Synergistic Effect of CTAB as VPCI for Mild Steel

VISHAL SAINI* and HARISH KUMAR

Material Science & Electrochemistry Laboratory, Department of Chemistry
Chaudhary Devi Lal University, Sirsa, Haryana – 125055, India
Material Science & Electrochemistry Laboratory, Department of Chemistry
Janta Girls College, Ellenabad, Sirsa, Haryana – 125102, India
*E-mail address: dony84@rediffmail.com

ABSTRACT

Industrialization and modernization in now a days has made a strong demand of steel and their maintenance for a strong infrastructure for every country in the race of survival, stabilization, growth and competition. Atmospheric corrosion can aggressively accelerate the rate of degradation of steel during their manufacturing, processing, storage and transportation. In these cases, traditional methods to prevent corrosion are not suitable which provide scope of Vapour Phase Corrosion Inhibitors (VPCI) in industries, defense and daily life. Cetyltrimethylammoniumbromide (CTAB) was tested for mild steel in different aggressive atmospheric conditions by Weight loss test, Eschke test, Salt spray test, Sulphur dioxide (SO_2) test at 50^{o}C and results of these tests were supported by Metallurgical research microscopy and Scanning electron microscopy (SEM). Synergistic effect of CTAB were performed with Ethylamine (EA), N,N,N,N-Tetramethylethylenediamine (TMEDA) and N-Ethylaniline (NEA) to enhance the percentage corrosion inhibition efficiency (PCIE).

Keywords: Weight loss test, Eschke test, Salt spray test, Metallurgical research microscopy, SEM, Vapour phase corrosion inhibitors, Synergistic effect.

Introduction

Atmospheric components such as moisture, air pollutants (SO_2, H_2S, N_xO_y, CO_2 and Cl^-) and temperature have been reported as corrodents for metal corrosion. Corvo[1] and Moricelli et al.[2] studied the relationship between chloride ion concentrations with corrosion rate in atmospheric conditions. Ericsson[3] showed that NaCl can cause corrosion at very low concentration because it can induce corrosion by SO_2 on a carbon steel surface. NaCl can enhance 14 times rate of corrosion by SO_2 at 9% relative humidity. In an another report of Blucher et al.[4], they have investigated adverse effect of CO_2 on corrosion of Al. Vuorinen et al.[5] and a list of authors have worked on organic compounds as VPCIs. Organic substances have been studied as VPCI for mild steel were morpholine derivatives and diaminohexane derivatives[5], fatty acid thiosemicarbazides[6], cyclohexylamine and dicyclohexylamine[7-8], amine carboxylates[9], ammonium caprylate[10], benzoic hydrazide derivatives[11-12], polyamines[13], bis-piperidiniummethyl-urea and β–amino alcoholic compounds[14]. Apart from organic substances, natural compounds like wood bark oil[15] and thyme[16-17] have also been used as VPCIs. Cano et al.[18] recently have proposed mechanism of inhibition of dicyclohexamineisonitrite and dicyclohexaminenitrite against corrosion due to vapours of acetic acid and formic acid on carbon steel. Zubielewicz et al.[19] studied the electrochemical behaviour of mixed anodic inhibitors. Batis et al.[20] evaluated the performance of two primers, first natural rust converter and other on organic primer coating containing VPCI against atmospheric corrosion for reinforcing steel. Lyublinski[21] studied synergistic corrosion management systems by use of corrosion inhibitors. In continuation to our earlier study[22-27], in the present study, the inhibiting properties of Cetyltrimethylamoniumbromide (CTAB) was investigated on mild steel at 85% relative humidity and 50°C by Weight loss test, Salt spray test in a solution of 3.0% NaCl, Eschke test, SO_2 test, Metallurgical research microscopy and Scanning electron microscopy. Synergistic effect of CTAB were also tested with Ethylamine (EA), N,N,N,N-Tetramethylethylamine (TMEDA) and N-Ethylaniline (NEA) to enhance the percentage corrosion inhibition action of CTAB.

Materials and Methods

Many research papers, articles and reviews have been reported to the study of techniques such as Adsorption isotherm technique[28], Weight loss technique[29], Potentiodynamic polarization measurements[30], Electrodynamical impedance meseaurment[31], Audioradiography[32] and Capacitance measurments[33]. Tormoen et al.[34] reported three new techniques namely Surface-enhanced Raman spectroscopy, Scanning Kelvin probe microscopy and Contact angle analysis to monitor the adsorption of VPCI on metallic surface in real time. Materials, equipments and methods used in my present study are explained as below:

Material

Mild steel (ASTM-283) coupons of dimensions 3.5cm × 1.5cm × 0.025cm and of chemical 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 (w/w) were used.

Equipments

Weighing Balance

Single Pan Analytical Balance, Precision 0.01mg, Model AB 135-S/FACT, Source Mettler Toledo, Japan.

Humidity Chamber

Thermotech TIC-4000N Temperature Controller, Humidity controller with course and fine adjustments, AC Frequeny 50-60Hz, Max. Voltage 300V, Source Make-Associated Scientific Tech., New Delhi.

Salt Spray Chamber

Thermotech TIC-4000N Temperature Controller, Pumping system Pt-100, AC Frequeny 50-60Hz, Max. Voltage 300V, Source Make-Associated Scientific Tech., New Delhi.

Air Thermostat

Nine adjustable Chambered, Electrically controlled, Accuracy ± 0.1°C.

Metallurgical Research Microscope

CXR II from Laomed, Mumbai, India

Scanning Electron Microscope

JEOL 5900LV scanning electron microscope.

All chemicals used for study were of AR grade with 99% minimum assay. Along with them triply distilled water (conductivity $<1\times10^{-6}$ $ohm^{-1}cm^{-1}$) and sulphuric acid were also used.

