2-MercaptoBenzoThiazole and 2-Amino-5-Mercapto-1,3,4-ThiaDiazole as Corrosion Inhibitors for 304 Stainless Steel

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2-Mercaptobenzothiazole and 2-amino-5-mercapto-1,3,4-thiadiazole have been shown to control the corrosion of 304 stainless steel in 1.0M sulphuric acid solution by using weight loss, polarization resistance, scanning electron microscopy and Auger electron spectroscopy techniques. Inhibition efficiency increases with the increase in concentration and decreases with the rise in temperature (from 20 to 40°C). Various corrosion parameters like Tafel slopes, corrosion rate, heat of adsorption and activation energy have been calculated. 2-Mercaptobenzothiazole is chemisorbed on the surface of 304 stainless steel whereas 2-amino-5-mercapto-1,3,4-thiadiazole is physically absorbed. Both the investigated compounds are cathodic inhibitors.

A highly corrosion resistant passive film is formed on the surface of 304 stainless steel due to atmospheric oxidation of chromium present in the alloy. This passive film mainly consists of chromium-oxyhydroxide. Therefore 304 stainless steel is widely used for various applications. However, it suffers from corrosion when it is exposed to aggressive environment like sulphuric acid solution. Therefore, it is very important to control its corrosion in such media by employing some feasible technique. Many organic compounds have been used as corrosion inhibitors for protecting metals from corrosion [1-6]. Nitrogen and sulphur containing organic compounds have proved to be good inhibitors for controlling the corrosion of different kinds of steel in various corrosive environments [7-11].

The present investigation is concerned with the study of 2-mercaptobenzothiazole (MBT) and 2-amino-5-mercapto-1,3,4-thiadiazole (AMTD) as corrosion inhibitors of 304 stainless steel in 1.0M sulphuric acid solution. Investigations have been carried out using weight loss and electrochemical polarization techniques with 100, 200 and 400 ppm concentration of the inhibitors at 20, 30 and 40°C. Scanning electron micrographs of 304 stainless steel surface have been taken in presence and absence of the inhibitors to get some information about the film present on the surface. Auger electron spectroscopy is used to investigate the adsorption of inhibitors on 304 stainless steel surface.

EXPERIMENTAL

All the chemicals used were of AR grade and the solutions were prepared using double distilled water. 304 Stainless steel sheets (composition C = 0.045, Mn = 1.47, S = 0.008, P = 0.060, Si = 0.37, Ni = 7.98, Cr = 17.04 and Fe balance) were supplied by Swastic (India) Foils Pvt. Ltd. Rectangular specimens of size 2x4 cm were

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used for weight loss experiments. For electrochemical studies, the specimens had a working area of 1x1 cm with a 4 cm long stem to make electrical contact. All specimens were polished successively with 1/0, 2/0, 3/0 and 4/0 grades of emery papers and were then thoroughly cleaned with water and acetone. The weight loss experiments were carried out in 100, 200 and 400 ppm of MBT and AMTD in 0.1M sulphuric acid solution at 20, 30 and 40°C. The electrochemical studies were performed using a potentiostat / galvanostat (Model CL 95, Elico Make). The surface morphology was studied by scanning electron microscope (Model JSM-840, JEOL Make). Auger electron spectroscopy (AES) analysis were carried out using scanning Auger microprobe (SAM) (PHI Model 590A, U.S.A.). For studying their surface characteristics, the specimens were exposed to 1.0M sulphuric acid solution for 12 hours before recording AES spectra. The results of analysis were plotted on the graph in dN/dE *vs* electron energy showing the various elemental peaks.

RESULTS AND DISCUSSION

Weight loss Method

Table 1 shows the percentage inhibition efficiency of the two inhibitors obtained by weight loss method at different temperatures. Both the inhibitors are effective in controlling the corrosion of 304 stainless steel in 1.0M sulphuric acid solution but MBT is more effective than AMTD. Inhibition efficiency increases with the increase in temperature from 20 to 40°C.

