

# INHIBITION OF MILD STEEL CORROSION IN FORMIC ACID BY THIOUREA, 2-AMINO [4-p-CHLORO PHENYL] THIAZOLE AND DIFFERENT DERIVATIVES OF THEIR CONDENSATION PRODUCTS

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## ABSTRACT

The inhibitive effect of thiourea, 2-amino [4-p-chlorophenyl] thiazole and different derivatives of their condensation products, N-2[4-p-chlorophenyl] 2-thiazolyl] thiocarbamide on the corrosion of mild steel in 20% formic acid solution has been studied using weight loss and electrochemical polarisation techniques. Different concentrations of inhibitors and temperatures have been tested. The inhibition efficiencies calculated by both the techniques are in fairly good agreement except at higher concentrations of some inhibitors. The results observed have been discussed in the light of the molecular structures of the compounds and their adsorption on the surface of the corroding metal. All the inhibitors have been found to be good inhibitors. The polarisation measurements indicate that these inhibitors influence both anodic and cathodic reactions and thereby they contribute to reduce the corrosion rate.

**Keywords :** Mild steel, corrosion inhibition, formic acid, thiourea, thiazole, thiocarbamides.

## INTRODUCTION

Corrosion of mild steel in organic acids is an active area of research. Organic compounds containing N and S have proved to be good inhibitors for the prevention of corrosion under acidic conditions (1-4). Thiourea (4-7) and thiazoles (8-9) have been recognised as inhibitors for corrosion of many metals in different inorganic and organic acidic media. Improvement in the inhibitive performance due to products resulting from condensing two different inhibitor molecules has also been reported earlier for various metals in different environments (10-11). Thus, it is interesting to investigate the improved performance of the condensation products of thiourea and some of the thiazoles as corrosion inhibitors of mild steel in formic acid solutions.

In the present investigation, the inhibitive effect of thiourea and 2-amino [4-p-chlorophenyl] thiazole separately and of their condensation product, N-2[4-p-chlorophenyl] 2-thiazolyl] thiocarbamide, with different groups attached to it, on the corrosion of mild steel in 20 percent formic acid solution have been studied at 25, 35 and 45°C.

## EXPERIMENTAL

Mild steel of composition C-0.12%, Mn-0.11%, Si-0.02%, P-0.02%, S-0.02%, Ni-0.02%, Cu-0.01% Cr-0.01% and remainder Fe was used for the preparation of test electrodes. Analytical grade formic acid and double distilled water was used in the preparation of the experimental solution. Thiourea, 2-amino [4-p-chlorophenyl]-thiazole, 2-amino [4-p-chlorophenyl] thiocarbamide, N-2 [4-p-chlorophenyl].5-phenyl azothiazolyl] thiocarbamide, N-2[4-p-chlorophenyl] 5-o-methyl phenyl azothiazolyl] thiocarbamide and N-

2 [4-p-chlorophenyl] 5-o-methoxy phenyl azothiazolyl] thiocarbamide were synthesized in the laboratory and were recrystallized before use.

For weight loss experiments, specimens of 3x3 cm were mechanically polished with 1/0 to 4/0 grade emmery papers followed by cleaning with soap and finally degreased with acetone. The specimens were dipped in 300 ml of 20% formic acid without and with inhibitors for 24 hours. The loss in weight was determined after removing the specimens from the electrolyte. The test electrodes were washed thoroughly with distilled water, dried and weighed. Inhibition efficiencies were calculated from weight loss (2) and electrochemical techniques (12).

For electrochemical studies electrodes of 1x1 cm with a 4 cm long tag for electrical contact were used. The part of the stem adjacent to the electrode was coated with a lacquer. In a three necked glass assembly, platinum foil of size 2x2 cm and a Luggin type saturated calomel electrode were used as counter and reference electrodes, respectively. Potentiostatic polarisation experiments in nondeaerated and unstirred solution without any salt were carried out using a Wenking Model POS 73. The addition of up to 0.5 M sodium formate to 20% formic acid was not considered since it does not affect the anodic and cathodic polarisation curves to any appreciable degree. The shape of these curves remains identical, both in the presence and the absence of the salt (13). Therefore, sodium formate was not added to the formic acid for the inhibition study. The steady state potential was recorded after it attained a constant value. All the experiments were performed in an air thermostat with an accuracy of  $\pm 0.2^\circ\text{C}$ .

### RESULTS AND DISCUSSION

The inhibition efficiencies of thiourea (additive-I), 2-amino [4-p-chlorophenyl] thiazole (additive-II), N-2[4-p-chlorophenyl] 2-thiazolyl] thiocarbamide (additive-III), N-2 [4-p-chlorophenyl] 5-phenyl azothiazolyl] thiocarbamide (additive-IV), N-2[4-p-chlorophenyl] 5-o-methylphenyl azothiazolyl] thiocarbamide (additive-V) and N-2 [4-p-chlorophenyl] 5-o-methoxyphenyl azothiazolyl] thiocarbamide (additive-VI) at their different concentrations (50, 100, 150, 200 and 250 ppm) evaluated by weight loss and electrochemical techniques have been recorded and are presented in Table 1. The percentage inhibition efficiency calculated by both techniques are in fairly good agreement. The variation in the inhibition efficiency of all the tested inhibitors with their concentration at 25°C has been illustrated in Fig. 1.