Methods

Vapour Pressure Determination Test

A definite amount of exactly weighed VPCI was 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 electrically controlled air thermostat maintained at the constant temperature of 50^0C for 10 days. Change in weight of VPCIs was observed by analytical balance and vapour pressure of investigated VPCI was determined by weight loss of VPCI for time of exposure by equation 1.

$$P = \frac{W}{At}\left[\frac{2\pi RT}{M}\right]^{1/2} \quad \text{-------------------- (1)}$$

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

Weight Loss Test

Mild steel coupons were mechanically polished successively with the help of emery papers grading 100, 200, 300, 400 and 600µ and then thoroughly cleaned with plenty of triple distilled water, ethanol and acetone. Then coupons were dried with hot air blower and stored in desiccators over silica gel. Weight loss tests were carried out in an electronically controlled air thermostat maintained at a constant temperature of 50^oC. After recording the initial weights of mild steel coupons, they were kept in different isolated chambers of air thermostat having fixed amount of VPCI at a constant temperature of 50^oC for 24 hours of exposure time. A uniform thin film of VPCI was adsorbed onto the metal coupon surface 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^oC for 10 days. Blank coupons untreated with VPCI were also kept in humidity chamber for the same duration in the same corrosive environment. After exposing the coupons for 10 days, coupons were taken out from the humidity chamber and washed initially under running tap water. Loosely adhering corrosion products were removed with the help of rubber cork and coupon was again washed dried and then weighed again. Corrosion rate in miles per year (mpy) and PCIE were calculated by using equations 2 and 3 respectively.

$$\text{Corrosion Rate (mpy)} = \frac{534 \; X \; W}{DAT} \quad \text{---------------} \; (2)$$

Where, W = weight loss (in mg), D = density of mild steel (in g/cm^3), A = area of coupon (in sq. inch), T = exposure time (in hour).

$$\text{Percentage Inhibition Efficiency} = \frac{CRo - CR}{CRo} \; X \; 100 \quad \text{-------------} \; (3)$$

Where, CR_o = corrosion rate in absence of inhibitor and CR = corrosion rate in presence of inhibitor.

Salt Spray Test

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% NaCl solution maintained at 50^{o}C for duration of 10 days along with blank coupons. After exposing coupons for 10 days, coupons were treated in same manner as treated in weight loss test to remove corrosion products and then CR and PCIE were calculated.

Eschke Test

Kraft papers of suitable size were dipped in the VPCI for 30 seconds and then dried to adsorb uniform layer of inhibitor on Kraft papers. Mild steel coupons were wrapped in VPCI impregnated Kraft papers and then kept in humidity chamber maintained at 85% relative humidity maintained at 50^{o}C for first 12 hours and 25^{o}C for next 12 hours alternately for 10 days. This temperature cycle was maintained in two sets because of formation and condensation of vapours of VPCI on mild steel surface regularly. After exposing coupons for 10 days, coupons were treated in same manner as treated in weight loss test to remove corrosion products and then CR and PCIE were calculated.

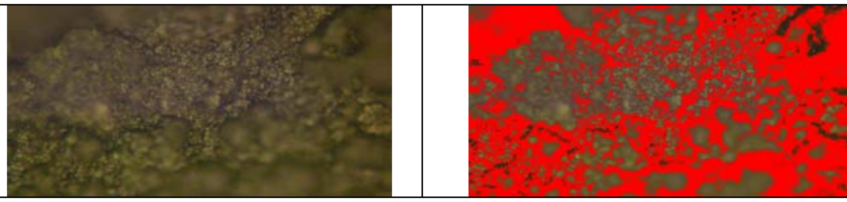
SO_2 Test

SO_2 test was carried out on the mild steel coupons as in weight loss test. SO_2 gas was prepared by dissolving 0.04 g of sodium thiosulphate in 30mL 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 50^{o}C 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 coupons for 10 days, coupons were treated in same manner as treated in weight loss test to remove corrosion products and then CR and PCIE were calculated.

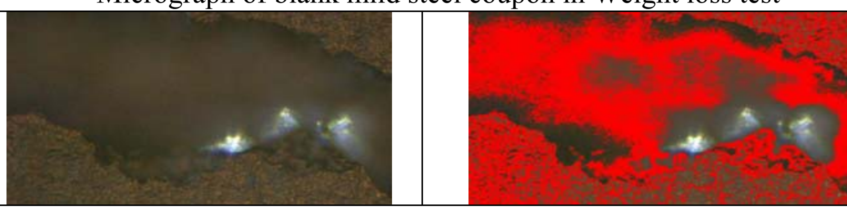
Metallurgical Research Microscopy

This test was employed to know about nature and type of corrosion using metallurgical research microscope. To investigate the corrosion inhibition efficiency of investigated VPCIs, micrographs of the corroded coupons treated with investigated VPCI were subjected to porosity study and morphology of surface. By the obtained results a comparative study of that porosity and surface morphology was carried which provided the information about the number of pores, size of pores, percentage porosity and area covered by the pores on the surface of coupon after the four different corrosion experiments. Percentage porosity (PP) and total objects (TO) shows the roughness of surface. On the other hand maximum perimeter and maximum area object ratio (A/O) provide the information about the size and depth of the pores on the surface of mild steel. Micrographs of blank corroded coupons were taken after exposure of different aggressive environments for 10 days are shown in Table-1.

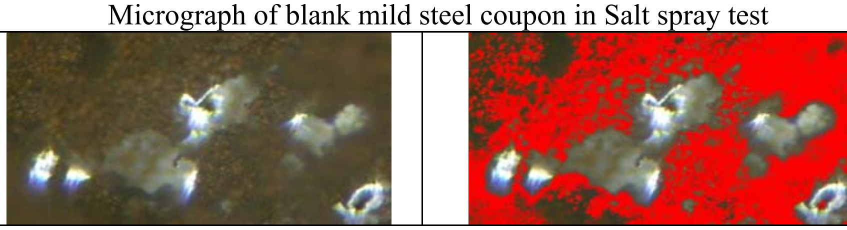
Table-1 Micrographs of blank mild steel coupon in different corrosion tests



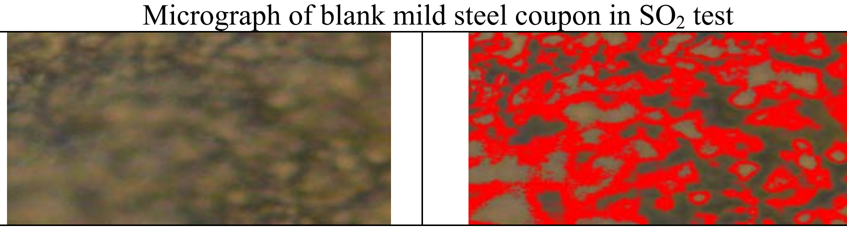
Micrograph of blank mild steel coupon in Weight loss test