Table 1

Corrosion rate in MPY (Corr) and Inhibition Efficiency (IE%) Data by Weight Loss & Polarization Methods

Specimen 304 SS; Medium 1.0 M Sulphuric acid without and with Inhibitors

Inhibitor	Wt. loss Method						Pol.Resist.Method		
Conc	20°		30°		40°		20°	30°	40°
(ppm)	Corr	IE%	Corr	IE%	Corr	IE%	IE	IE	IE
nil	179.9	(-)	325.4	(-)	440.1	(-)	-	-	-
Inhibitor	**MBT**								
100	11.3	(93.7)	53.2	(83.6)	127.0	(71.1)	89.7	80.4	68.1
200	5.6	(96.8)	35.4	(89.1)	114.1	(74.0)	93.1	85.0	71.9
400	5.3	(97.0)	21.3	(93.4)	84.3	(80.8)	96.4	89.6	77.7
Inhibitor	**AMTD**								
100	50.4	(71.9)	104.9	(67.7)	154.6	(64.8)	68.8	65.3	62.8
200	15.0	(91.6)	54.9	(83.1)	100.2	(77.2)	87.3	82.5	80.2
400	9.2	(94.8)	37.3	(88.5)	67.0	(84.7)	91.3	86.8	83.5

In case of AMTD there is an appreciable increase in inhibition efficiency as the inhibitor concentration is increased from 100 to 200 ppm and after that only a slight increase is observed when the concentration is further raised to 400 ppm.

Polarisation Resistance Method

Corrosion current density (I_{corr}) values were calculated from the linear polarization resistance data using Stern-Geary equation. Corrosion rates and percentage inhibition efficiency calculated from these are summarised in Table 1. Results of weight loss method and electrochemical polarization techniques are almost the same. Slight difference in the percentage inhibition efficiency values may be attributed to the two specimens not having strictly identical surfaces.

Anodic and cathodic Tafel slope values are recorded in Table 2. Cathodic Tafel slope values in presence of the inhibitor are slightly higher. Anodic Tafel slope values in presence of AMTD are slightly higher while with MBT these values are quite high. Damaskin [12] has pointed out that these changes in slope in presence of inhibitors may be attributed to

(i) Increased adsorption of organic substance,
(ii) A change in the mechanism of the process,
(iii) Formation of oxides on the metal surface in presence of oxidising inhibitor and
(iv) Gradual formation of compounds which are more effective inhibitors than the compounds initially adsorbed.

Increase of anodic Tafel slope values in case of MBT may be due to the adsoprtion of MBT through its delocalized electrons or formation of Fe-OH-MBT complex on the metal surface.

Table 2

Variation of OCP (in mV) and Tafel slopes (b_a & b_c in mV/decade)

Specimen 304 SS; Medium 1.0 M Sulphuric acid without and with Inhibitors

conc		20°			30°			40°	
(ppm)	OCP	b_a	b_c	OCP	b_a	b_c	OCP	b_a	b_c
nil	-460	65	65	-445	75	65	-435	75	60
Inhibitor	**MBT**								
100	-437	220	85	-419	220	80	-431	210	70
200	-432	225	85	-416	225	85	-425	230	60
400	-426	225	90	-430	230	86	-430	230	70
Inhibitor	**AMTD**								
100	-424	85	75	-430	95	75	-430	95	70
200	-409	85	70	-421	90	75	-430	80	70
400	-390	95	65	-408	90	70	-422	85	75

Open circuit potential (OCP) value in absence and presence of the inhibitors are also recorded in Table 2. OCP shifted towards less negative values in presence of MBT and AMTD and in both cases the shift is more with increase in the concentration. When the temperature is increased from 20 to 30°C OCP value shifts towards positive direction in presence of MBT but in the negative direction in case of AMTD. On further increasing the temperature to 40°C OCP value shifts in negative direction in presence of MBT as well as AMTD. The OCP becomes almost constant after about 30 minutes. Since the OCP shift is little, it is difficult to draw any clear conclusion about the nature of the inhibitors but considering the shift in OCP with the addition of inhibitors, it seems that the inhibitors are of mixed type.