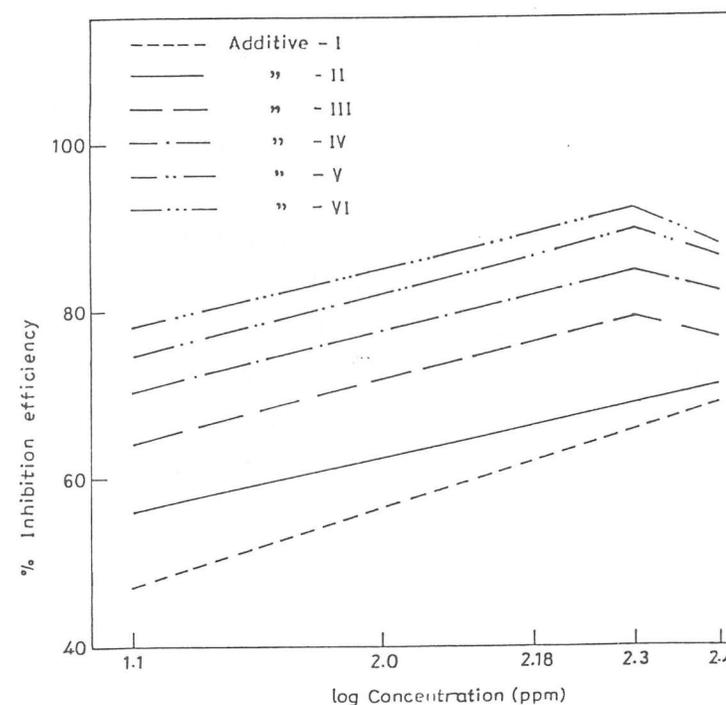


Fig. 1: Variation in % inhibition efficiency with concentration of the inhibitors at 25°C.

Table 1 : Inhibition efficiency (%IE) of the inhibitors at their different concentrations for the corrosion of mild steel in 20% formic acid by weight loss and electrochemical techniques at different temperatures.

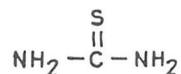
Inhibitors and concentration (ppm)	% IE					
	25°C		35°C		45°C	
	Weight loss	Electrochemical	Weight loss	Electrochemical	Weight loss	Electrochemical
<b>Thiourea</b>						
50	47.23	45.05	52.76	51.02	54.55	54.29
100	55.70	54.29	61.29	61.09	63.22	63.69
150	62.54	61.10	63.59	64.52	65.29	66.89
200	65.47	65.32	66.59	66.12	69.42	69.80
250	68.08	69.10	70.74	71.82	72.72	72.46
<b>2-amino [4-p-chlorophenyl] thiazole</b>						
50	56.35	56.35	62.67	62.85	65.70	65.33
100	61.56	61.10	67.28	66.12	69.83	69.80
150	65.80	63.69	70.96	70.49	73.76	74.30
200	67.43	66.89	72.58	72.46	75.21	76.01
250	70.03	71.16	76.50	74.30	78.93	77.09
<b>N-2 [4-p-chlorophenyl] 2-thiazolyl] thiocarbamide</b>						
50	61.89	61.98	69.12	70.49	71.07	71.16
100	72.64	72.46	79.72	78.12	82.44	80.05
150	76.87	75.45	82.49	82.62	85.12	83.78
200	79.15	78.12	85.02	84.51	88.02	87.18
250	76.22	80.05	82.94	86.20	84.50	88.52
<b>N-2 [4-p-chlorophenyl] 5-phenyl azothiazolyl] thiocarbamide</b>						
50	68.08	69.10	73.27	72.46	76.03	76.01
100	78.83	78.12	83.87	83.02	86.78	85.55
150	83.06	82.62	85.71	85.21	89.26	88.52
200	85.02	84.15	88.94	87.12	90.91	89.04
250	82.41	86.20	84.33	88.25	87.19	90.88
<b>N-2 [4-p-chlorophenyl] 5-o-methyl phenyl azothiazolyl] thiocarbamide</b>						
50	74.59	73.70	78.80	78.12	81.40	80.05
100	83.39	83.40	88.25	87.12	90.29	89.04
150	85.99	86.20	89.63	89.04	91.12	91.29
200	89.57	89.53	91.01	90.23	92.36	91.87
250	86.31	90.45	89.17	91.09	90.08	92.76
<b>N-2 [4-p-chlorophenyl] 5-o-methoxy phenyl azothiazolyl] thiocarbamide</b>						
50	77.85	78.12	82.02	81.38	83.06	82.62
100	86.32	86.82	90.32	88.25	91.32	90.88
150	90.55	90.45	91.71	91.49	93.39	92.76
200	91.85	91.29	93.31	92.59	94.42	93.54
250	88.27	92.06	88.47	93.54	90.29	94.50

The inhibition efficiency of additives were found to increase continuously with increase in their concentration. However, the percentage inhibition efficiencies of additive-III to VI determined by weight loss method showed a declining tendency above the concentration of 200 ppm. The decrease in inhibition efficiency between 200 and 250 ppm for these additives is observed at each experimental temperature. Surprisingly such a decrease in inhibition efficiency at 250 ppm was not observed when evaluated by electrochemical method, instead it increased continuously at all temperatures. It is difficult to explain this discrepancy in the inhibition efficiency values calculated by using different techniques because both positive and negative difference between two values for each inhibitor at their different concentrations has been observed.

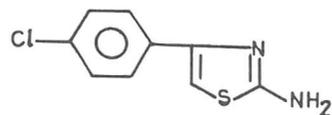
Inhibition efficiencies of the order of 65 and 67 percent were obtained at 25°C and at 200 ppm of the additives I and II respectively, by weight loss and electrochemical techniques. However, the condensation product of these two additives, additive-III, exhibited 79 percent inhibition efficiency at the same concentration and temperature. The inhibition efficiency of the condensation product further improved from 79 to 92 percent as derivatives of this compound synthesized on substituting di-azophenyl, di-azo-o-methyl phenyl and di-azo-o-methoxy phenyl groups of the thiazole of the condensation product were used as inhibitor. Successive increase in the inhibition efficiency of the derivatives from IV to VI is in agreement with the theoretical prediction. Thus, the observed inhibition efficiency at different concentrations and temperatures follow the trend : Additive VI > V > IV > III > II > I. An increase in temperature invariably increases the inhibition efficiency of all inhibitors at all concentrations.

