

**STUDY THE PERFORMANCE OF VOLATILE CORROSION INHIBITORS IN****PROTECTION OF MILD STEEL IN NEUTRAL AND HCl ENVIRONMENTS.****P.Kannan<sup>a</sup>, K.Lavanya<sup>b</sup>, K.S.Anuratha<sup>c</sup> M.Natesan\***

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**Abstract**

Apprehend the corrosion of the mild steel (MS) in various environment has been studied. Amide like OTP, OTS, OTC and DCHA.BTZ compounds exploited as VCI in this paper and tentative its corrosion rate and its inhibition power in corrosive Neutral and HCl medium. Weight loss mode used to calculate the former parameter. Surface characterization had been analyzed SEM and FTIR. Electro chemical studies of EIS and Tafel polarization and its parameter were computed by characterization. And find OTS and DCHA.BTZ were best VCI in acid and neutral medium via the above characterizations. The thermodynamic property adsorption isotherm has been calculated.

**Key Words**

Mild Steel, Volatile Corrosion Inhibitor, Inhibition Efficiency, Corrosion Rate, Environment.

**1. Introduction**

Corrosion is universal process which can't apprehend but can control. Day by day, the new chemical compounds were synthesized and being discover for the treatment of corrosion. Among them volatile corrosion inhibitor (VCI) which, could easily vaporized and give a best passive film on the mild steel. There are various investigation has been done on volatile corrosion inhibitor, by using aliphatic amine and salicylic acid and their salts. In this work, reveal the behavior of OTP, OTS, OTC and DCHA.BTZ in Acid and Water (steam) mediums. The choice of the VCI is depends on its vaporization power and deposit on the surface of metal [1]. There are numerous investigations on corrosion inhibition studies by aliphatic amines, salicylic acid and their salts as vapor phase corrosion inhibitors for various industrial metals and alloys [2-5]. In some place natural products have been used as inhibitor which could not be a VCI. They gave its protection as much it could on mild steel in HCl medium [6]. Inhibition effect depends on the inhibitor due some specialization fact like, chain length, size of the molecule and strength of bonding to the metal. On this fact propylamine derivative showed poly inhibition effect under different environment exhibited its efficiency as best [7]. Under the immersion condition Sodium dihydrogen orthophosphate implied highest inhibition action than that the other [8]. Cyclohexylamine has high thermal stability in power plant and have VCI characteristic too, in pipeline. Aromatic compound such as, naphthalene has been a VCI at 250-350 °C in the HCl environment. Bayer synthesized cylcohexylamine and dicyclohexylamine as volatile corrosion inhibitor on iron [9]. Mostly, polyamine and polyaniline having larger size, electron donating atoms, is to be a VCI for mild steel. In these account VPMA acts as an effective corrosion inhibitor for steel in 2M sulphuric acid medium. The inhibition efficiencies increase by an increase in concentration of VPMA and decrease in temperature [10]. Most of the weight loss

method investigated through immersion condition when mild steel immersed in the HCl has 1M concentration. Basically more acidic there will be high corrosion chance, in order to arrest them Bipyrazole organic compound used on it [11]. Most of the heterocyclic compound having lone pair electron are proficient inhibition on mild steel in acid medium [12]. Because these molecules can donate their lone pair electron to the metal surface and thereby reduce the oxidized state of metal, to avoid corrosion [13]. Among azole compound pyrazole [14], triazole [15], tetrazole [16] were found to be an extraordinary performance on mild steel in corrosive medium. Benzotriazole in sulphuric acid medium of 0.5M concentration has contributed its efficiency 99.7% and 85.7 of double layer capacitance about 20 hours, than that its derivatives [17]. But, in the 6 hrs immersion period exhibit 89% of inhibition, compared with same concentration of H<sub>2</sub>SO<sub>4</sub> [18]. From the literature survey, not much more article on corrosion behavior of mild steel in water gas (steam) and HCl acid gas medium by using Amide as a volatile corrosion inhibitor (VCI). This article described the corrosion behavior of mild steel in a forth mentioned medium using SEM, FTIR, EIS and Tafel technique.

## 2. Experimental data

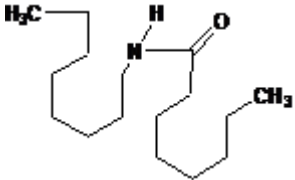
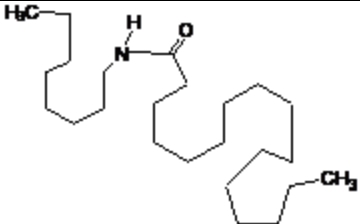
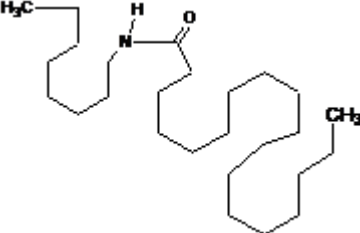
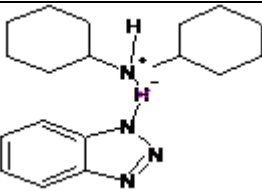
Corrosion tests were done in VCIM at 50<sup>0</sup> C. Before experiment the specimens were polished with grit emery paper, degreased by acetone, washed by distilled water and dried in hot air. Then specimens were weighed, and suspended in the hooks and calculate the inhibition efficiency and corrosion rate in the presence and absence of inhibitor in the HCl and water medium of environment.

### 2.1. Synthesis

The synthesis of OTP, OTS, OTC and were prepared by the equimolar mixture of octylamine (Aldrich) with corresponding acids such as palmetic, stearic, caprylic acid(Merck) by

stirring them at room temperature. And DCHABTZ was synthesised by incorporate dicyclohexylamine and benzotriazole (Aldrich). Finally, the synthesized inhibitor were characterized by FTIR. The molecular structure and weight of the amide inhibitor were shown below Table 1.

