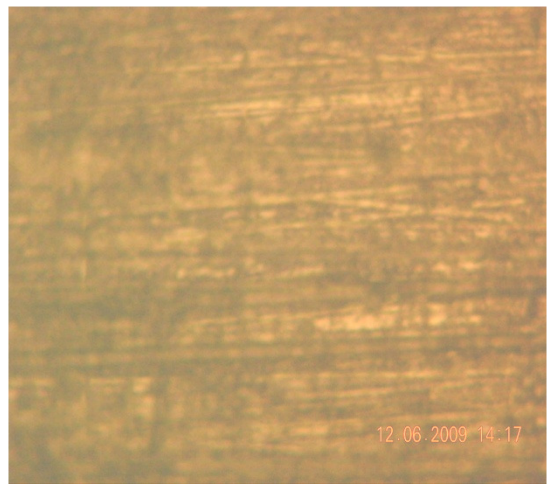


Blank mild steel coupon

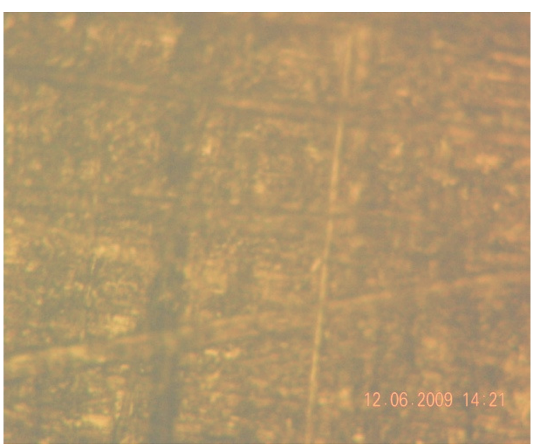
Blank mild steel coupon



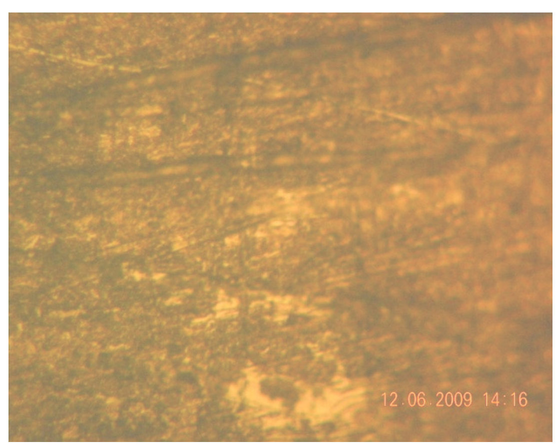
Mild steel coupon treated with DAPA



Mild steel coupon treated with EA



Mild steel coupon treated with TU



Mild steel coupon treated with BI

Figure-6
Metallurgical micrographs of mild steel coupons blank and treated with different VPCIs

References

1. Free M.L., Klang W. and Ryu D.Y., Prediction of Corrosion Inhibition Using Surfactants, *Corrosion*, **60** 837-844 **(2004)**

2. Rozenfeld I.L., Corrosion Inhibition, New York, McGraw Hill Inc **(1982)**

3. Kuznestor Y.L., Organic inhibitors of Corrosion of metals, Plenum Press, New York 70 **(1996)**

4. Jones D.A., Principles and Preventions of Corrosion, 2nd Ed, Upper Saddle River, Prentice Hall, NJ, 503 **(1996)**

5. Bregmann J.L., Corrosion Inhibition, Macmillan Co., New York **(1963)**

6. Singh D.D.N. and Banerjee M.K., *Anticorrosion Method*, **31** 4-8 **(1984)**

7. Stupnisek-Lisac E., Cinotti V. and Retchenabach D., *J. Appl. Electrochem*, **29,** 117-122 **(1999)**

8. Subrumanian A., Natsen M., Murlitharan V.S., Balakrishan K. and Vasudevan T., An overview: vapor phase corrosion inhibitors, *Corrosion*, **56** 144-155 **(2000)**

9. Sastri V.S., Corrosion Inhibitors Principles and Applications, John Wiley & Sons, New York 787 **(1998)**

10. Rajgopalan K.S. and Ramaseshan G., *J. Sci. Ind. Res.*, **19A,** 275-280 **(1960)**

11. Subrumanian A., Gopalakrishan R., Bhupati C.S., Balakrishan K., Vasudevan T. and Natesan M.N.S., *Bull. Electrochem*, **14,** 739-744 **(1998)**

12. Saurbier K., Rengaswamy M.V., Hchultze G.W., Geke J., Penninger J. and Robmeler H., *Corros. Sci,* **33,** 351 **(1992)**

13. Vuarinew E.K., *Br. Corros. J.*, **29,** 120 **(1994)**

14. Sekine I., Sambongih M., Hogiuda H., Oshibe T., Yuasa M., Imohama T., Shibata Y. and Wake T., *J. Electrochem. Soc,* **139,** 167 **(1992)**

15. Muralitharan S., Pitchumani S., Ravichaneran S. and Iyur S.V.K., J. *Electrochem. Soc*, **142,** 478 **(1995)**

16. Zhang D.Q., Gao L.X., *Mater. Perform.*, **42,** 40 **(2003)**

17. Quraishi M.A., Jamal D., Synthesis and evaluation of some organic vapor phase corrosion inhibitors, *Ind. J. Chem. Tech.*, **11,** 459-464 **(2004)**

18. Quraishi M.A. and Jamal D., *Corrosion*, **58,** 387 **(2002)**

19. Tuken Yazici T. and Erbil B., *Progress in organic coating*, **50,** 115 **(2004)**

20. Starostina M., Smorodin A. and Galor L., *Meter. Perform.*, **38,** 52 **(2000)**

21. Rajendran S., Apparao B.V. and Palaniswamy N., Corrosion and its Control, Proc. of International Conf. on Corrosion, Mumbai **(1997)**

22. Quraishi M.A., Bhardwaj V. and Jamal D., *Ind. J. Chem. Tech.*, **12,** 98 **(2005)**

23. Persiantsava V.P., Chemistry Review in Corrosion, Soviet Scientific Reviews of Mascow, OSSR, **8,** 64 **(1987)**

24. Subrumanian A., Natesan M., Balakrishan K. and Vasudevan T., *Bull. Electrochem.,* **15,** 54 **(1999)**

25. Dogra S.K., Dogra S., Physical Chemistry through Problems, Wiley Eastern Limited, New Delhi, 231 **(1986)**

26. Narayan R., An Introduction to Metallic Corrosion and its Prevention, 1st ed, Oxford and IBH **(1983)**

27. Furman A. and Chandler C., Test methods for Vapour Corrosion Inhibitors, Proc. 9th Eur. Sym. Corros. Inhib., Ann. Univ., **11,** 465 **(2000)**