The effectiveness of these inhibitors may be explained assuming the adsorption process as the cause of inhibition. The extent of adsorption of different inhibitors at a fixed concentration would depend on the surface area of the inhibitor molecules and the number and position of active centres such as N, S and O atoms along with delocalised  $\pi$  electron density on the aromatic ring. The structures of the tested inhibitors are :

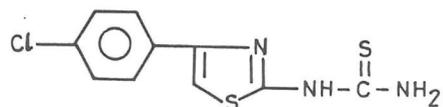
(1) Thiourea



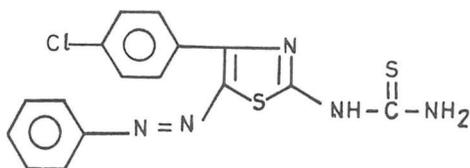
(2) 2-Amino [4-p-chlorophenyl] thiazole



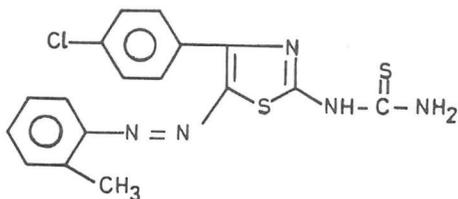
(3) N-2 [4-p-chlorophenyl] 2-thiazolyl] thiocarbamide



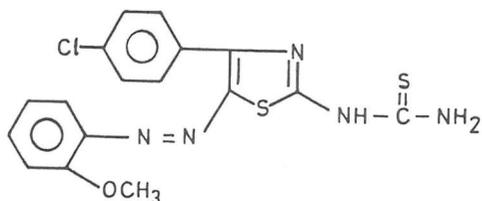
(4) N-2 [4-p-chlorophenyl] 5-phenyl azothiazolyl] thiocarbamide



(5) N-2 [4-p-chlorophenyl] 5-O-methyl phenyl azothiazolyl] thiocarbamide



(6) N-2 [4-p-chlorophenyl] 5-O-methoxy phenyl azothiazolyl] thiocarbamide



The inhibition efficiency data recorded in Table 1 reveals that on increasing the concentration of thiourea from 50 to 250 ppm, inhibition efficiency increases from 47 to 68 percent. With a rise in temperature from 25 to 45°C the percentage inhibition efficiency increases up to 72 percent at 250 ppm. Thus, thiourea may be considered to show appreciable inhibition efficiency at 250 ppm and at higher temperature the efficiency is even slightly improved. The adsorption of thiourea on the corroding surface being considered as the cause of inhibition, it could take place via functional nitrogen and sulphur atoms. Lower values of inhibition efficiency may be attributed to the smaller size of the additive which could however be improved by substituting hydrogen atoms in the molecule with other groups so that the number of active centres and lone pairs of electrons at these sites as well as the surface area of the molecule is appreciably increased (3,5).

On the other hand, inhibition efficiency of 2-amino[4-p-chlorophenyl] thiazole is greater (56%) than that of thiourea (47%), at 50 ppm. In fact, additive - II has more active centres and larger surface area than thiourea. The adsorption of additive-II may take place via functional N and S atoms as well as through the delocalised  $\pi$  electrons of the phenyl groups and thus, covering larger surface area. Consequently, an increase in inhibition efficiency is expected when thiourea is replaced by this compound. The results of the present investigation are in agreement with the theoretical prediction. In order to achieve further increase in inhibition efficiency additive III to VI were synthesized by condensing additive I and II and then preparing its different derivatives.

The additives III to VI can be considered to be made up of both thiourea and 2-amino [4-p-chlorophenyl] thiazole, in parts. These additives should show greater inhibition efficiency than additive I and/or II. It is to be

noticed that additive III shows an increase in inhibition efficiency over any of the inhibitors I or II. The inhibition efficiency of additive III is quite large, 79%, in comparison to the respective values 65% and 67% for additives I and II, at 200 ppm. This increase in inhibition efficiency may be attributed to increase in the number of active centres as well as the surface area. The inhibitor has two 'S' and three 'N' atoms as active centres and in addition a phenyl group. Looking at the structure of the additive III, it appears that it should have shown much larger inhibition efficiency than that actually observed. But, depending upon the geometry of the molecule, all the active centres may not be able to participate in the coordination bonding with the metal ions on the surface and hence, the expected result is not achieved. Nevertheless, the increase in inhibition efficiency is the indicative of the fact that larger surface area of the electrode is covered by the molecules of the third additive than those covered by any of the first two additives.

Further, an increase in the inhibition efficiency by 6% is observed when di-azophenyl group is substituted in the additive-III. In di-azophenyl group two nitrogen atoms are present as the key atoms for adsorption. In addition, the  $\pi$  electron density of benzene ring may also enhance the adsorbability of the molecules. This explains the higher inhibition efficiency shown by the additive-IV in comparison to that of the additive-III.

The di-azophenyl group being common to all additives from IV to VI gives further improvement in the inhibition efficiency due to an increase in the  $\pi$  electron density on phenyl ring by substitution of electron donating groups such as methyl ( $-\text{CH}_3$ ) and methoxy ( $-\text{OCH}_3$ ) groups on the phenyl ring. Hence, further improvement in IE shown by additive V and VI is due to increased electron density due to the phenyl ring. The additive VI shows larger inhibition efficiency than additive V. This enhancement in inhibition efficiency is conceivable in the light of better electron donating property of

$-\text{OCH}_3$  than that of  $-\text{CH}_3$  group. The relative change in the inhibition efficiency observed during the investigation by successively changing the additive from IV to VI indicates that it is the phenyl ring of the dia-azophenyl group which is mainly involved in the adsorption process. The two nitrogen atoms would have been away from the electrode surface to have any impact on the extent of adsorption.