Table 1. Structures of VCI's

S.No	Structure	Molecular formula & weight	Vapour pressure (mmHg)	Name of VCI
1		C <sub>16</sub> H <sub>33</sub> NO & 255.4393	2.5653×10 <sup>-3</sup>	OTC
2		C <sub>24</sub> H <sub>49</sub> NO & 367.652	1.9667×10 <sup>-3</sup>	OTP
3		C <sub>26</sub> H <sub>53</sub> NO & 395.7051	1.2740×10 <sup>-3</sup>	OTS
4		C <sub>18</sub> H <sub>29</sub> N <sub>4</sub> & 301.4498	1.253×10 <sup>-3</sup>	DCHABTZ

## 2.2. *Materials and Medium*

The solution of 0.01N HCl and distill water used as electrolyte solution separately as two different environments. The specimen carbon steel's were made with following chemical composition of Carbon-0.07%, sulphur- nil, phosphorous-0.008%, silicon – nil, manganese - 0.34%, Fe – balance.

## 2.3. *Gravimetric Measurements*

The Gravimetric test was conducted to evaluate the inhibition effect of the VCI. Specimens of mild steel were made with dimensions of 5 cm x 1 cm x 0.1cm and a hole was drilled in each for suspending purpose. The test specimens' mill scales were removed by using the pickling solution as given before. Prior to the tests, the metal surface was polished with 1/0, 2/0, 3/0 and 4/0 emery papers, degreased with trichloroethylene, and dried. The specimens were weighed with accuracy of 0.1mg. After initial weighing, the test specimens were exposed in a 1000 ml of glass desiccators with an open weighing bottle containing the solution of inhibitor in Isopropyl alcohol. The specimens were held by hooks in the desiccators over a 500ml of electrolyte solution like (HCl and Water). This setup was kept in a thermostat water bath maintained at 50°C. This arrangement produced a continuous under saturation of water vapours at 100% relative humidity. One cycle included a 5 hours exposure in the thermostat. The experiments were carried out in the absence and in the presence of inhibitor. The observations were made at the end of the test period. Specimens were then cleaned using pickling solution. Washed, dried and reweighed. Mass loss was then found to determine the corrosion rate. The

specimens were weighed prior and after the tests. The corrosion rate was calculated by formula

(1), and the inhibition efficiency (IE) by formula (2, 3 and 4) respectively.

$$CR = \frac{W_1 - W_2}{A \times T} \rightarrow (1)$$

$$IE \% = \frac{W_1 - W_2}{W_1} \times 100 \rightarrow (2)$$

$$IE \% = \frac{R_{ct}(i) - R_{ct}}{R_{ct}(i)} \times 100 \rightarrow (3)$$

$$IE \% = \frac{R_p(i) - R_p}{R_p(i)} \times 100 \rightarrow (4)$$

Where, A is the specimen area (in m<sup>2</sup>), W<sub>1</sub> is initial mass of the specimen, and W<sub>2</sub> is the specimen mass (in g) after the exposure period, T is the exposure period (in hours), the experiments were carried out in triplicate. i.e. the gravimetric corrosion rate was listed as an average value for the three specimens studied under identical experimental conditions.

$R_{ct}(i)$  and  $R_p(i)$  are the charge transfer resistance and polarization resistance with inhibitor and  $R_{ct}$  and  $R_p$  are blank respectively.

#### 2.4. Potentiodynamic Measurement

The polarization measurement has been taken with help of this electrode system working and counter electrode mode were consider as a one, and saturated calomel electrode as reference one. The potential value in this paper was referred to SCE. The potentio dynamic measurements were started by changing step wise 60mV/m on a PGP20IP potentiostat/ galvanostatic. The anode potential could find at the steady potential. Tafel polarization drawn via interchanges the potential (E) and log I, the parameter  $b_a$  and  $b_c$  were evaluated.

#### 2.5. Electrochemical Impedance Spectroscopy

The cell configuration of EIS was done by the electrochemical measurement unit solartron 1280b.  $R_{ct}$  and Cdl value obtain from the difference between the values of real axis. They employed amplitude of  $\pm 20$ mV, frequency ranging 0.5Hz to 100 KHz.

#### 2.6. Fourier Transformation Infrared Spectroscopic Studies (FTIR)

Surface analyses of adsorbed film, on the mild steel during the gravimetric tests in the presence of inhibitor were obtained by FTIR spectrum.

### 3. Results and Discussion

#### 3.1. Weight loss method

The inhibition effect of volatile corrosion inhibitor, on the carbon steel after 5Hrs exposure at 100% RH was discussed by weight loss method. Two environments like, acid and

water. And calculate the corrosion rate and inhibition efficiency of the VCI's which is shown in the table 2 and 3 respectively. In all environments DCHAB shows that it is high and best inhibition on iron in the corresponding environments.

Table 2. Effect of VCI's on MS in Acid environment.

Serial no	Inhibitor	Weight loss (g)	Inhibition efficiency (%)	Corrosion rate ( $\mu\text{m}/\text{y}$ )
1	Blank	8	-	0.7132
2	DCHA.BTZ	2.4	70	0.2139
3	OTP	2.1	74	0.1872
4	OTC	0.8	90	0.0772
5	OTS	0.1	98	0.0133

Table 3. Effect of VCI's on MS in Neutral environment.

Serial no	Inhibitor	Weight loss (g)	Inhibition efficiency (%)	Corrosion rate ( $\mu\text{m}/\text{y}$ )
1.	Blank	6	-	0.5349
2.	OTS	3.4	43	0.3031
3.	OTC	2.6	56	0.2340
4.	OTP	1.6	72	0.1471
5.	DCHA.BTZ	0.7	88	0.0649



The nyquist plot of the carbon steel with this five inhibitor were drawn which is exposed about 5hrs in the  $H_2S$  environment is shown in the fig.1. It shows that the corrosion behavior of mild steel in the sense of resistance to the corrosive medium in the presence and absence of inhibitor. The VCI's doesn't amend the mechanism dissolution of metal. Hence, it's purely depends on the charge transfer process. All experimental plots approximately have a semi-circular shape. The impedance measurement shows that the inhibition of the VCIs is characterised by increasing diameter of the arc which is acting the resistance  $R_{sol}$  is the solution resistance between the reference and working electrode. When the aggressive chemicals such as sulphur, water, ionic species permeate the inhibitor film to the active site of the metal, the corrosion of metals become measurable, so that is associated parameters, the double layer capacitance (Cdl) and charge transfer resistance (Rct) can be estimated.

