

Effect of Organic Inhibitor on Corrosion
of Mild Steel in Hydrochloric Acid

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The inhibition effect of thiourea, hexamethylenetetramine and N-N'-dicyclohexylthiourea on mild steel corrosion in hydrochloric acid solutions has been examined by means of a hydrogen-evolution measurement and the surface observation of corroded specimens. The evolution-rate of hydrogen by the steel was kept constant in the acid solution with thiourea. In contrast, the evolution-rate reduced with time in the acid solution with the other inhibitors. The inhibitor concentration at which the inhibitor efficiency was over 90% was 500ppm for thiourea and only 50ppm for the other inhibitors. The surface of corroded specimens was much smoother in the acid solution with hexamethylenetetramine than in the acid solution with thiourea, regardless of the corrosion-rate. Thus, hexamethylenetetramine has been found as an excellent inhibitor for the corrosion of mild steel in hydrochloric acid solution.

1. Introduction

Hydrochloric acid has been widely used in pickling and in descaling for various industrial equipments because of its strong dissolving action. At the same time, organic inhibitors have been developed and used to minimize the acid attack on the metal during the operation which caused undesirable results such as the excessive consumption of acid, destructing valuable metal and enlarging surface roughness of the metal (1, 2). Therefore, it is important and significant to make clear the action and the function of inhibitors that have been used and what will be utilized in acid cleaning processes.

In the present work, the corrosion behavior of mild steel was

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examined in hydrochloric acid solutions with thiourea, hexamethylenetetramine or N, N'-dicyclohexylthiourea through hydrogen-evolution measurements. Then, the inhibition effect of the inhibitors was discussed on the basis of the data on corrosion-rate, inhibitor efficiency and surface roughness of corroded specimens.

2. Experimental

A mild steel was used as the test material in this experiment. Table 1 shows the percentage of carbon and of elements other than iron present in the steel. Test pieces were 32mm width, 42mm length and 4mm thick, and being polished with 600 grade emery paper.

Table 1 Elemental analysis(%) of test material

C	Si	Mn	P	S
0.13	0.0026	0.44	0.012	0.026

As test solutions, 500ml of 1.0, 2.5 and 5.0 v/o HCl solution was used with or without inhibitors. Thiourea, hexamethylenetetramine and N, N'-dicyclohexylthiourea were used as a inhibitor, respectively. The former two were added in the acid solution after dissolving them in the same solution, while the last one was added as its methyl alcohol solution because of the poor solubility in water and acid solutions. The inhibitor concentrations were varied in the range of 5 to 500ppm in the test solutions.

Corrosion tests for the steel were carried out using the apparatus shown in phot. 1. That is, the test piece was immersed in the acid solution and then the hydrogen liberated by the piece was collected on the solution in the burette, and being measured its volume at every five or ten minutes for one hour. The test solutions were exposed in air. The temperature of test solutions and air were kept at 20 ± 1 °C throughout experiments. After testing, the test pieces were rinsed in distilled water using a supersonic cleaner for five minutes and then dried. The surface profiles of corroded specimens were observed using a Jalysurf 10 surface profilemeter.

3. Results and discussion

The data on the hydrogen-evolution by the steel was summarized in Figs. 1, 2 and 3. The volume of hydrogen in these figures was expressed as the volume at S T P, V_{STP} , which was converted from

the volume of hydrogen observed, V_{obs} by the following equation,

$$V_{\text{STP}} = \frac{P_{\text{obs}} - P_{\text{L}}}{760} \times \frac{273}{293} \times V_{\text{obs}}$$