The decrease in inhibition efficiency at 250 ppm for additive III to VI would have occurred due to mutual interaction between inhibitor molecules adsorbed at the adjacent sites. The observed data reveal that this is true particularly for bulky molecules and it is quite obvious. It is evident from data on Table 1 that an increase in temperature and concentration leads to an improvement in the protective power for all the additives. Similar increase in inhibitive efficiency of thiourea and its compound with the increase in temperature has been reported earlier for Al- $\text{HNO}_3$  system (3). This enhancement in inhibitive efficiency at higher temperatures has been attributed to the higher activation energy for the adsorption and the higher rate of diffusion of bulky inhibitor molecules, at elevated temperatures, from the bulk of solution to the interface (14).

The anodic polarisation behaviour of mild steel was studied in 20 percent formic acid containing different concentrations of additives at temperatures 25, 35 and 45°C. The curves in Fig. 2 illustrate the anodic polarisation behaviour of mild steel in the presence of 50, 100, 150, 200 and 250 ppm of additive-VI at 25°C. The shape of the curve is not modified on adding the additives or increasing their concentrations. However, on increasing the concentration of the inhibitor, the curves are gradually shifted towards lower current density region. The nature of the anodic polarisation curves observed for other additives exhibit similar trend at all the concentrations and temperatures (25, 35 and 45°C).

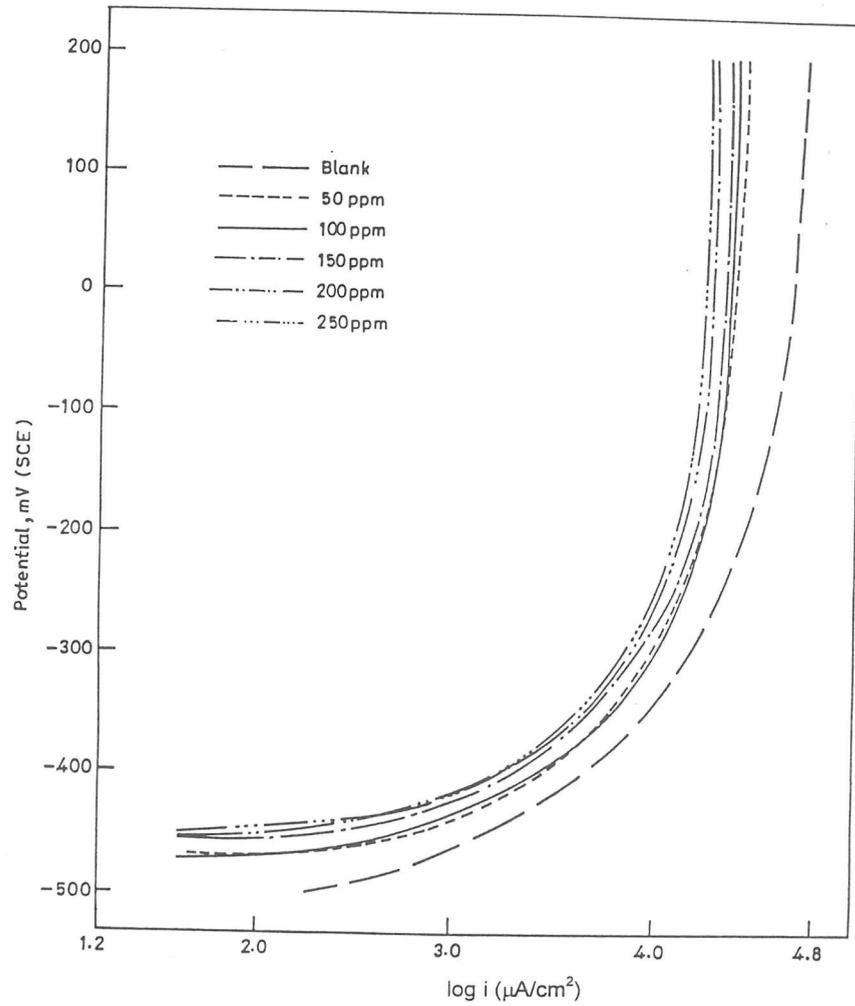


Fig. 2 : Anodic polarisation curves for different concentrations of additive - VI at 25<sup>0</sup>C

It is realized from these observations that the additive molecules retard the corrosion process without changing the mechanism of corrosion. The magnitude of the shift in current density is directly proportional to the concentration of inhibitors, indicating that the inhibitive property of these compounds is concentration dependent.

Fig. 3 illustrates the potentiostatic anodic polarisation curves for all the additives studied at 25°C and 250 ppm (similar curves were obtained at 35 and 45°C). The shift towards lower current density was observed to be maximum for additive-VI indicating its maximum effectiveness with respect to its interference with anodic reaction. The observed shift in anodic polarisation curves due to each of the inhibitor follows the same trend as that followed by