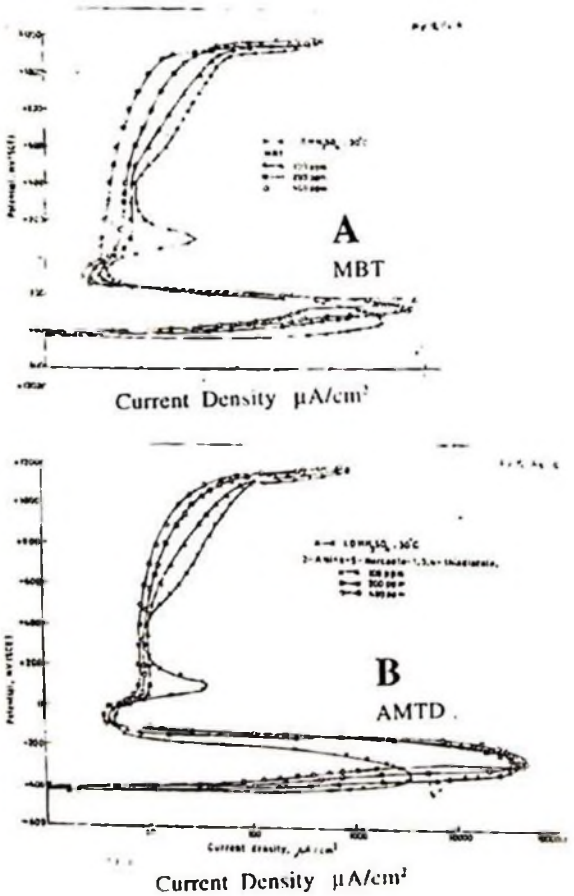


Fig.1 Anodic polarization curves of 304 stainless steel in 1.0M sulphuric acid solution
Current density 0-10³ μa/cm²\ Potential - 600 to + 1200 mV
Inhibitor 0.100.200 & 400 ppm
A In presence and absence of MBT.
B In presence and absence of AMTD

Anodic polarization curves for 304 stainless steel in 1.0M sulphuric acid solution in absence and presence of MBT and AMTD have been shown in Figs. 1A and B. It is evident from these that critical current density values in presence of the inhibitors are higher than in their absence and it increases with the increase in concentration of MBT and AMTD from 100 to 400 ppm. Such a behaviour has also been reported by Trabanelli and co-workers [13] in case of sulphur containing organic compounds. This may be due to the fact that during anodic polarization, at lower anodic potentials in the active region, MBT and AMTD molecules form a soluble complex with Fe^{2+} thus decreasing the concentration of the ions in the immediate vicinity of the electrode. This leads to a higher critical current density to compensate for the decreased concentration of the ions so that the anodic passivation may occur. However, the passivation current density and breakdown potential values are lower in presence of both the inhibitors.

Figs.2A & 2B show the cathodic polarization curves plotted for 304 stainless steel in absence and presence of different concentration of MBT and AMTD in 1.0M sulphuric acid solution at 30°C. Cathodic polarization curves shifted considerably towards lower current density values in presence of both the investigated inhibitors. Thus complete anodic and cathodic polarization curves suggest that both MBT and AMTD reduce cathodic reaction only and act as cathodic inhibitors.

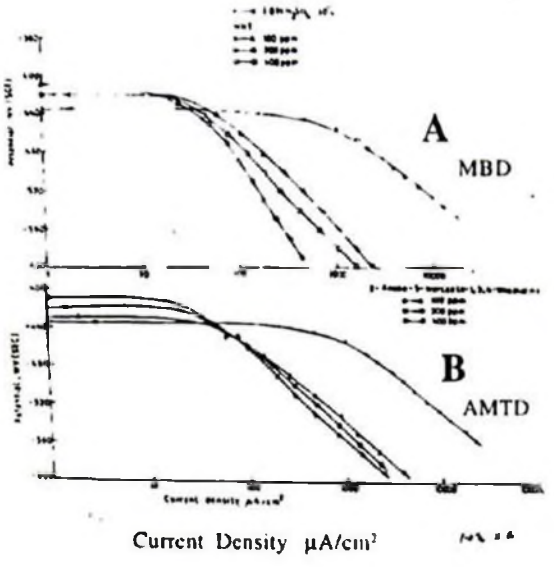


Fig.2 Cathodic polarization curves of 304 stainless steel in 1.0M sulphuric acid solution
Current density 0-10⁵ μa/cm²\ Potential - 600 to - 400 mV
Inhibitor 0,100,200 & 400 ppm
A in presence and absence of MBT
B in presence and absence of AMTD

Plots of log [θ/(1 - θ)] *vs* log C are linear for the adsorption of both MBT and AMTD on 304 stainless steel surface at all the three experimental temperatures. Thus the adsorption of MBT and AMTD obey Langmuir's adsorption isotherm.

Table 3 shows the values of heat of adsorption and activation energy for corrosion reactions. Heat of adsorption increases with the increase in concentration of the inhibitors from 100 to 400 ppm. The values of heat of adsorption suggest that MBT is chemisorbed on the surface of 304 stainless steel. Lower values of heat of adsorption for AMTD show that adsorption of AMTD is physical in nature.