Micrograph of blank mild steel coupon in Salt spray test



Micrograph of blank mild steel coupon in SO_2 test



Micrograph of blank mild steel coupon in Eschke test

Results of metallurgical research microscopy of blank mild steel coupon after different corrosion tests are reported in Table-2 from which it is clear that in weight loss test 9774 pores cover 8886066.4820μ^2 area due to uniform corrosion in humid environment by which 68.90% surface become porous. In this test, numbers of pores are very high but A/O ratio is not very high as compared to that of salt spray test. In salt spray test, percentage porosity (69.94%) is almost equal to that of weight loss test but the numbers of pores (13,380) and the porous area (10960879.5014μ^2) on the mild steel surface are high due to corrosive action of direct exposure of chloride ions on the surface of mild steel coupon. In this test, perimeter of pore (52323.4375μ) and A/O ratio are high due to large size and high depth of pores respectively. In SO_2 test, although the numbers of pores (3387) are very low as compared to other corrosion experiments yet the percentage porosity (86.62%) are highest in this test. In this test the size of pores (78541.5913μ) and A/O ratio are very high due to high depth of the pores by the acidic action of SO_2 environment which provide evidence in favour of mechanism of pits formation on the surface of coupon by the acidic action of SO_2. In Eschke test, depth of pores is very low due to small size of pore of perimeter (20138.1682μ) but total objects (6448) are high due to roughness of surface by the action of corrodents of environment.

Table-2 Metallurgical research microscopy results of blank mild steel coupon.

	TO	**PP**	**MP(μ)**	**MA (μ^2)**
Weight Loss Test	9774	68.9	55805.5407	8886066.4820
Salt Spray Test	13380	69.94	52323.4375	1096879.5014
SO_2 Test	3783	86.62	78541.5913	9770443.2133
Eschke Test	6448	69.11	20138.1682	4461322.7147

Scanning Electron Microscopy

This technique gives the morphology study of mild steel coupons after treatment of different corrosion tests which provide the evidences in support of inhibition data of investigated VPCIs, type of corrosion and for mechanism of inhibition. In this test, coupons were studied at different resolutions on different spots on the mild steel coupons for complete information about the inhibition mechanism after treating with different tests. SEM of blank mild steel coupons was also taken for the comparative study of metal specimens which are given in Figure-1. Micrographs of the blank coupons clearly provide the evidence of pitting and crevice corrosion in corroding environments.

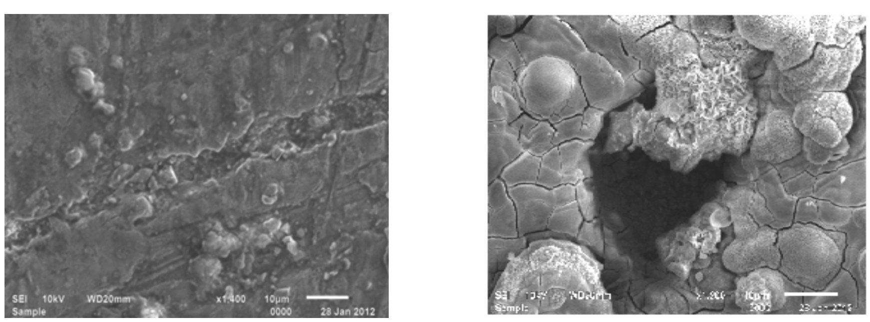


Figure-1 SEM of blank mild steel coupon.

Results and Discussion

Vapour Pressure Determination Test

Vapour pressure of CTAB was found to be 40.93 X 10^{-4} mmHg at 50^{o}C by which CTAB can easily adsorbed on the surface of mild steel coupon and form a barrier film for water vapours and corrosive aggressive contents of atmosphere around the coupons and protect coupons from corrosion by the formation of protective layer.

Results of Weight Loss Test, Salt Spray Test, SO_2 Test and Eschke Test

Results obtained by Weight loss test, Salt spray test, SO_2 test and Eschke test for mild steel in different aggressive environments and PCIE of CTAB are shown in Table-3. From which it is clear that PCIE of CTAB is averagely near about 50%. Weight loss and corrosion rate of mild steel coupons treated with CTAB are compared with blank coupons in Figure-2 and Figure-3.

It is clear from these Figures that weight loss and corrosion rate for mild steel coupons, treated with CTAB, in all tests are significantly low as compared to that of blank mild steel coupons. This inhibitor is a cationic surfactant containing a long hydrophobic chain which provides the active site for formation of barrier film on the surface of mild steel to protect the mild steel from corrosion loss. Further, PCIE of CTAB is compared in Figure-4 from which it is clear that the PCIE of CTAB is near about 50%.

Table-3 Weight Loss, CR and PCIE of CTAB in various corrosion tests performed on Mild steel coupons treated with CTAB and on Blank coupons

	Wt. Loss (mg) (Blank)	**CR(mmpy) (Blank)**	**Wt. Loss (mg) (Treated)**	**CR (mmpy) (Treated)**	**PCIE**
Wt. Loss Test	14.8	5.10	8.2	2.82	44.70
Salt Spray Test	10.2	3.51	4.1	1.41	50.69
SO_2 Test	15.2	5.24	8.6	2.96	43.51
Eschke Test	8.3	2.86	4.1	1.41	50.70

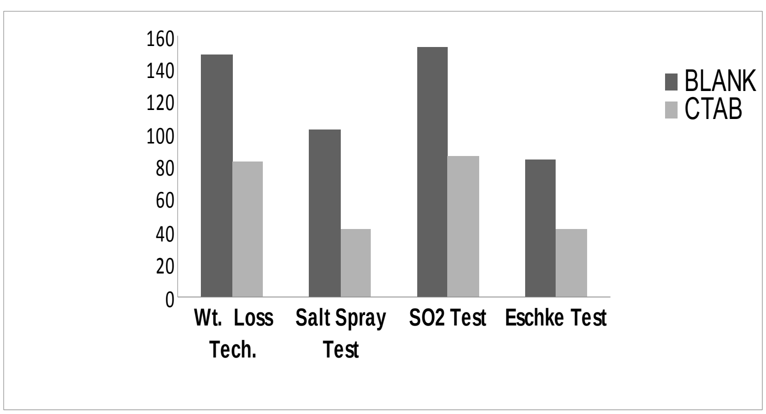
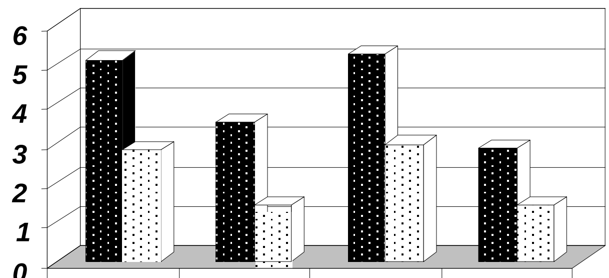


Figure-2 Weight loss of Mild steel coupons treated with CTAB and of Blank coupons in various corrosion tests.