The Cdl and Rct values are shown in the table only for which has highest inhibition efficiency in weight loss method1 & 2 for acid, neutral respectively. And shows that OTS and DCHABTZ having highest value of Rct and Cdl value of  $14571 \text{ ohm cm}^2$ ,  $3.508 \times 10^7 \mu\text{F/cm}^2$  and value of  $9872 \text{ ohm cm}^2$ ,  $3.654 \times 10^5 \mu\text{F/cm}^2$  in both environment respectively than the other (which doesn't shown). The impedance spectrum shown fig.1&2 Inhibition efficiency can also be calculated with this. Inhibition efficiency has been computed by equation 3

Table 4. Electrochemical Impedance Studies in Acid medium

Inhibitor used	$R_{ct}$ ohm $cm^2$	$C_{dl}$ $\mu F/cm^2$	Inhibition efficiency (%)
Blank	2389	$3.005 \times 10^{-5}$	-
OTS	14571	$3.508 \times 10^{-7}$	83

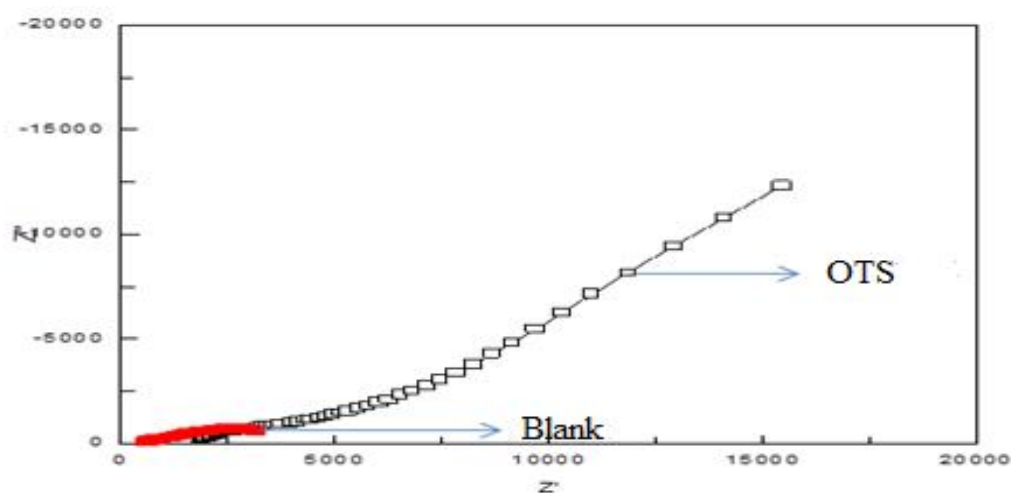


Fig .1. Impedance diagram for the blank and OTS in acid medium.

Table 5. Electrochemical Impedance Studies in Neutral Medium

Inhibitor used	$R_{ct}$ ohm $cm^2$	$C_{dl}$ $\mu F/cm^2$	Inhibition efficiency (%)
Control	2082	$2.51 \times 10^{-4}$	-
DCHA.BTZ	9872	$3.654 \times 10^{-5}$	78

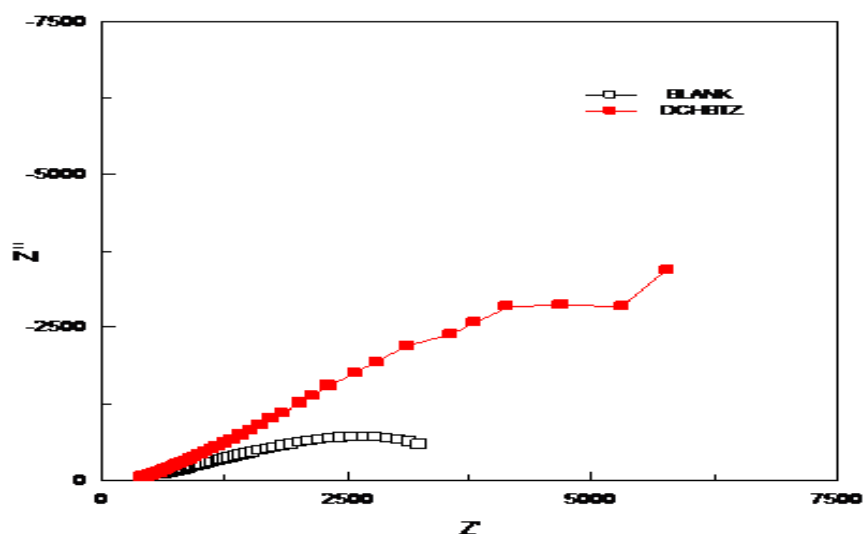


Fig .2. Impedance diagram for the blank and DCHABTZ in neutral medium.

### 3.3. Tafel polarization Technique

Tafel Polarization monitoring is an effective electrochemical method of measuring corrosion. Monitoring the relationship between electrochemical potential and current generated between electrically charged electrodes in a process stream allows the calculation of the corrosion rate. LPR is most effective in aqueous solutions, and has proven to be a rapid response technique. In our studies the current produced by the blank i.e. without inhibitor is in the

increasing order increase with increase in volt apply. But it is totally inversely related, the current produced by the best inhibitor is very low, when compare with other remaining inhibitors. With this account, which shows the best inhibition in measurement is OTS and DCHABTZ in acid and water environments respectively. Retained inhibitors shows that less inhibition than the others (which doesn't show). Tafel graph took only for which represented highest inhibition in weight loss in the given below Fig.3 and 4, the parameter values are given in below table 6 and 7 acid and neutral medium respectively. Inhibition efficiency could be calculated from the equation (4).