Table 3

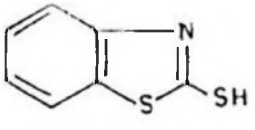
Heat of Adsorption (ΔH in k.cal) and Activation Energy (E in k.cal) Values

Specimen 304 SS:
Medium 1.0 M H_2SO_4 without and with Inhibitors

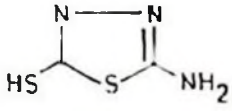
Conc	MBT		AMTD	
(ppm)	-ΔH	E	-ΔH	E
0	-	8.3	-	8.3
100	12.5	18.6	2.4	9.8
200	14.8	20.8	4.5	12.4
400	17.5	25.1	6.5	14.3

The activation energy for the inhibited systems are higher than that of uninhibited system and it increases with increase in concentration of both MBT and AMTD. Both the inhibitors give good efficiency at lower than at higher temperature. This suggests that MBT and AMTD belong to first category of inhibitors according to the classification by Putilova [1].

Molecular structures of MBT and AMTD are given below:

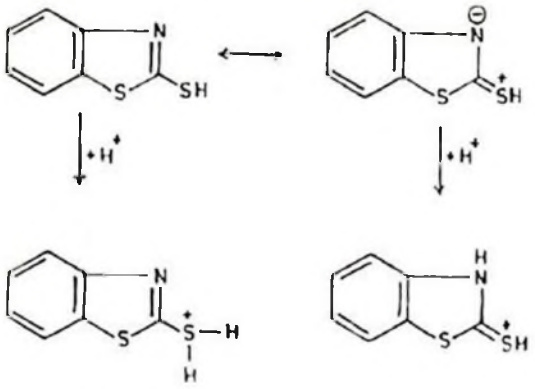


MBT



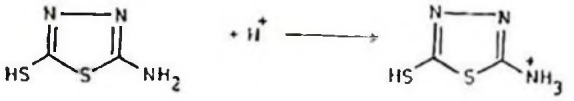
AMTD

The sulphur in the ring of MBT will not be protonated because its lone pair electron is delocalized with π-electrons of benzene ring. But exocyclic sulphur can be protonated. MBT can exist in two resonance forms; exocyclic sulphur of both forms can be protonated in acidic medium due to high electron density available at nitrogen in the ring and exocyclic sulphur.



This suggests that the adsorption of MBT on steel surface would occur through exocyclic sulphur of the molecule which would result in the formation of a strong bond with the metal atoms. This fact have also been confirmed by the high heat of adsorption values in the presence of MBT.

In sulphuric acid solution -NH_2 group of AMTD is quaternised and acquires a positive charge.



The nitrogen of -NH_2 group will become an active centre for the adsorption of the inhibitor molecule on 304 stainless steel surface. Stimulation of the anodic dissolution process at anodic potentials in the active region is perhaps due to the formation of a complex of the inhibitor molecule with iron and/or chromium in the steel which is highly soluble in the acidic environment.

Figs. 3A, B and C show the scanning electron micrographs of 304 stainless steel in 1.0M sulphuric acid solution in absence and presence of 200 ppm of MBT and AMTD