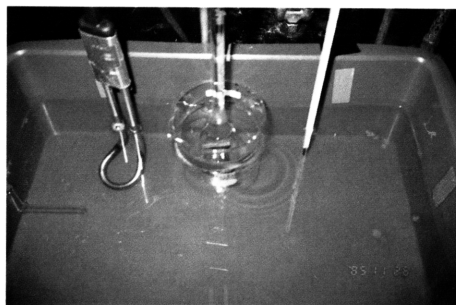
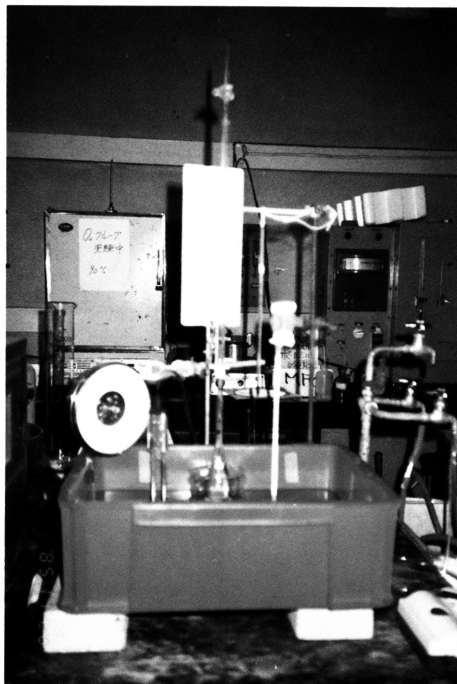
where, P_{obs} is the barometric pressure observed and P_{L} is the vapour pressure of water at 293 K, i.e., 17.5mmHg.

Fig. 1 shows the effect of hydrochloric acid concentrations and also that of thiourea on the hydrogen-evolution by the steel. The volume of hydrogen liberated increased linearly with time regardless of the concentrations of acid and thiourea.

The evolution-rate of hydrogen increased in proportion to the concentration of acid. While, in 5% HCl solutions with thiourea, the evolution-rate of hydrogen reduced with increasing the concentration of thiourea except in the solution containing 5ppm of thiourea. Thus, the constancy of the evolution-rate of hydrogen,

i.e., the linear relationship between the volume of hydrogen liberated and time was clearly observed in all curves listed in Fig. 1, although the evolution-rate of hydrogen depended on the concentration of hydrochloric acid and thiourea.

Figs. 2 and 3 show the effect of hexamethylenetetramine and N, N'-dicyclohexylthiourea, respectively. In contrast to the attack by the acid solutions with thiourea, the evolution-rate of hydrogen, i.e., the corrosion rate of the steel reduced with time even in the lowest concentration of these inhibitors. Thus, the inhibition effect on the steel was found to be more pronounced with the above



phot. 1 Apparatus of hydrogen-evolution measurements

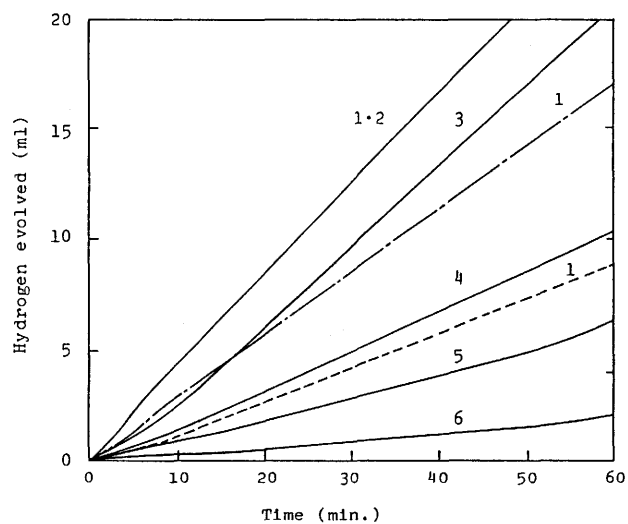


Fig.1 Effect of hydrochloric acid concentration and of thiourea on steel corrosion in 5v/o hydrochloric acid