Table 6. Polarization parameters for MS in presence of VCI after 5 hrs exposure at acid medium

Inhibitors	$i_{cor}$ ( $\mu A/cm^2$ )	Tafel slope (mV/Decade)		$R_p$ K Ohm.cm <sup>2</sup>	Inhibition efficiency (%)
		$B_a$	$-B_c$		
Blank	$3.6426 \times 10^{-5}$	233.4	101.23	10	--
OTS	$2.3302 \times 10^{-7}$	669.47	636.72	92	89

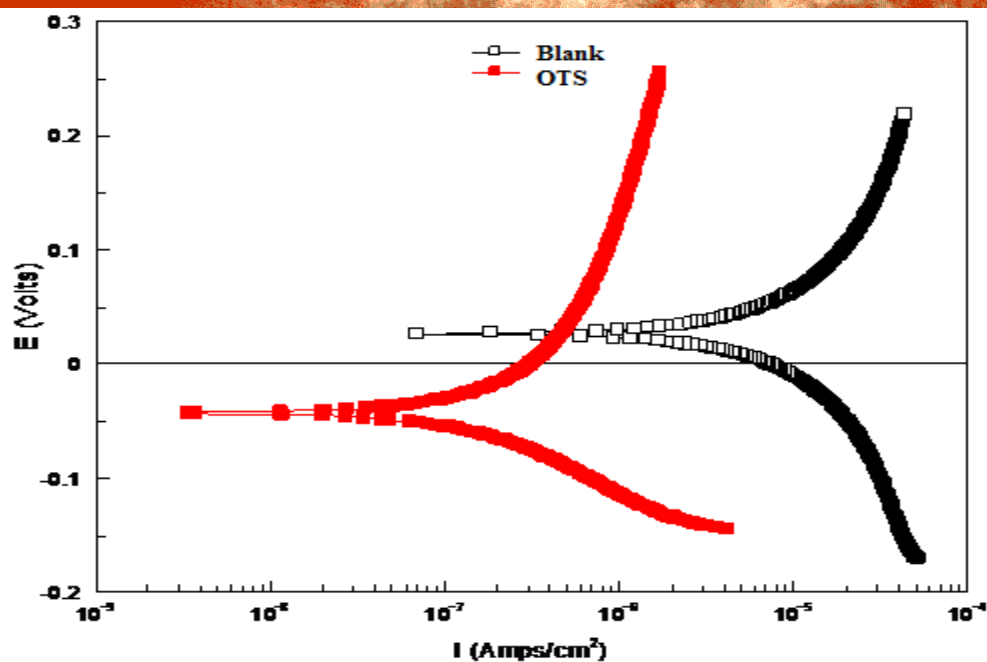


Fig .3. Tafel Polarization curve of Blank with OTS in acid medium

Table 7. Polarization parameters for MS in presence of VCI after 5 hrs exposure  
at neutral medium

Inhibitors	$i_{cor}$ ( $\mu A/cm^2$ )	Tafel slope (mV/Decade)		$R_p$ ( $K\Omega cm^2$ )	Inhibition efficiency (%)
		Ba	-Bc		
Control	$0.961 \times 10^{-6}$	102.4	97.607	5	--
DCHA.BTZ	$4.337 \times 10^{-7}$	316.0	360.24	76	93.4

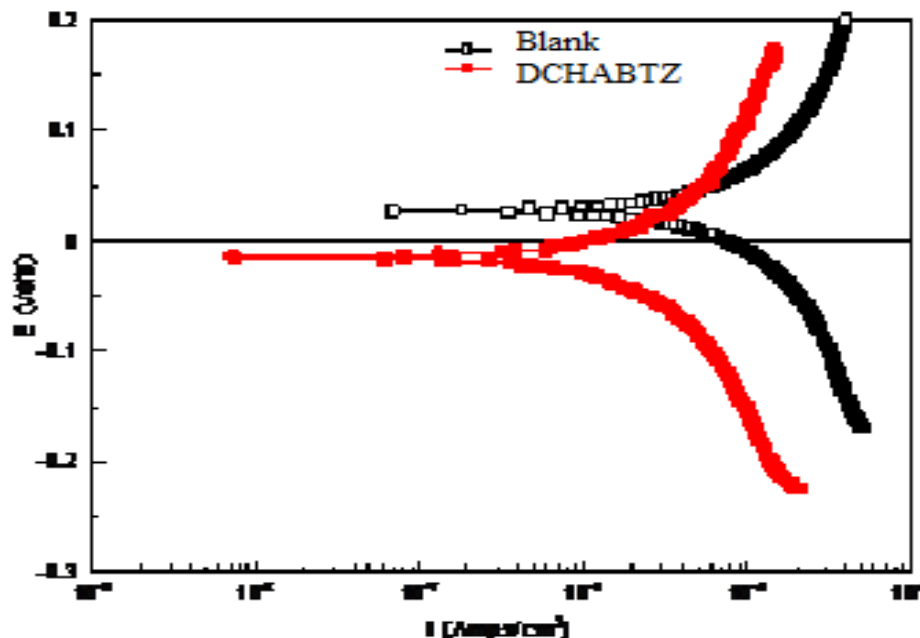


Fig. 4. Tafel Polarization curve of Blank with DCHA BTZ in neutral medium

### 3.4. Adsorption Isotherm

As mentioned weight % of VCI [19] took for the demonstrations. And it obeyed the adsorption isotherm. Adsorption Isotherms of VCI on MS in both Acid and Neutral medium had shown in the fig 5 and 6 respectively. And it implied the maximum adsorption occurred 1.2%, at which maximum inhibition efficiency observed