	Wt. Loss	Salt Spray	SO2 Test	Eschke Test
■ BLANK	5.1	3.51	5.24	2.86
■ CTAB	2.82	1.41	2.96	1.41

Figure-3 CR of Mild Steel Coupons treated with CTAB and of Blank coupons in various corrosion tests.

It is clear from data that CTAB is showing good corrosion inhibition property against the direct contact of chlorides ions on mild steel coupons. Chloride ions accelerate the rate of corrosion by penetration of the barrier layer of protective agent on surfaces but CTAB form a stable barrier film on the surface of mild steel coupon which can't be penetrated by chlorides ions easily.

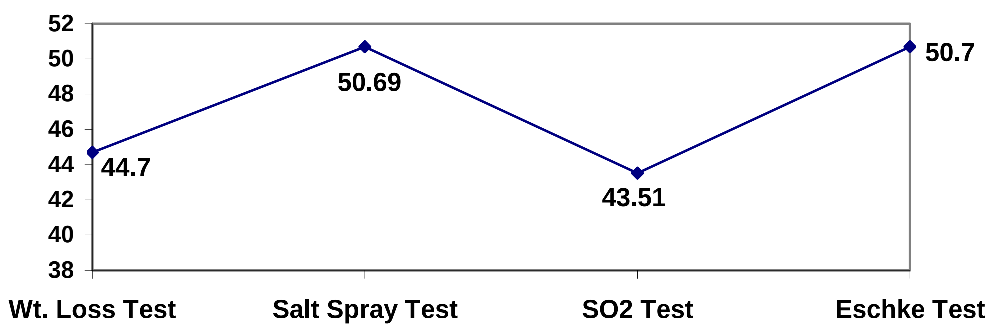


Figure-4 PCIE of CTAB in various corrosion tests

Low inhibition efficiency of CTAB in acidic medium of SO_2 is due to less basic strength of CTAB by which its tendency to neutralize the acidic character of SO_2. From the data obtained by Eschke test, it is clear that CTAB performs very significant role against the corrosion at high temperature due to direct contact of vapours of CTAB to the surface of mild steel coupon. Visual observations of mild steel coupons are also given in Table-4.

Table-4 Visual observations of mild steel coupon surface after performed various corrosion tests.

VPCI	Salt Spray Test	Eschke Test	SO_2 Test	
Blank	Clear pits and crevices were visible		Uniform corrosion	Pitting corrosion
CTAB	Clear clean surface No any pits and crevice No corrosion product		Clear clean surface No corrosion product No corrosion product	Slightly tarnishing No any pits and crevice

Metallurgical Research Microscopy of CTAB

Results of metallurgical research microscopy and micrographs of mild steel coupons treated with CTAB after corrosion tests are reported in Table-5 and Table-6 respectively. By comparison of the data obtained by different corrosion tests, it is clear that PP is significantly low in all tests due to good inhibition action of CTAB against the atmospheric corrosion. In weight loss test, 4036 pores cover 47929.3629μ^2 area due to uniform corrosion in humid environment by which 27.78% surface become porous.

Table- 5 Micrographs of mild steel coupons treated with CTAB in different corrosion tests.

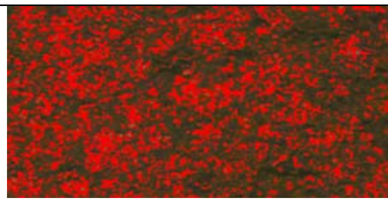
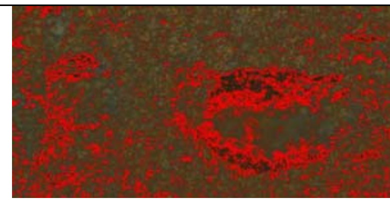
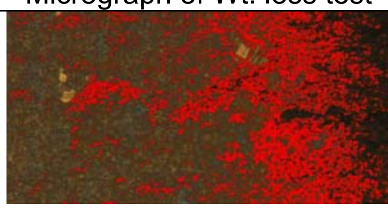
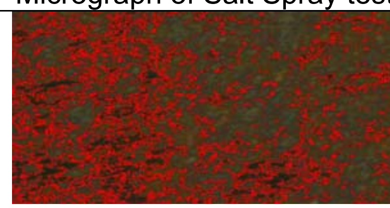
 Micrograph of Wt. loss test	 Micrograph of Salt Spray test
 Micrograph of SO_2 test	 Micrograph of Eschke test

Table-6 TO, PP, MP of pore and MA covered by pore on mild steel coupon treated with CTAB in various corrosion tests

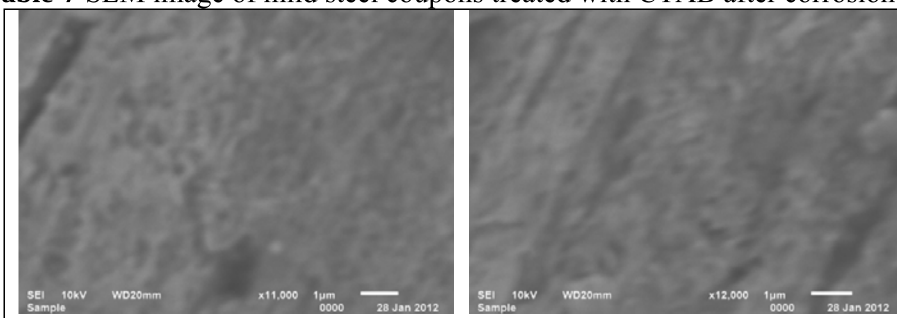
	TO	PP	MP(μ)	MA (μ^2)
Weight Loss Test	4036	27.78	6097.9254	47929.3629
Salt Spray Test	4302	23.68	12387.2353	53054.0166
SO_2 Test	8068	30.05	15877.3849	65837.9501
Eschke Test	3885	23.86	2653.8388	3560.9418

In this test A/O ratio is not very high which represent the uniform type of corrosion on surface of mild steel coupon in humid environment. In salt spray test, PP (23.68%) is little bit low but the numbers of pores (4302) are high due to corrosive action of chloride ions. In this test, perimetre of pore (12387.2353μ) and A/O ratio are some high due to large size and high depth of pores respectively. In SO_2 test, numbers of pores (8068) and percentage porosity (30.05%) are increased but its A/O ratio is decreased which provide evidence in favour of prevention mechanism of pits on the surface of coupon by action of CTAB. In Eschke test, depth of pores are very low due to small size of pore of perimeter (2653.8388 μ) but TO (3885) are high due to roughness of surface by action of corrodents of environment. Micrographs of all tests show that almost smooth surface of mild steel coupon without any corrosion products are obtained after the treatment of coupon with CTAB.