HCl (v/o); 5.0; —, 2.5; ---, 1.0; ----

Inhibitor (ppm); 1;0, 2;5, 3;10, 4;50, 5;100, 6;500

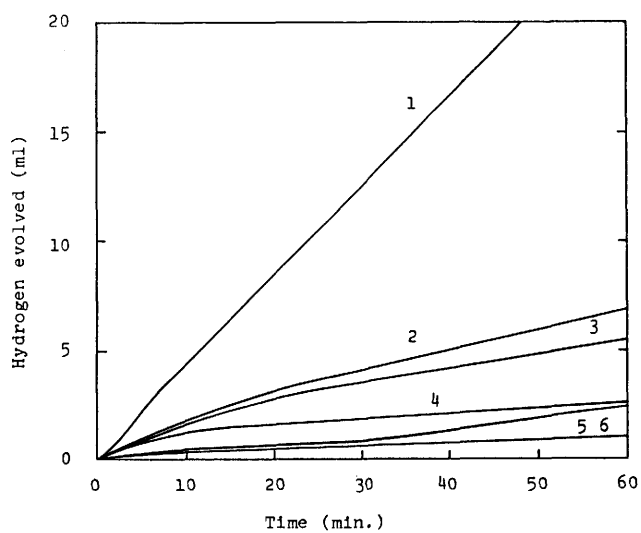


Fig.2 Effect of hexamethylenetetramine on steel corrosion in 5v/o hydrochloric acid

Inhibitor (ppm); 1;0, 2;5, 3;10, 4;50, 5;100, 6;500

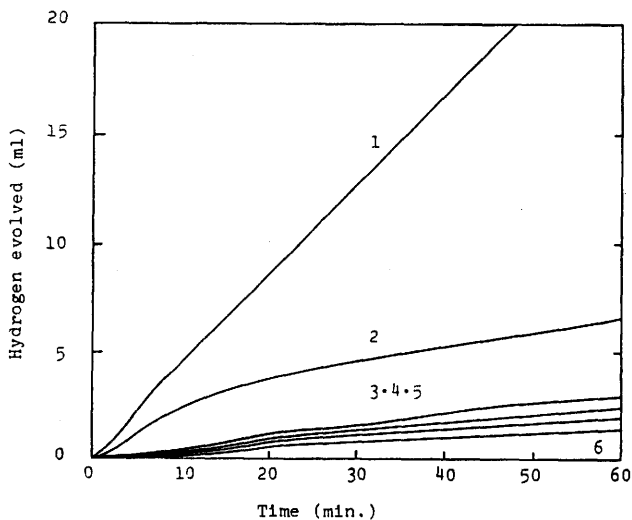
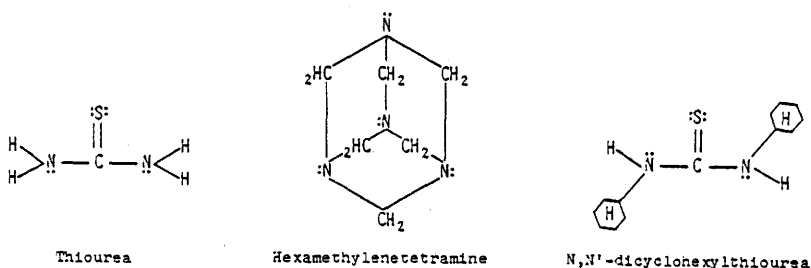


Fig.3 Effect of *N,N'*-dicyclohexylthiourea on steel corrosion in 5% hydrochloric acid
Inhibitor (ppm); 1;0, 2;5, 3;10, 4;50, 5;100, 6;500

two inhibitors than with thiourea. This will be closely related to the adsorption behavior of the inhibitors at the metal/solution interface. The chemical formulas of inhibitors used are as follows;



In general, most corrosion inhibitors of the adsorption film type, such as amines, have functional groups with N and / or S atom having lone electron pair in their molecules, which are able to adsorb on metal surfaces, and also hydrophobic groups in their structures. These inhibitors prevent corrosion by adsorbing on the clean metal surface with their functional groups, and retarding the diffusion of water to the metal surfaces with their hydrophobic groups (3).