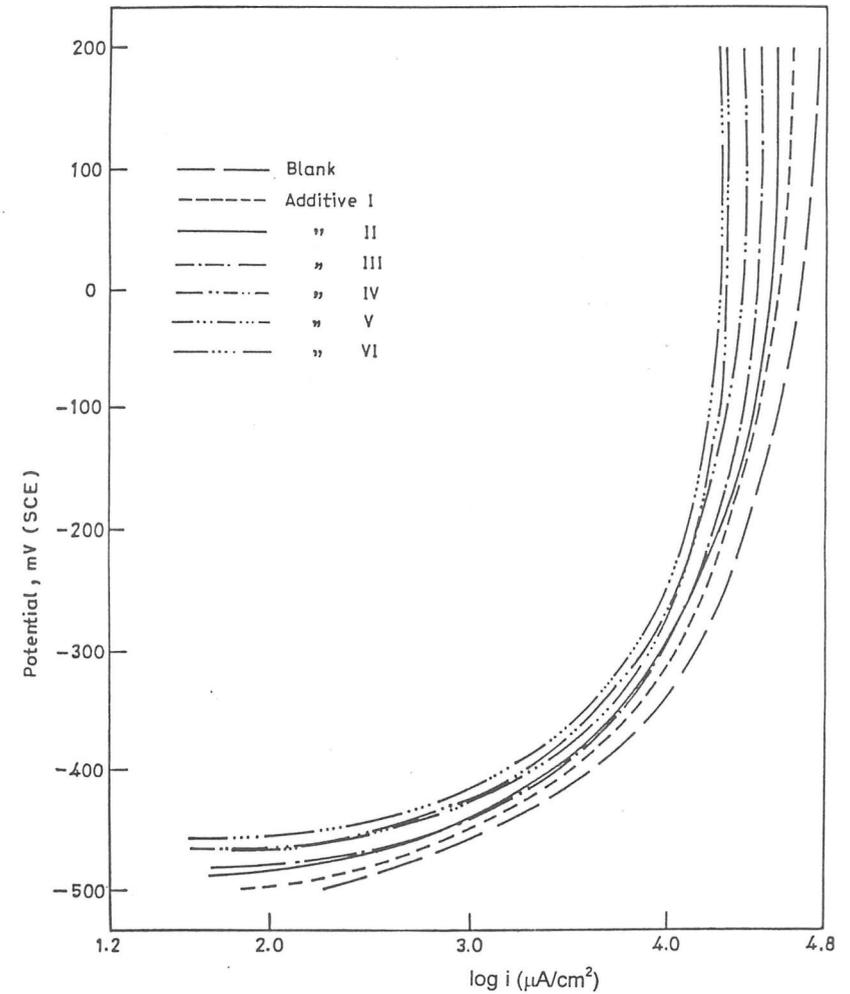


Fig. 3 : Anodic polarisation curves of mild steel in the presence of different additives at 25<sup>0</sup>C

their inhibition efficiencies.

The anodic parameters such as corrosion current ( $i_{corr}$ ), corrosion potential ( $E_{corr}$ ), limiting current ( $i_L$ ) and the ratio of limiting current with and without inhibitor ( $i_L/i_L^0$ ) in the electrolyte obtained from the polarisation curves are presented in Tables 2, 3 and 4 at temperatures 25, 35 and 45°C, respectively for all the additives. It is apparent from the data in these tables that there is a decrease in  $i_{corr}$ ,  $i_L$  and  $i_L/i_L^0$  values with increase in the concentration of the additives at each temperature. The decrease in  $i_{corr}$  with the addition of the inhibitor and of the ratio of limiting current densities with and without the addition of the inhibitors ( $i_L/i_L^0$ ) may be explained on the basis of the adsorption of these molecules on electrode surface, thereby decreasing the surface area available for the anodic reaction. The displacement of  $E_{corr}$  in the presence of these inhibitors slightly in the positive direction is observed.

The cathodic polarisation curves of mild steel in the presence of different concentration of additive VI at 25°C are shown in Fig. 4. It is evident from the figure that on increasing the concentration of the additive cathodic polarisation curve shifts towards the lower current density region. The observed trend for other additives at all concentration and temperature is similar. Further, at a fixed concentration of 250 ppm, for different additives the relative downward shift is again in accordance to their inhibition efficiency as shown in Fig. 5. This indicates that all the additives are able to prevent the cathodic process along with the anodic process.

Thus, from the above discussion it may be concluded that adsorption phenomenon is mainly responsible for the inhibition caused by these molecules. Assuming that the area covered by the inhibitor is directly related to the reduction in the corrosion rate, the inhibition process should follow

Table 2 : Corrosion parameters from anodic polarisation curves of mild steel in 20% formic acid containing different concentrations of additives, at 25°C.

Inhibitors and concentration (ppm)	$i_{corr}$ ( $\mu A/cm^2$ )	$i_{corr}/i_{corr}^0$	$E_{corr}$ (mV)	$i_L$ ( $mA/cm^2$ )	$i_L/i_L^0$
Blank	288.40	-	-520	56.23	-
<b>Thiourea</b>					
50	158.49	0.55	-515	52.48	0.93
100	131.83	0.46	-510	50.12	0.89
150	112.20	0.39	-510	45.71	0.81
200	100.00	0.35	-505	43.65	0.78
250	89.13	0.31	-505	41.69	0.74
<b>2-amino [4-p-chlorophenyl] thiazole</b>					
50	125.89	0.44	-518	45.71	0.81
100	112.20	0.39	-515	43.65	0.78
150	104.71	0.36	-510	39.81	0.71
200	95.50	0.33	-508	38.02	0.68
250	83.18	0.29	-508	36.31	0.65
<b>N-2 [4-p-chlorophenyl] 2-thiazolyl] thiocarbamide</b>					
50	109.65	0.38	-510	39.81	0.71
100	79.43	0.28	-512	38.02	0.68
150	70.79	0.25	-508	34.64	0.62
200	63.10	0.22	-505	31.62	0.56
250	57.54	0.20	-505	30.20	0.54
<b>N-2 [4-p-chlorophenyl] 5-phenyl azothiazolyl] thiocarbamide</b>					
50	89.13	0.31	-512	34.64	0.62
100	63.10	0.22	-510	33.11	0.59
150	50.12	0.17	-508	30.20	0.54
200	45.71	0.16	-504	26.30	0.47
250	39.81	0.14	-504	25.12	0.45
<b>N-2 [4-p-chlorophenyl] 5-o-methyl phenyl azothiazolyl] thiocarbamide</b>					
50	75.86	0.26	-510	31.62	0.56
100	47.86	0.17	-508	28.84	0.51
150	39.81	0.14	-508	25.12	0.45
200	30.20	0.10	-505	21.88	0.39
250	27.54	0.10	-502	19.95	0.35
<b>N-2 [4-p-chlorophenyl] 5-o-methoxy phenyl azothiazolyl] thiocarbamide</b>					
50	63.10	0.22	-508	27.54	0.49
100	38.02	0.13	-505	25.12	0.45
150	27.54	0.10	-504	22.91	0.41
200	25.12	0.09	-500	19.05	0.34
250	22.91	0.08	-505	17.38	0.31