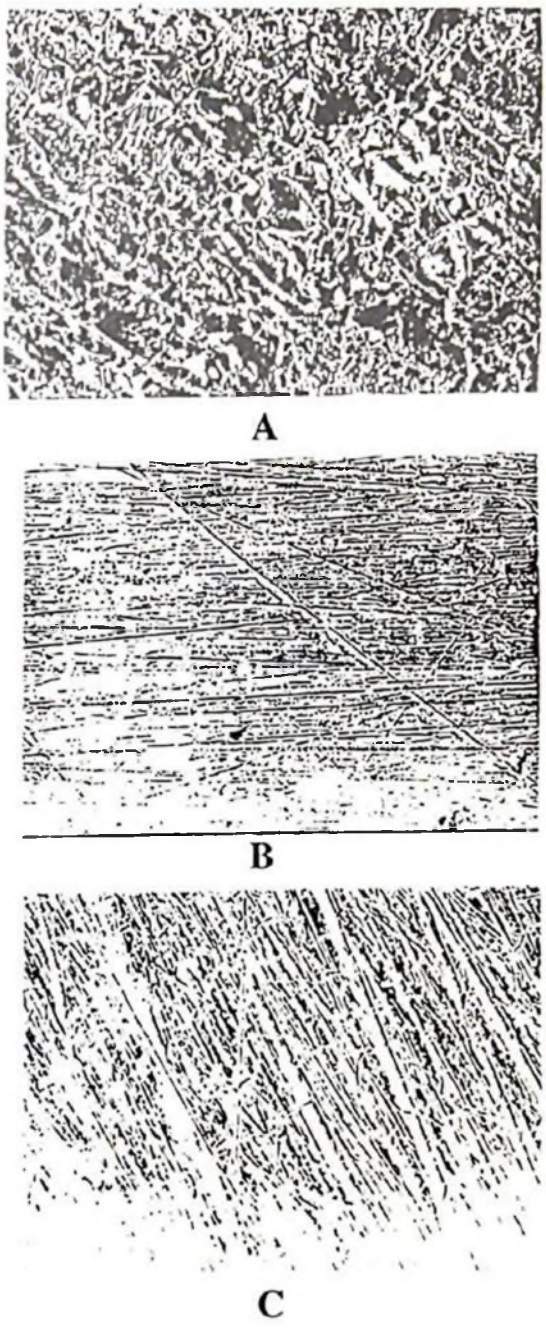


Fig.3 SEM micrograph (X800) of 304 stainless steel surface exposed for 12 hours to 1.0M sulphuric acid solution containing

(A) no inhibitor
(B) in presence of 200 ppm of MBT
(C) in presence of 200 ppm of AMTD.

respectivley. Micrograph in Fig.3a shows that the surface of 304 stainless steel is corroded heavily in 1.0M sulphuric acid solution. The condition of the surface is much better when 200 ppm of MBT or AMTD was added to the solution (Figs 3 b & c). Improved surface conditions confirm that MBT and AMTD provided a good corrosion resistance to 304 stainless steel surface.

Figs. 4A, B and C show the AES spectra of 304 stainless steel exposed to 1.0M sulphuric acid solution in absence and presence of the investigated inhibitors. It is clear from spectra in Fig. 4b that more intense sulphur and nitrogen peaks at 153 eV and 383 eV respectively are obtained alongwith the peaks of elements like O, Cr, Fe and C (Fig. 4a) in the presence of 200 ppm of MBT. Higher intensity of sulphur and nitrogen peaks suggests that MBT molecules are strongly adsorbed on the surface of 304 stainless steel. In presence of 200 ppm of AMTD, a small peak of nitrogen is also observed alongwith all other peaks obtained in the absence of the inhibitors. Presence of nitrogen on the surface of 304 stainless steel suggests that inhibitor molecules are present on the surface of 304 stainless steel even though the inhibitor has been found to be adsorbed physically on the surface of 304 stainless steel.

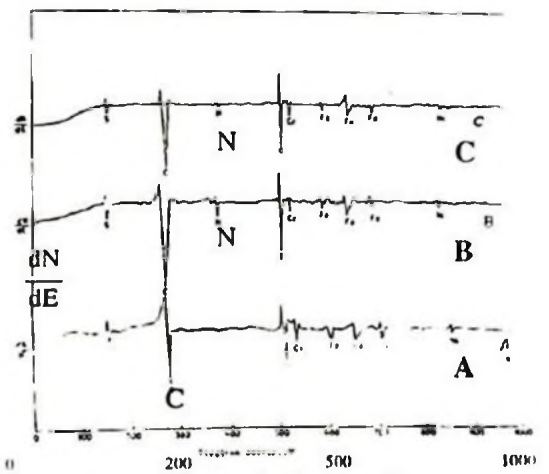


Fig.4 AES spectra of 304 stainless steel exposed to 1.0M sulphuric acid solution for 12 hours

(a) no inhibitor
(b) in presence of 200 ppm of MBT
(c) in presence of 200 ppm of AMTD.

CONCLUSIONS

1. Inhibitors efficiency increases with the increase in concentrtion of both the investigated inhibitors and decrease with the increase in temperature from 20 to 40°C.

2. Critical current density increases in presence of both the inhibitors.

3. Both the compounds investigated are cathodic inhibitors. Both the inhibitors are effective but MBT is more effective than AMTD.

4. Adsorption of MBT and AMTD on the surface of 304 stainless steel obey Langmuir adsorption isotherm equation. MBT is chemisorbed on the surface of 304 stainless steel whereas AMTD is physically adsorbed.

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