Scanning Electron Microscopy

By comparison of SEM images of coupons treated with CTAB as shown in Table-7, it is clear CTAB show very excellent corrosion inhibition properties against the aggressive environments. SEM images of CTAB have no any corrosion product even at very high resolution of 11000 and 12000 but have some cracks which indicate the crevice corrosion of mild steel in acidic environment. Clearness of SEM images of coupon treated with CTAB provide the evidence in favor of very good PCIE of CTAB.

Table-7 SEM image of mild steel coupons treated with CTAB after corrosion test.



SEM of coupons treated with CTAB

Mechanism of Inhibition

The probable mechanism of inhibition action of CTAB contains the following features:

a) Presence of a long hydrophobic chain in the molecule of CTAB provide it ability to form a barrier film on the surface of mild steel to protect the mild steel surface from water vapours and corrosive contents of atmosphere.
b) Absence of any lone pair donor atom and low vapour pressure and vapour density is the cause of low PCIE of CTAB.

Synergistic Effect of CTAB

CTAB is a suitable vapour phase corrosion inhibitor due to presence of a long hydrophobic chain in the molecule of CTAB which provide it ability to form a barrier film on the surface of mild steel to protect the mild steel from water vapours and corrosive contents of atmosphere around the mild steel. But absence of any lone pair donor atom and low vapour pressure and vapour density is the cause of low PCIE of CTAB. To increase the PCIE of CTAB, synergistic effect of CTAB with EA, TMEDA and NEA was tested by Weight loss test, Eschke test, Salt spray test, SO_2 test, Metallurgical research microscopy and SEM.

Vapour Pressure Determination Test

Vapour pressures of combinations of CTAB with different VPCIs were determined by vapour pressure determination test performed as given in the experimental section of this manuscript. Results of this test for different combinations of CTAB are given in Table-8.

Table-8 Vapour Pressures of combinations of CTAB with different VPCIs

Combinations of CTAB	**Vapour Pressure (10^{-2}mmHg)**
CTAB + EA	85.33
CTAB + TMEDA	161.02
CTAB + NEA	106.01

Weight Loss Test

To determine the synergistic effect of CTAB, different combination of CTAB with different VPCIs were tested through weight loss test. By the results of this test, weight loss, CR and PCIE of the combinations were determined which are given in Figure-5. Results of this test are clearly showing the synergistic effect of CTAB in which PCIE of CTAB in the combination are very good as compared with the individual performance as shown in Figure-6.

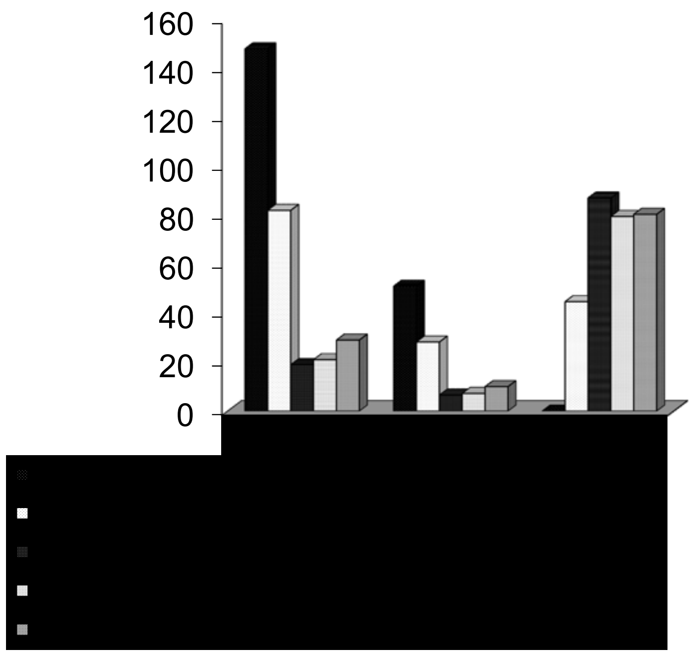


Figure-5 Weight loss(x10^{-1}mg), CR(x10^{-4}mpy) and PCIE of CTAB with different VPCIs obtained from Weight loss test.

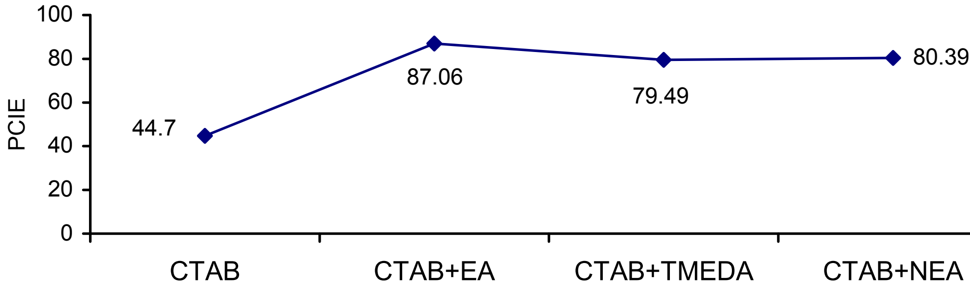
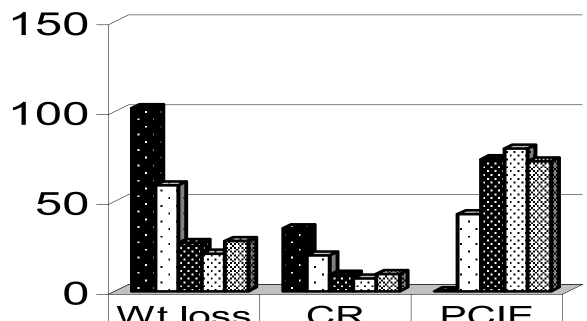