Table 3 : Corrosion parameters from anodic polarisation curves of mild steel in 20% formic acid containing different concentrations of additives, at 35°C.

Inhibitors and concentration (ppm)	$i_{Corr}$ ( $\mu A/cm^2$ )	$i_{Corr}/i_{Corr}^0$	$E_{Corr}$ (mV)	$i_L$ ( $mA/cm^2$ )	$i_L/i_L^0$
Blank	512.86	-	-520	79.43	-
<b>Thiourea</b>					
50	251.19	0.49	-512	54.95	0.69
100	199.53	0.39	-508	50.12	0.63
150	181.97	0.35	-505	47.86	0.60
200	173.78	0.34	-500	45.71	0.58
250	144.54	0.28	-490	43.65	0.55
<b>2-amino [4-p-chlorophenyl] thiazole</b>					
50	190.55	0.37	-510	52.48	0.66
100	173.78	0.34	-510	47.86	0.60
150	151.36	0.30	-506	45.71	0.58
200	141.25	0.28	-505	41.69	0.52
250	131.83	0.26	-500	39.81	0.50
<b>N-2 [4-p-chlorophenyl] 2-thiazolyl] thiocarbamide</b>					
50	151.36	0.30	-505	45.71	0.58
100	112.20	0.22	-500	41.69	0.52
150	89.13	0.17	-498	39.81	0.50
200	79.43	0.15	-495	36.31	0.46
250	70.79	0.14	-492	34.64	0.44
<b>N-2 [4-p-chlorophenyl] 5-phenyl azothiazolyl] thiocarbamide</b>					
50	141.25	0.28	-508	39.81	0.50
100	87.10	0.17	-500	38.02	0.48
150	75.86	0.15	-495	34.64	0.44
200	66.07	0.13	-492	33.11	0.42
250	60.26	0.12	-495	31.62	0.40
<b>N-2 [4-p-chlorophenyl] 5-o-methyl phenyl azothiazolyl] thiocarbamide</b>					
50	112.20	0.22	-505	38.02	0.48
100	66.07	0.13	-508	36.31	0.46
150	56.23	0.11	-500	33.11	0.42
200	50.12	0.10	-495	30.20	0.38
250	45.71	0.09	-490	28.84	0.36
<b>N-2 [4-p-chlorophenyl] 5-o-methoxy phenyl azothiazolyl] thiocarbamide</b>					
50	95.50	0.17	-500	36.31	0.46
100	60.26	0.12	-505	33.11	0.42
150	43.65	0.09	-500	30.20	0.38
200	38.02	0.07	-490	28.18	0.35
250	33.11	0.06	-485	26.30	0.33

Table 4 : Corrosion parameters from anodic polarisation curves of mild steel in 20% formic acid containing different concentrations of additives, at 45°C.

Inhibitors and concentration (ppm)	$i_{Corr}$ ( $\mu A/cm^2$ )	$i_{Corr}/i_{Corr}^0$	$E_{Corr}$ (mV)	$i_L$ ( $mA/cm^2$ )	$i_L/i_L^0$
Blank	870.96	-	-535	100.00	-
<b>Thiourea</b>					
50	398.11	0.46	-530	70.79	0.71
100	316.23	0.36	-520	63.09	0.63
150	288.40	0.33	-525	56.23	0.56
200	263.03	0.30	-518	50.12	0.50
250	239.88	0.28	-520	47.86	0.48
<b>2-amino [4-p-chlorophenyl] thiazole</b>					
50	302.00	0.35	-530	63.09	0.63
100	263.03	0.30	-525	57.54	0.58
150	223.87	0.26	-520	52.48	0.52
200	208.93	0.24	-525	47.86	0.48
250	199.53	0.23	-515	44.67	0.45
<b>N-2 [4-p-chlorophenyl] 2-thiazolyl] thiocarbamide</b>					
50	251.19	0.29	-525	54.95	0.55
100	173.78	0.20	-518	50.12	0.50
150	141.25	0.16	-510	45.71	0.46
200	112.20	0.13	-508	41.69	0.42
250	100.00	0.11	-508	39.81	0.40
<b>N-2 [4-p-chlorophenyl] 5-phenyl azothiazolyl] thiocarbamide</b>					
50	208.93	0.24	-520	52.48	0.52
100	125.89	0.14	-518	47.86	0.48
150	100.00	0.11	-525	43.65	0.44
200	95.50	0.11	-515	38.02	0.38
250	79.43	0.09	-510	36.31	0.36
<b>N-2 [4-p-chlorophenyl] 5-o-methyl phenyl azothiazolyl] thiocarbamide</b>					
50	173.78	0.20	-515	47.86	0.48
100	95.50	0.11	-510	43.65	0.44
150	75.86	0.09	-508	39.81	0.40
200	70.79	0.08	-505	36.31	0.36
250	63.10	0.07	-505	33.11	0.33
<b>N-2 [4-p-chlorophenyl] 5-o-methoxy phenyl azothiazolyl] thiocarbamide</b>					
50	151.36	0.17	-508	39.81	0.40
100	79.43	0.09	-505	38.02	0.38
150	63.10	0.07	-500	34.64	0.35
200	56.23	0.06	-495	31.62	0.32
250	47.86	0.05	-490	30.20	0.30