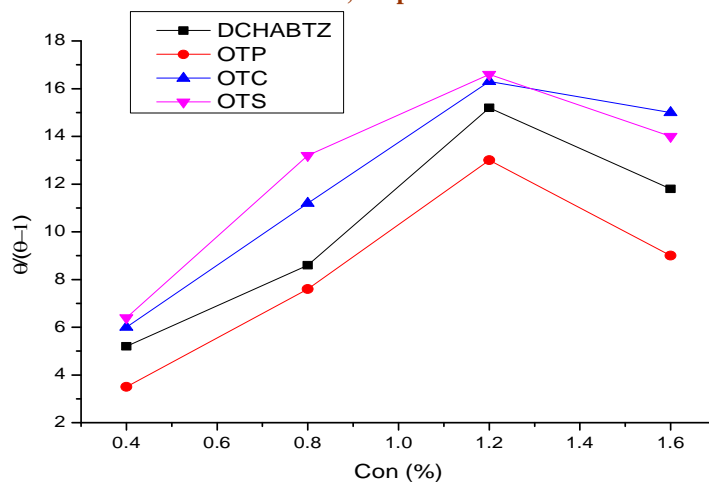


Fig .5. Adsorption isotherms in acid medium

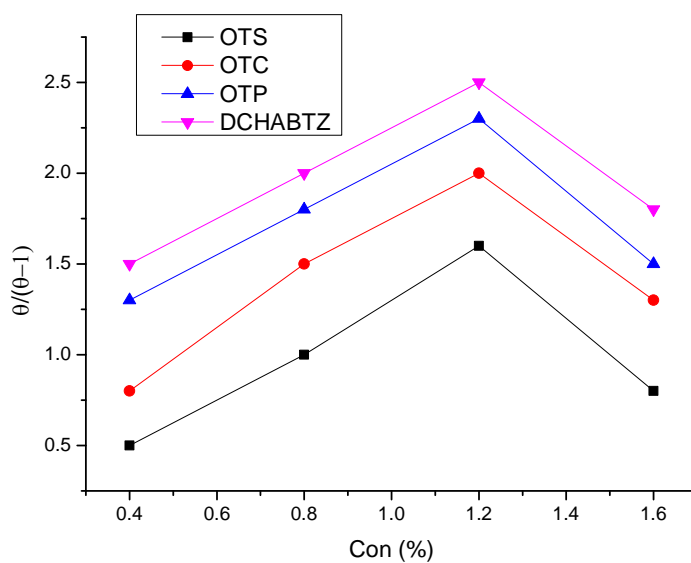


Fig .6. Adsorption Isotherms in neutral medium

The gradual increase of the adsorption of VCI in the above isotherm figures implies that 1.2wt% was the maximum adsorption on the MS. Hence, we made the former Wt % for the all

VCI to determine the inhibition efficiency in both acid and neutral medium. And parameters are shown in the following.

Table 8. Polarization parameters for MS in presence of 1.2wt % of VCI in Acid medium

Inhibitors	$i_{cor}$ ( $\mu A/cm^2$ )	Tafel slope (mV/Decade)		$R_p$ ( $K\Omega cm^2$ )	Inhibition efficiency (%)
		Ba	-Bc		
Blank	1.5	112	133	12.6	-
DCHA.BTZ	0.2636	197.7	155.3	45	72
OTP	0.16	137	170	58	78
OTC	0.05	219	66.8	63	80
OTS	0.0399	218	187	82	85

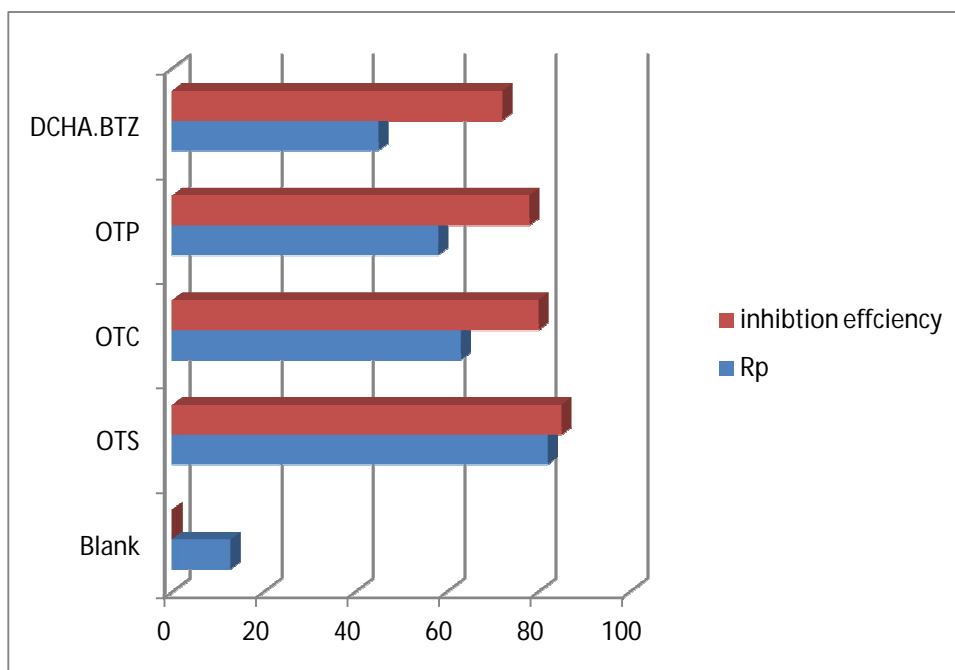


Fig.7.  $R_p$  and IE of inhibitors in acid medium.



Table 9. Polarization parameters for MS in presence of 1.2wt % of VCI in  
Neutral medium

Inhibitors	$i_{cor}$ ( $\mu A/cm^2$ )	Tafel slope (mV/Decade)		$R_p$ ( $K\Omega cm^2$ )	Inhibition efficiency (%)
		Ba	-Bc		
Blank	2.3	165	167	54	-
OTS	0.1	141	216	117	54
OTC	0.08	112	140	177.5	69
OTP	0.05	155	85	186	71
DCHABTZ	0.02	136	114	346	84

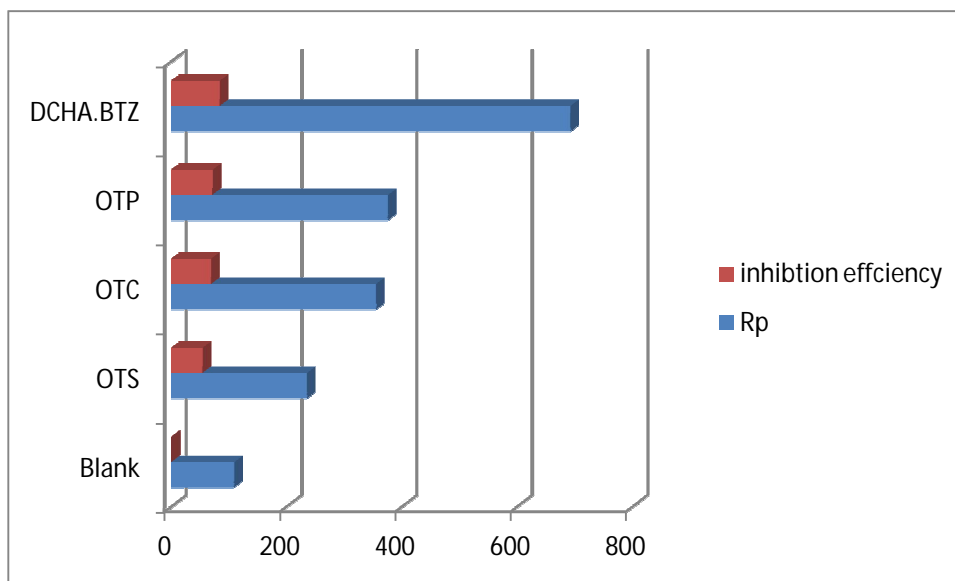


Fig.8.  $R_p$  and IE of inhibitor in neutral medium.