Figure-6 PCIE of CTAB with different combination of VPCI in Weight Loss Test

From Figure-5, it is clear that the weight loss and CR of combinations of CTAB with different VPCIs are very low as compared to that of CTAB. It is due to increase in vapour pressure and vapour density of the combinations. It is observed that specific sites of active functional groups for the adsorption of VPCIs are increased and enhanced PCIE of combinations. From Figure-6, it is clear that CTAB is performing efficiently VPCI in combinations with EA, TMEDA and NEA as compared to the other combinations. In all combinations, PCIE of combinations are more than that of individual in which PCIE exceeds from 44.70% (CTAB). Figure-6 shows that PCIE of the different combinations with CTAB is in following order: CTAB+EA > CTAB+NEA > CTAB+TMEDA

Salt Spray Test

To determine the synergistic effect of CTAB, different combinations of CTAB with different VPCIs were tested by the effect of chloride ions on mild steel coupon through salt spray test. By the results of this test, weight loss, CR and PCIE of mixtures were determined which are given in Figure-7.



	Wt.loss	CR	PCIE
BLANK	102	35.1	0
CTAB	59	20	43.01
CTAB+EA	27	9.3	73.5
CTAB+TMEDA	21	7.2	79.49
CTAB+NEA	28	9.7	72.36

Figure-7 Weight loss($\times 10^{-1}$mg), CR($\times 10^{-4}$mpy) and PCIE of CTAB with different VPCIs obtained from Salt spray test.

Results of this test clearly show the synergistic effect of CTAB in which PCIE of CTAB in the combination are high as compared with the individual performance as shown in Figure-8. From this figure it is shown that the PCIE of mixtures are higher than that of individual CTAB in salt spray test. Effect of direct spray of chloride ions on the mild steel coupon can be easily explained by the PCIE in this test.

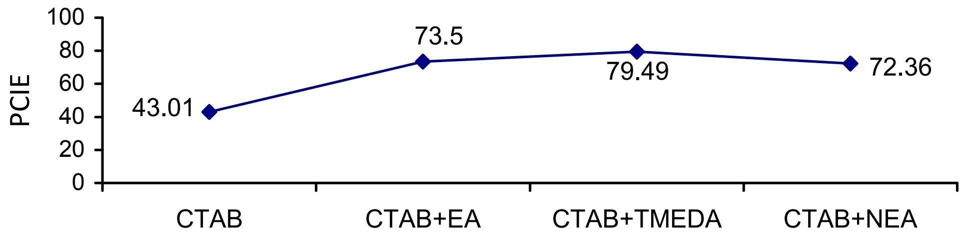


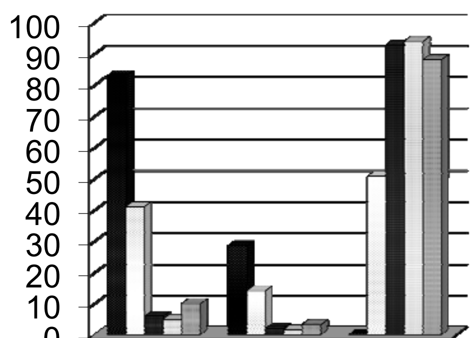
Figure-8 PCIE of CTAB with different combinations of VPCIs in Salt spray test.

Due to direct contact of NaCl salt on the surface and its hydrolysis products accelerate the corrosion rate due to which PCIE is slightly lower than that of weight loss test from Figure-8, it is shown that PCIE of different combinations of VPCI with CTAB is in order:

CTAB+TMEDA > CTAB+EA > CTAB+NEA

Eschke Test

To determine the synergistic effect of CTAB, different combinations of CTAB with different vapour phase corrosion inhibitors were tested by direct contact of VPCIs on the mild steel coupon through Eschke Test. By the results of this test, weight loss, corrosion rate and percentage corrosion inhibition efficiencies of different combinations were determined which are shown in Figure-9.



	Wt.loss	CR	PCIE
BLANK	83	28.6	0
CTAB	41	14.1	50.69
CTAB+EA	6	2.1	92.79
CTAB+TMEDA	5	1.7	94.06
CTAB+NEA	10	3.4	88.11

Figure-9 Weight loss($\times10^{-1}$mg), CR($\times10^{-4}$mpy) and PCIE of CTAB with different VPCIs obtained from Eschke test.

Results of this test clearly show the synergistic effect of CTAB in which PCIE of CTAB in the combinations are higher than that of CTAB individually as shown in Figure-10. Effect of direct contact of VPCI on the mild steel coupon can be easily explained by the PCIE in this test. Due to direct contact of VPCI on the surface of mild steel, VPCI produces a barrier film on the mild steel surface by the adsorption of its vapour to protect the steel from the water vapours and aggressive corrodents of atmosphere. From the results of this test, it is clear that PCIE for combinations are very good and CTAB perform an efficient VPCI due to its synergistic effect.

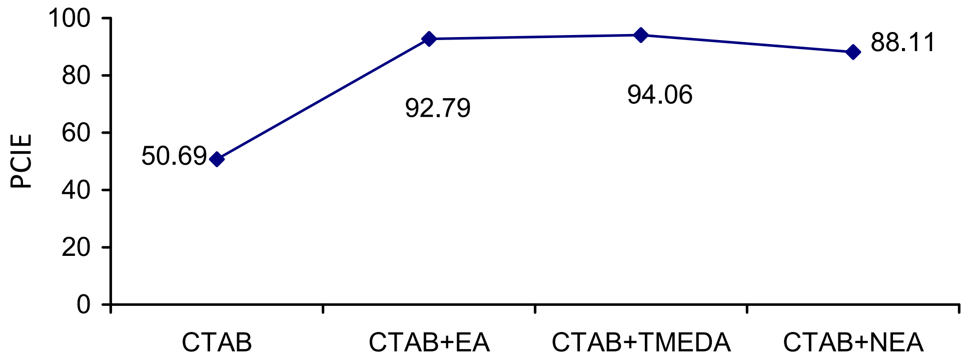


Figure-10 PCIE of CTAB with different combination of VPCIs in Eschke Test.