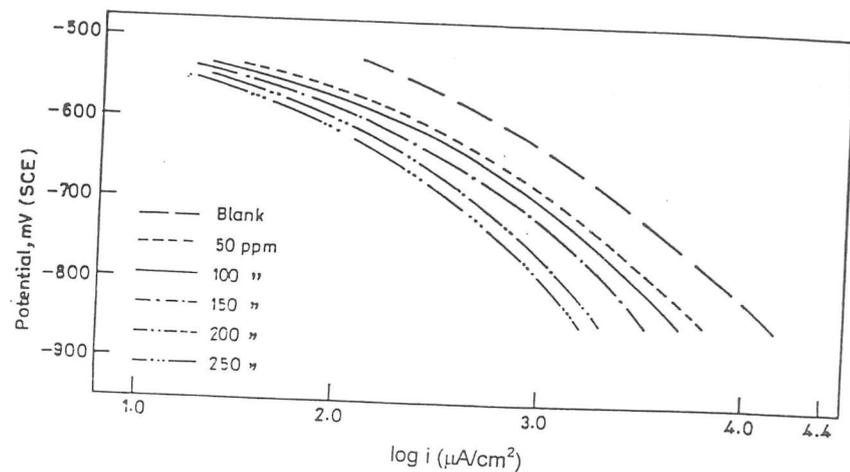


Fig. 4: Cathodic polarisation curves for different concentrations of additive - VI at 25°C

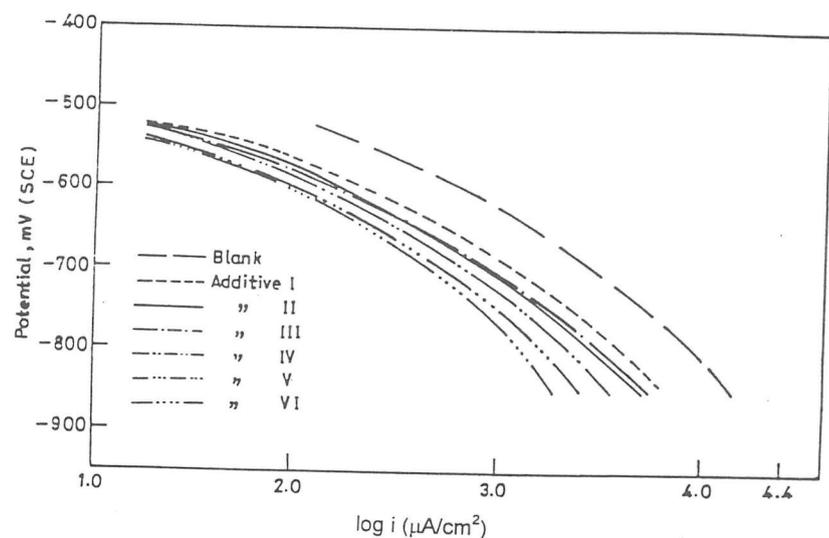


Fig. 5: Cathodic polarisation curves of mild steel in the presence of different additives at 25°C

either the isotherm of Langmuir or those of Temkin or Frumkin. The experimental equation of Frumkin's isotherm (15,16) is

$$\theta / (1 - \theta) \exp(f\theta) = KC$$

where, 'K' is the equilibrium constant for the adsorption reaction, 'C' is the concentration of the inhibitor in mole litre<sup>-1</sup>, 'θ' is the degree of coverage and 'f' is parameter connected with the variation of adsorption energy with coverage. For f=0, the Langmuir's isotherm is obtained and its validity is confirmed from the linearity of the log θ/(1-θ) vs log C plot. Temkin's isotherm results from the value of f > 0 and hence, there should exist a linear dependence of θ upon log C (17).

Langmuir and Temkin's plots are shown in Fig. 6 and 7. For calculation of θ values, the inhibition efficiency obtained from electrochemical technique has been used. However, some deviation from linearity is expected in certain cases beyond 200 ppm if θ is calculated from the weight loss data. In both cases, all investigated compounds give a straight line, at 25°C. Thus, the adsorption of these inhibitors obey Langmuir as well as Temkin's adsorption isotherm.

The heat of adsorption was calculated, from the plots of log θ / (1-θ) vs, 1/T, for all the inhibitors at 100 ppm as shown in Fig. 8. The values of heat of adsorption thus obtained are -1.84, -3.68, -4.60, -5.52, -4.14 and -4.14 Kcal/mole for inhibitions I to VI, respectively. It appears from these values that inhibitor IV is most strongly adsorbed followed by inhibitor - III, inhibitors - V and VI, inhibitor - II and lastly inhibitor - I. The above sequence is not exactly similar to that obtained for their inhibition efficiency. Probably the size of the inhibitors also plays an important role along with the heat of adsorption in determining their inhibition efficiency. The inhibition efficiency increases regularly with the increase in the size from inhibitor - I to VI.