The data on the hydrogen-evolution by the steel suggest that the adsorption layer on the steel surface was formed more tightly

and stably with hexamethylenetetramine and N, N'-dicyclohexylthiourea which have the both groups in their structures, than with thiourea.

Next, assuming that the reduction reaction of dissolved oxygen on the steel surface and the dissolution of hydrogen liberated into the acid solution were negligible (4), we converted the evolution-rate of hydrogen by the steel to the corrosion-rate of the steel on the basis of the following over-all reaction,

$$\text{Fe} + 2\text{H}^+ \longrightarrow \text{Fe}^{2+} + \text{H}_2$$
 That is, as 1ml of hydrogen liberated at STP was equivalent to 2.493mg of iron dissolved, the mean corrosion-rate over one hour of the steel ($\text{mg}/\text{dm}^2 \cdot \text{hr}$) was calculated.

Fig. 4 shows the relationship between the inhibitor concentration and the mean corrosion-rate of the steel. The corrosion-

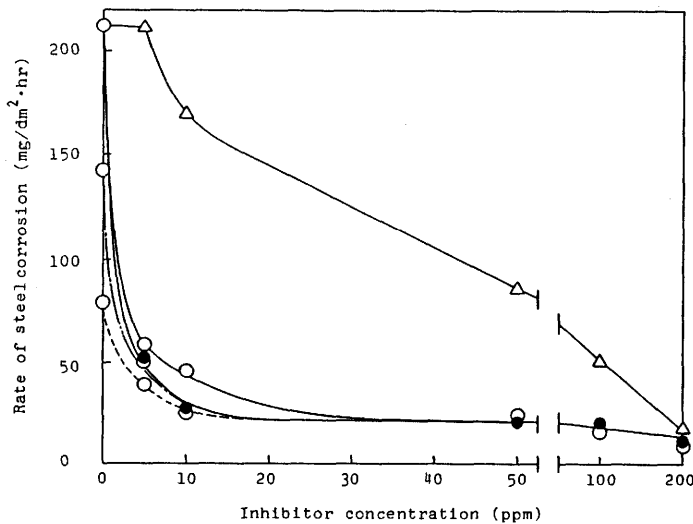


Fig. 4 Relation between inhibitor concentration and corrosion-rate on mild steel

HCl (v/o); 5.0; —, 2.5; ---, 1.0; - · - · -
 Δ; Thiourea, O; Hexamethylenetetramine
 ●; N,N'-dicyclohexylthiourea

rate was reduced effectively even in 5ppm of the inhibitors except thiourea. It is interesting to note that the corrosion-rate with hexamethylenetetramine was found to be independent on the hydrochloric acid concentrations in the range of 1.0~5.0 v/o HCl solution.

In Table 2 are listed the data on corrosion-rate, inhibitor efficiency and surface roughness of corroded specimens for thiourea and hexamethylenetetramine series in 5 v/o HCl solution. The inhibitor efficiency was calculated from the following equation,

Table 2 Mean corrosion-rates, inhibition efficiencies and surface roughness of test specimens obtained in 5v/o hydrochloric acid

	Inhibitor concentration (ppm)	Thiourea				Hexamethylenetetramine			
		Corr. rate (mg/dm ² ·hr)	Efficiency (%)	Ra (μm)	Rmax (μm)	Corr. rate (mg/dm ² ·hr)	Efficiency (%)	Ra (μm)	Rmax (μm)
1hr	0	212	0	0.27	2.8	212	0	0.27	2.8
	10	171	19	0.36	2.1	46	78	0.11	0.4
	50	87	59	0.24	1.7	22	90	0.11	0.4
	100	52	75	0.22	0.6	16	93	0.10	0.2
	500	17	92	0.21	0.8	9	96	0.08	0.2
5hrs	0	—	—	0.86	4.2	—	—	0.86	4.2
	500	—	—	0.61	3.0	—	—	0.17	0.7