### 3.5. SEM Spectral Details

#### *Acid medium*

SEM image reveals that the specimens are containing the corroded iron and unaffected specimen in their surface after exposure in Acid environment. The amount of surface defects decreases by the inhibitor of OTS on the MS. The best coordinate bond layer distribution was observed on specimen containing inhibitor which shows in the fig.9

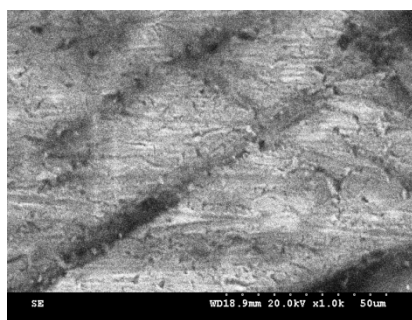


Fig.9(a). Shows Specimen with OTS

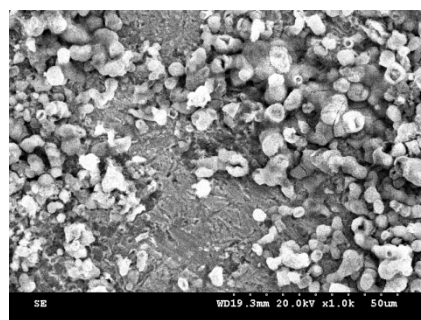


Fig.9(b). Blank

On comparing the above two images, image which is not having the inhibitor shows highly corroded particle on the MS surface. When compare with the first image there is no that much amount of corroded particle. Form the SEM analysis shows that OTS inhibitor is shows high inhibition efficiency among the others (which doesn't).

#### *Neutral medium*

SEM image reveals that the specimens are containing the corroded iron and unaffected specimen in their surface after exposure at neutral environment. The amount of surface defects decreases by the inhibitor of DCHA.BTZ on the MS. The best coordinate bond layer distribution was observed on specimen containing inhibitor which shows in the fig.10

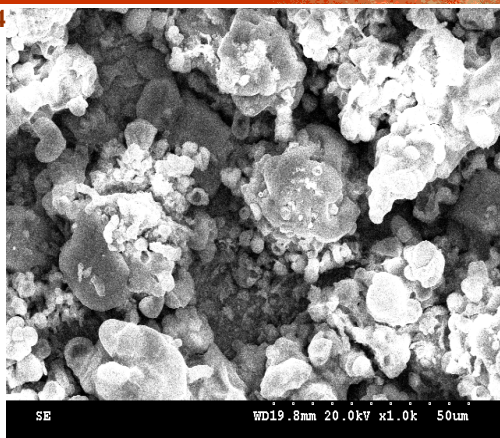


Fig .10(a). Blank

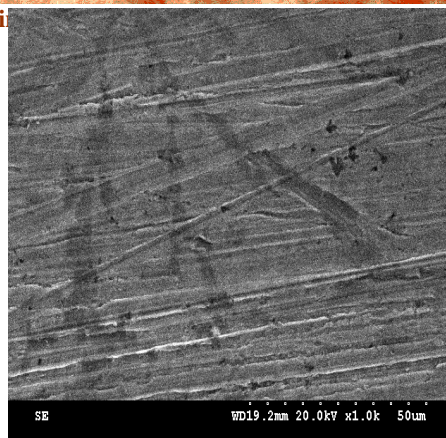


Fig .10(b). Specimen with DCHA.BTZ

### 3.6.FT-IR Spectrum Analysis

FTIR spectral details for VCIs and their surface film on mild steel after 5 hrs exposure at 100% RH in neutral medium. The synthesized VCI compounds and their inhibitive film formed on the surface of mild steel after 5hrs exposure at 100% RH in neutral medium has been studied using the FTIR spectral analysis. The mechanism for inhibition of corrosion on mild steel by the VCI compounds is clear from the spectral data obtained in the below table. FTIR spectrums and tables portrait for the best inhibitor, which has best inhibition in both medium.

It is seen from FTIR spectral data of VCI film formed on the metal surface in the Corrosive medium A, that the C-N stretching frequency of DCHA.BTZ has shifted from 1364 to 1408  $\text{cm}^{-1}$ . It suggests that nitrogen atoms present in inhibitor are coordinated to MS resulting in the formation of inhibitor – Fe complex on metal surface. Similarly N-H, N=N,  $\text{NH}^+$  absorption frequencies 3394, 1566  $\text{cm}^{-1}$  shifted to , 3834, 1636  $\text{cm}^{-1}$ , respectively in neutral environment . The

shift in the value is due to the donation of lone pair of electrons of N atoms present in the VCI compound to Fe resulting in the formation of inhibitor-Fe complex.

From the FTIR spectral analysis it is clear that inhibitor – Fe complex is formed on the metal surface. The higher inhibition efficiency of DCHA.BTZ may be due the presence of 3 nitrogen atoms when compared to other inhibitors. The high lone pair electrons present in the DCHA.BTZ formed thick non- visible complex on the metal surface to reduce the corrosion rate of metal in comparison with other VCIs. FT-IR spectra of the VCI compounds and iron specimens after 5 hrs film forming period were recorded and the corresponding figures are shown in the followings.