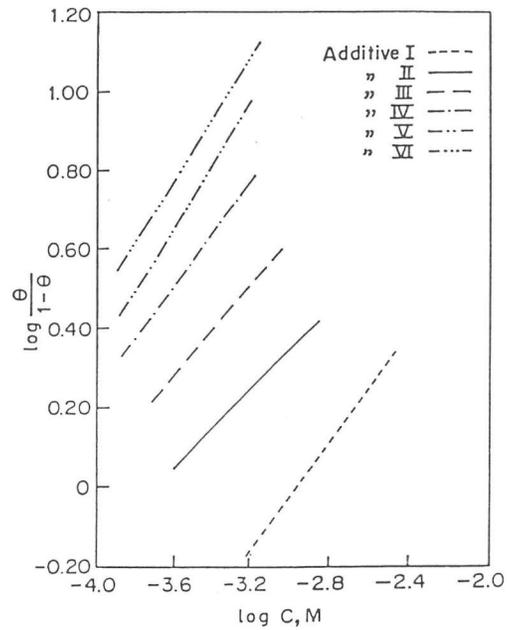


Fig. 6 : Langmuir plots for the additives at 25<sup>0</sup>C

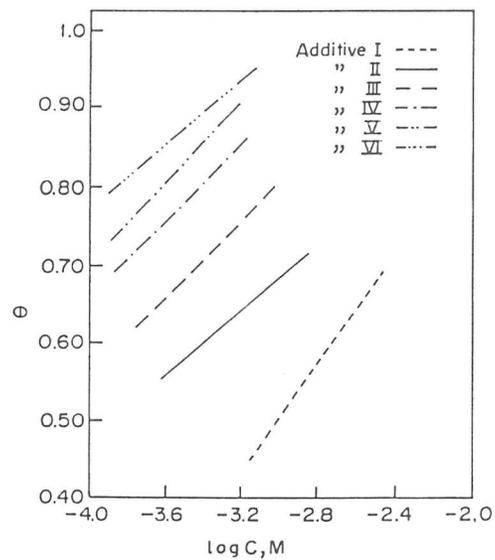


Fig. 7 : Relation between surface coverage  $\theta$  and  $\log C$  for mild steel in 20% HCOOH, at 25<sup>0</sup>C.

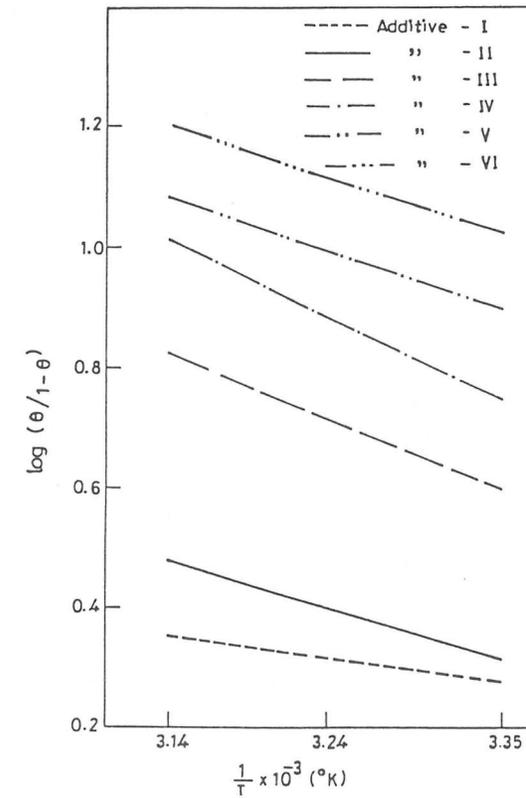


Fig. 8 : Calculation of heat of adsorption.

Fig. 9 and 10 show the optical microphotographs for mild steel in 20% formic acid solution in the absence and presence of 200 ppm of additive VI. at 1000 x magnification. On comparing these microphotographs, it appears that in the presence of N-2[4-p-chlorophenyl] 5-o-methoxy phenyl azothiazolyl] thiocarbamide some change in the surface morphology due to the presence of the adsorbed layer of inhibitor molecules are observed.

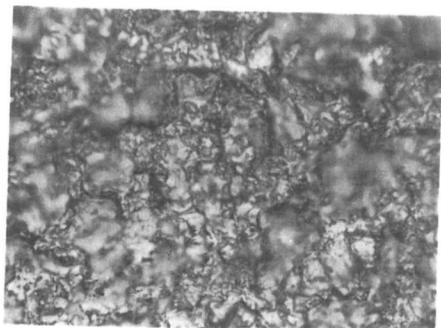


Fig. 9 : Mild steel in 20% formic acid solution (1000x)

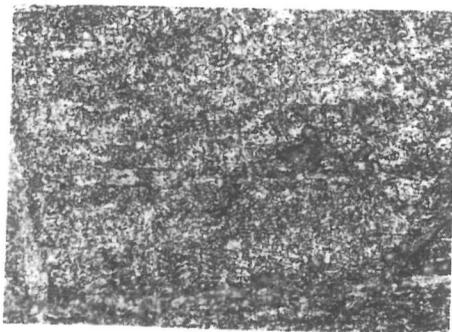


Fig. 10 : Mild steel in the presence of Additive VI (1000 x)

### CONCLUSIONS

1. All the inhibitors tested are found to be effective for the corrosion of mild steel in 20% formic acid.
2. The inhibition efficiency of each tested inhibitor were found to be dependent on the inhibitor concentration and experimental temperature.

3. The order of the inhibition efficiency of the inhibitors may be represented as :

N-2 [4-p-chlorophenyl] 5-o-methoxy phenyl azothiazolyl] thiocarbamide > N-2 [4-p-chlorophenyl] 5-o-methyl phenyl azothiazolyl] thiocarbamide > N-2 [4-p-chlorophenyl] 5-phenyl azothiazolyl] thiocarbamide > N-2 [4-p-chlorophenyl] 2-thiazolyl] thiocarbamide > 2-amino [4-p-chlorophenyl] thiazole > thiourea

4. The adsorption of these molecules on the corroding surface could explain the observed inhibition efficiencies.
5. All the inhibitors were found to obey Langmuir, Temkin and Frumkin's adsorption isotherm in the whole range of concentration.

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