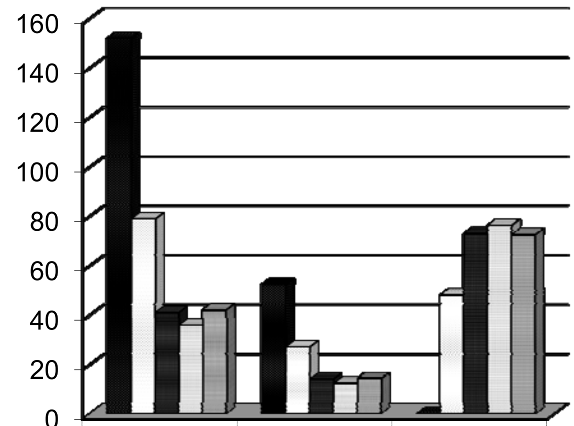
From Figure-10, it is clear that PCIE of different combinations of VPCI with CTAB is in order:

CTAB+TMEDA > CTAB+EA > CTAB+NEA

It has been discussed earlier that the PCIE of EA is in the range of 60% but in combination PCIE is enhanced and touched the peak of 80%. It is due to low vapour density and low molecular weight of the EA molecule. Due to high vapour pressure, the rate of condensation of the vapours of EA is very high and the vapour density is very low. By the combination, the vapour pressure of EA is reduced and it acts as a very good VPCI in combination. But by the direct contact of its combination on the surface of mild steel retard the rate of condensation of vapours and by adsorption, it protects the mild steel by barrier film formation.

SO_2 Test

To determine the synergistic effect of CTAB, different combinations of CTAB with different vapour phase corrosion inhibitors were tested by the effect of sulphate ions on the mild steel through SO_2 test. By the results of this test, weight loss, corrosion rates and percentage corrosion inhibition efficiencies of the combination were determined which are shown in Figure-11.



	Wt.loss	CR	PCIE
BLANK	152	52.4	0
CTAB	79	27.2	48.09
CTAB+EA	41	14.1	73.02
CTAB+TMEDA	36	12.4	76.32
CTAB+NEA	42	14.4	72.51

Figure-11 Weight loss($\times10^{-1}$mg), CR($\times10^{-4}$mpy) and PCIE of CTAB with different VPCIs obtained from SO_2 test.

Results of this test are clearly showing the synergistic effect of CTAB in which PCIE of CTAB in the combination are good as compared with the individual performance as shown in Figure-12. From these figures, it is shown that PCIE of different combinations of VPCI with CTAB is in order:

CTAB+EA > CTAB+NEA = CTAB+TMEDA.

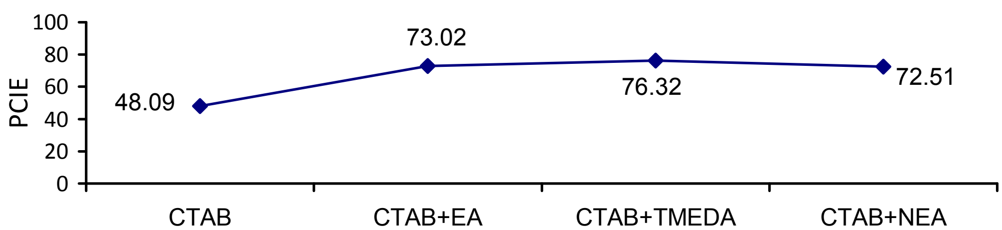


Figure-12 PCIE of CTAB with different combination of VPCI in SO_2 test.

From the results of combinations of CTAB with different VPCIs in weight loss test, salt spray test, Eschke test and SO_2 test, it is clear that CTAB perform as very good VPCI for mild steel under atmospheric corrosion. In combination of CTAB with EA, TMEDA and NEA vapour pressure rises to a level of best performance.

Conclusions

As a result of experimental work carried out on the performance of investigated vapour phase corrosion inhibitors, a deep analysis of corrosion parameters obtained by corrosion testing experiments, morphology of mild steel coupon show that CTAB perform excellent corrosion inhibition properties against the aggressive environments of SO_2 and NaCl at high relative humidity and high temperature. From the experimental study it is concluded that

i) Due to rise in vapour pressure of CTAB with combinations of EA, TMEDA and NEA, rate of adsorption of CTAB on mild steel coupon is increased by which CTAB form barrier layer on mild steel easily and protect mild steel from corrodents of environments.

ii) Presence of two lone pair donar atoms in TMEDA molecule increase the basic strength of combinations by which it can easily neutralize the acidic character of environment around coupon and retard the CR.

iii) Presence of alkyl group near the lone pair donar atom in EA and TMEDA enhance the basic strength due to +I effect and protect the mild steel easily by neutralize of acidic environment.

iv) Presence of benzene ring decreases the basic strength in NEA due to resonance stabilization by which PCIE of combination with NEA is relatively low in corrosion tests.

v) Metallurgical research microscopy and SEM give an idea of the uniform type and crevice type and pitting type of corrosion on mild steel in humid environment, NaCl environment and in SO_2 environment respectively.

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REFERENCES

[1] Corvo F.; Atmospheric Corrosion of Steel in Humid Tropical climates: Humidity, Temperature, Rainfall and Sun Radiation, *Corros*, 40, 4 (1984).

[2] Morcillo M., Chico B., Otero E. and Mariaca L., Effect of Marine Aerosol on Atmospheric Corrosion, *Mater. Perf.,* 38(4), 24 (1999).

[3] Ericsson R., The influence of SO_2 supply and Relative Humidity on the Atmospheric Corrosion of Steel, *Werks. Korros.*, 29, 400 (1978).

[4] Blucher B.D., Lindstrom R., Svensson J.E. and Johansson L.G., The effect of CO_2 on the NaCl-induced Atmospheric Corrosion of Aluminum, *J. Electrochem. Soc.*, 148, 127 (2001).

[5] Vuorinen E., Ngobeni P., Van der Klashorst G.H., Skinner W., De W.E. and Ernst W.S., Derivatives of Cyclohexylamine and Morpholine as Volatile Corrosion Inhibitors, *Brit. Corros. J.*, 29, 120 (1994).

[6] Quraishi M.A., Jamal D. and Singh R.N., Inhibition of Mild Steel Corrosion in the Presence of Fatty Acid Thiosemicarbazides, *Corros,*, 58 201 (2002).