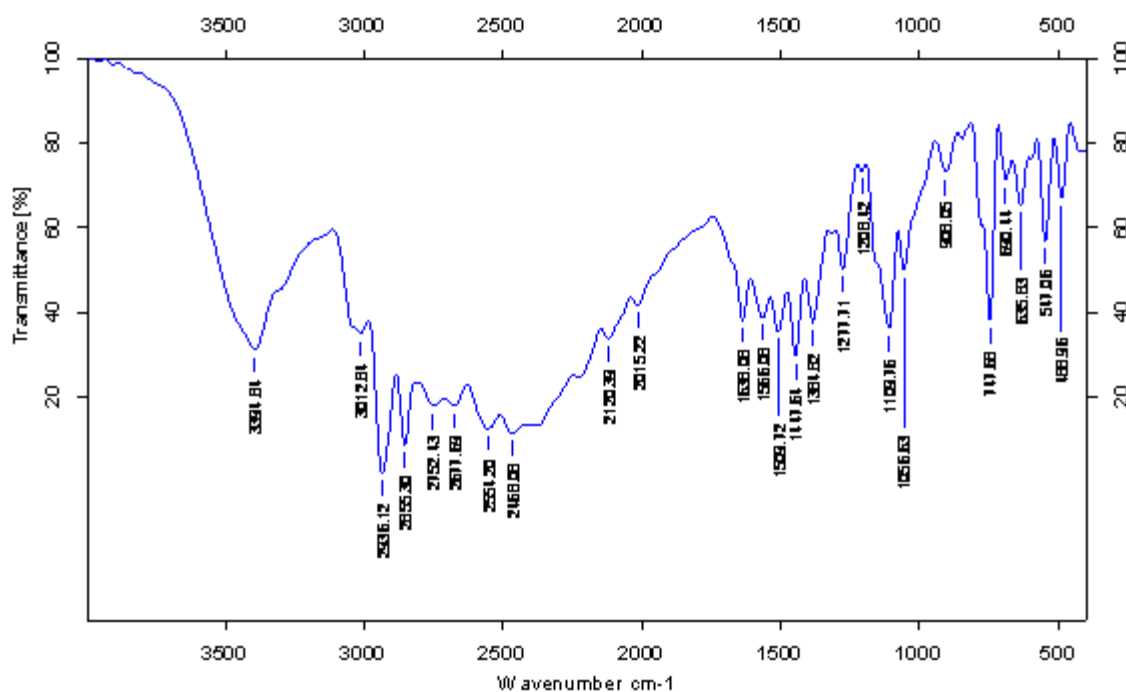


Fig .11(a). Shows the FT-IR spectrum of the DCHA.BTZ inhibitor

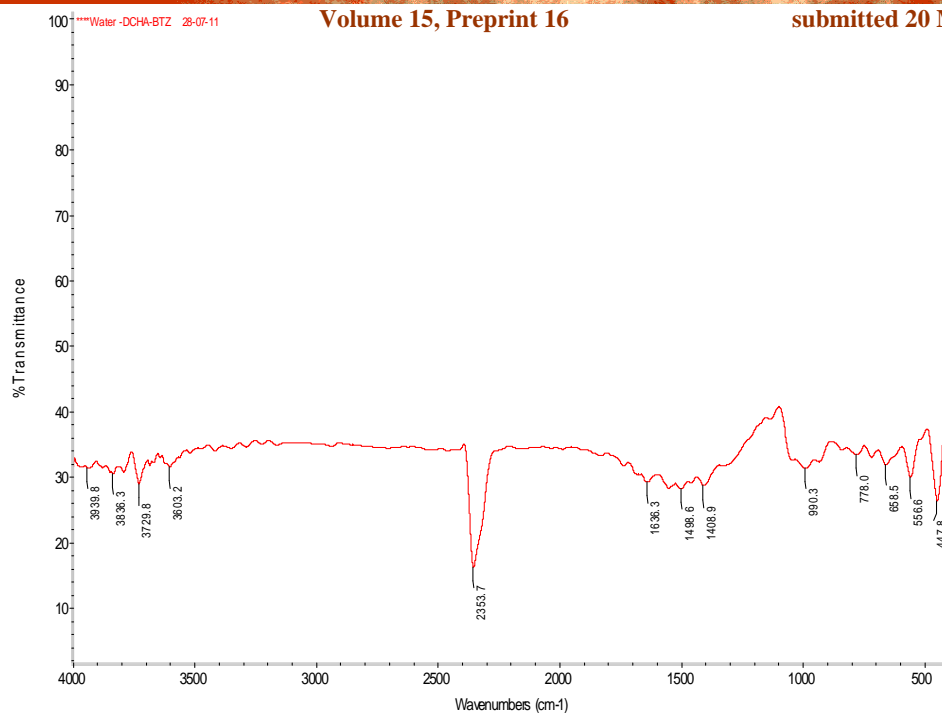


Fig .11(b). shows FT-IR absorption spectrum of the DCHA.BTZ inhibitor in neutral environment.

Table 10. Absorption frequencies of FTIR spectra recorded for DCHA.BTZ and in neutral medium.

Name of the inhibitor	Bond	Frequency range $\text{cm}^{-1}$	Measured band	
			Inhibitor $\text{cm}^{-1}$	MS Surface film $\text{cm}^{-1}$
DCHA.BTZ	C-N	1220-1020	1408	1364
	N-H	3650-3200	3834	3394
	N=N	1630-1575	1636	1566

The synthesized VCI compounds and their inhibitive film formed on the surface of mild steel after 5hrs exposure at 100% RH in both Acid medium has been studied using the FTIR spectral analysis. The mechanism for inhibition of corrosion on mild steel by the VCI compounds is clear from the spectral data obtained in the below table 4.16. It is seen from FTIR spectral data of VCI film formed on the metal surface in the Acid medium, that the C-N stretching frequency of OTS has shifted from 1103 to 931  $\text{cm}^{-1}$ . It suggests that nitrogen atoms present in inhibitor are coordinated to MS resulting in the formation of inhibitor – Fe complex on metal surface. Similarly N-H, C=O absorption frequencies 3426, 1635  $\text{cm}^{-1}$  shifted to 3604, 1646  $\text{cm}^{-1}$ , respectively in environment A. The shift in the value is due to the donation of lone pair of electrons of N atoms present in the VCI compound to Fe resulting in the formation of inhibitor-Fe complex. From the FTIR spectral analysis it is clear that inhibitor – Fe complex is formed on the metal surface. The higher inhibition efficiency of OTS may be due to the presence of 2 nitrogen atoms when compared to other inhibitors. The lone pair electrons and then strong C-N sigma bond is present in the OTS formed thick non-visible complex on the metal surface to reduce the corrosion rate of metal in comparison with other VCIs.

From the above FT-IR investigation it shows that the octylamine derivated amide compounds such as OTC, OTP, and OTS all are having the lone pair electron containing atom like oxygen and nitrogen. In the amide compounds the nitrogen atom was donated their lone pair electron to the metal to form the Fe- inhibitor coordinated bond. It can be seen from the value that the C-N value decreased and C=O value increased.