[7] Subramanian A., Kumar R.R., Natesan M. and Vasudevan T., The Performance of VPI Coated Paper for Temporary Corrosion Prevention of Metals, *ACMM*, 49 354 (2002).

[8] Subramanian A., Rajendran P., Natesan M., Balakrishnan K., and Vasudevan M., Corrosion Behavior of Metals in SO_2 Environment and Its Prevention by Some Volatile Corrosion Inhibitors, *ACMM*, 46, 346 (1999).

[9] Vuorinen E. and Skinner W., Amine Carboxylates as Vapor Phase Corrosion Inhibitors, *Brit. Corros. J.*, 37, 159 (2002).

[10] Skinner W., Preez F.D. and Vuorinen E., Evaluation of Vapor Phase Corrosion Inhibitors, *Brit. Corros. J.*, 34, 151(1999).

[11] Quraishi M.A. and Jamal D., Inhibition of Metals Corrosion by a New Vapor Phase Corrosion Inhibitor, *J. Metall. and Mater. Sci.*, 47, 45 (2005).

[12] Quraishi M.A., Bhardwaj V. and Jamal D., Prevention of Metallic Corrosion by Some Salts of Benzoic Hydrazide under Vapor Phase Conditions, *Ind. J. Chem. Tech.*, 12, 39 (2005).

[13] Zhang D.Q., Gao L.X. and Zhou G.D., Polyamine Compound as a Volatile Corrosion Inhibitor for Atmospheric Corrosion of Mild Steel, *Mate and Corros,* 58, 594 (2007).

[14] Khamis E. and Andis N.A., Herbs as New Type of Green, Inhibitors for Acidic Corrosion of Steel, *Material Wissenschaft and Werkstoff technik*, 33, 550 (2002).

[15] Poongothai N., Rajendran P., Natesan M. and Palaniswamy N., Wood Bark Oils as Vapor Phase Corrosion Inhibitors for Metals in NaCl and SO2 Environments, *Ind. J. Chem. Tech.*, 12, 641(2005).

[16] Premkumar P., Kannan K. and Natesan M., Thyme Extract of Thymus Vulgar L. as Volatile Corrosion Inhibitor for Mild Steel in NaCl Environment, *Asian J. Chem.*, 20, 445 (2008).

[17] Premkumar P., Kannan K. and Natesan M., Natural Thyme Volatile Corrosion Inhibitor for Mild Steel in HCl Environment, *J. Metall. and Mater. Sci.*, 50, 227 (2008).

[18] Cano E., Bastidas D.M., Simancas J. and Bastidas J.M., Dicyclohexylamine nitrite as volatile corrosion inhibitor for steel in polluted environments, *Corros.*,61, 473 (2005).

[19] Zubielewicz M. and Gnot W., Mechanisms of non-toxic anticorrosive pigments in organic waterborne coatings, *Progr. In Organ. Coating.,* 49, 358 (2004).

[20] Batis G., Kouloumbi N. and Soulis E., Sandblasting: The only way to eliminate rust?, *Anti Corros. Meth. and Mat.,* 45(4), 222 (1998).

[21] Lyublinski E.Y.; Synergistic Corrosion Management Systems for Controlling, Eliminating and Managing Corrosion. *WO patent 124058*, (2008).

[22] Kumar H., Saini V. and Yadav V., Study of Vapour Phase Corrosion Inhibitors for Mild Steel under different Atmospheric Conditions, *Int. J. Engg. & Innovative Tech.,* 3(3), 206-211 (2013).

[23] Kumar H. and Yadav V., Corrosion Characteristics of Mild Steel under different Atmospheric Conditions by Vapour Phase Corrosion Inhibitors, *Am. J. of Materials Sci. & Engg.* 1(3), 34-39 (2013).

[24] Kumar H. and Yadav V., CHA, BA, BTA & TEA as Vapour Phase Corrosion Inhibitors for Mild Steel under different Atmospheric Conditions, *J. Corros. Sci. & Engg.* 16, Preprint 4 (2013).

[25] Kumar H. and Saini V., Corrosion characteristics of vapour phase inhibitors for mild steel under different atmospheric condition, *J. Corros. Sci. & Engg.* 14, Preprint 5 (2012).

[26] Kumar H. and Saini V., DAPA, EA, TU and BI as Vapour Phase Corrosion Inhibitors for Mild Steel under Atmospheric Conditions, *Res. J. of Chem. Sciences,* 2(2), 10-17 (2012).

[27] Kumar H. and Yadav V., BIA, DPA, MBTA and DMA as Vapour Phase Corrosion Inhibitors for Mild Steel under different Atmospheric Conditions, International Letters of Chemistry, Physics and Astronomy, 1, 52-66 (2014).

[28] Premkumar P., Evaluation of Menthol as Vapour Phase Corrosion Inhibitor for Mild Steel in NaCl Environment, *The Arab. J. Sci. Engg.,* 34(2C), 71 (2009).

[29] Abd S.S., Rehim E., Relay S.A.M., Saleh M.B. and Ahmed R.A., Corrosion Inhibition of Mild Steel in Acidic Medium using 2-amino Thiophenoland 2-Cyanomethyl Benzothiazole, *J. Appl. Electrochem.,* 31(4), 429 (2001).

[30] Quraishi M.A., Sardar R. and Jamal D., Corrosion Inhibition of Mild Steel in HCl by some Aromatic Hydrzides, *Mater. Chem. Phys*., 71 (3), 30 (2001).

[31] Rajappa S.K. and Venkatesha T.V., New Condensation Products as Corrosion Inhibitors for Mild Steel in an HCl medium, *Ind. J. Engg. Mater Sci.,* 9, 213 (2002).

[32] Quraishi M.A. and Jamal D., Dianils as New and Effective Corrosion Inhibitors for Mild Steel in Acidic Solutions, *Mater. Chem. Phys*., 78(3), 608 (2003).

[33] Prabhu R.A., Shanbhag A.V. and Venkatesha T.V., Influence of Tramadol [2-[(dimethylamino) methyl]-1-(3-methoxyphenylcyclohexanolhydrate] on corrosion inhibition of mild steel in acidic media, *J. App. Electrochem,* 37(4), 491 (2007).

[34] Tormoen G.W., Burket J.C., Dante J.F. and Sridhar N., Tri-Service Corrosion conference, (2005).