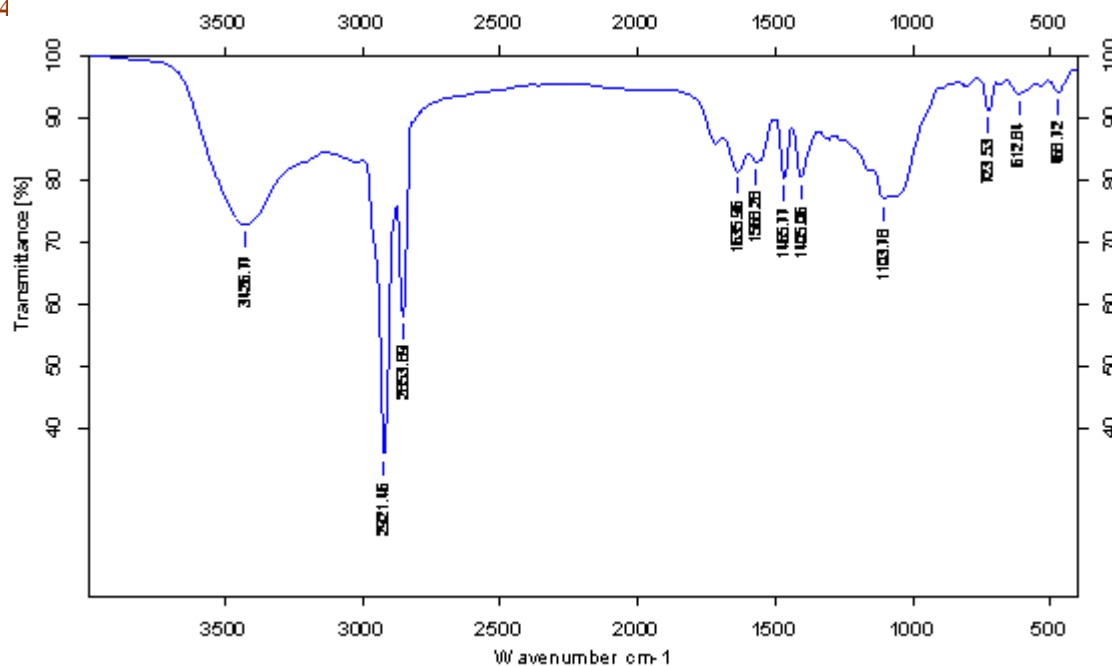


Fig .12 (a). shows the FT-IR spectrum of the OTS inhibitor

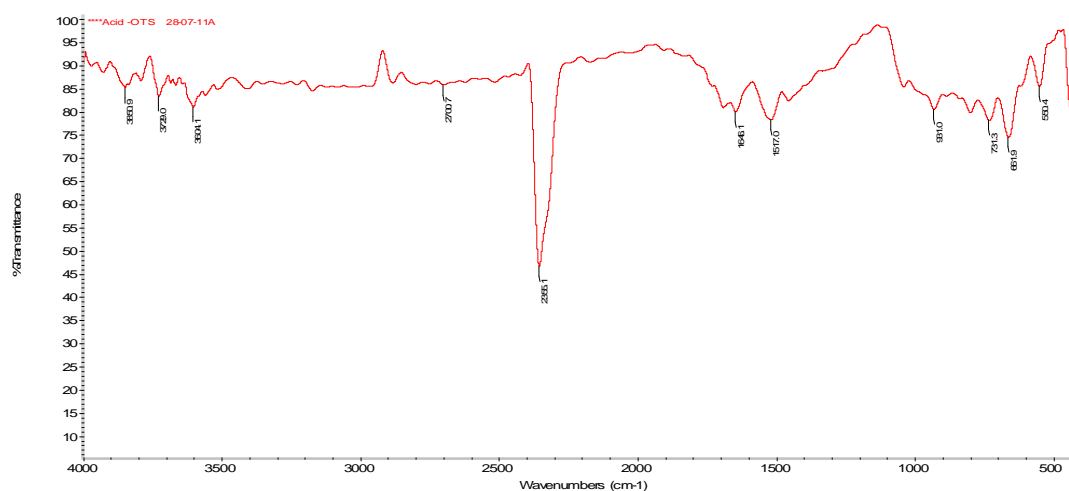


Fig .12 (b). Shows the FT-IR adsorption spectrum of the OTS in the acid environment

Table 11. Absorption frequencies of FTIR spectra recorded for OTS and in Acid medium.

Inhibitor	Bond	Frequency range $\text{cm}^{-1}$	Measured bond	
			Inhibitor $\text{cm}^{-1}$	MS Surface film $\text{cm}^{-1}$
OTS	N-H	3650-3200	3426	3604
	C=O	1800-1600	1635	1646
	C-N	1360-1080	1103	931

#### 4. Conclusion

From this study, the above compound OTS, OTP, OTC and DCHABTZ were could be used as a VCI. Even in the 1.2 % concentration gave the maximum adsorption power with the MS in the acid and neutral medium. And maximum inhibition efficiency occurred at 1.2% concentration around 90% in both medium. And SEM analysis shows the best adsorption of inhibitor via the clear surface on the metal surface.

Tafel explain that  $R_p$ ,  $i_{\text{cor}}$  and IE value respectively, 76 K Ohm.cm<sup>2</sup>,  $4.337 \times 10^{-7} \mu\text{A}/\text{cm}^2$  and 93.4% for DCHA.BTZ in water medium. In acid medium OTC has 92 KOhm.cm<sup>2</sup>,  $2.3302 \times 10^{-7} \mu\text{A}/\text{cm}^2$  and 89%. Better than the blank and else other inhibitors. EIS study implied the best  $C_{\text{dl}}$  and  $R_{\text{ct}}$  value of inhibitor were  $3.654 \times 10^{-5} \mu\text{F}/\text{cm}^2$  and 9872 ohm.cm<sup>2</sup>,  $3.508 \times 10^{-7} \mu\text{F}/\text{cm}^2$  and 14571 ohm.cm<sup>2</sup> of the inhibitors DCHA.BTZ and OTS in neutral, acid medium respectively.

FTIR accomplish how the adsorption took on the surface of the mild steel. Inhibitor DCHA.BTZ in water (steam) medium donating its lone pair of electron from its own nitrogen



atoms to iron surface. And OTS vouch it non-bonded electron as former compound did. This could realized, from the FTIR datas.

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