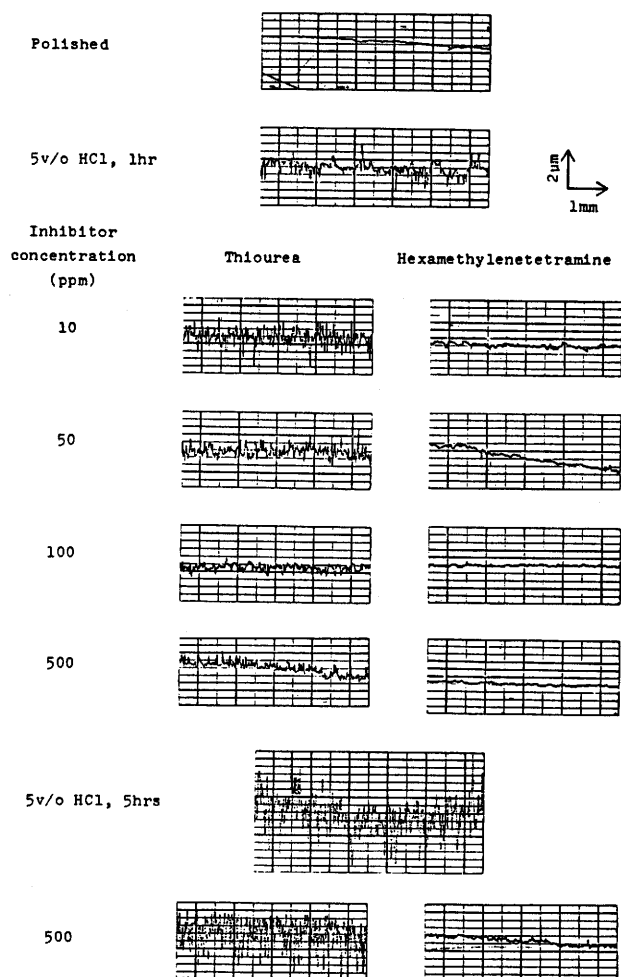


Fig.5 Surface profiles of corroded specimens

$$\text{Inhibitor efficiency(\%)} = \frac{R_o - R_i}{R_o} \times 100$$

, where R_o is the corrosion-rate in the absence of inhibitor and R_i is that in the presence of inhibitor. The average roughness, R_a , and the maximum roughness, R_{max} , were evaluated on the basis of the surface profiles of corroded specimens shown in Fig. 5. The inhibitor concentration at which the inhibitor efficiency was over 90% was 500ppm for thiourea, but only 50ppm for hexamethylenetetramine and also N, N'-dicyclohexylthiourea. These facts emphasize that the hydrophobic groups in the inhibitors played an important role to prevent the corrosion of steel in the acid solution.

The surface roughness of corroded specimens reduced with the increase of inhibitor concentrations, i.e., the decrease of corrosion-rates as can be clearly seen in Fig. 5. The R_a values were in $0.36 \sim 0.21 \mu\text{m}$ and the R_{max} being in $2.1 \sim 0.8 \mu\text{m}$ for the thiourea series. On the otherhand, the values of R_a and R_{max} were kept in $0.11 \sim 0.08 \mu\text{m}$ and in $0.4 \sim 0.2 \mu\text{m}$ for the hexamethylenetetramine series, respectively. The surface profiles of the specimens were much smoother for the latter series than for the former series, regardless of the corrosion-rates.

By lengthening the test time one to five hours, the surface roughness of the specimens enlarged remarkably with a similar mode in 5% HCl and the solution with 500ppm of thiourea. In market contrast to this, the surface roughness of the specimen with 500ppm of the other one remained smooth even in five hours testing.

The above results indicate that hexamethylenetetramine will act as an excellent inhibitor in pickling and descaling process with hydrochloric acid.

The authors will examine the inhibition mechanism of this compound using electrochemical polarization methods and surface observation techniques by ESCA in near future.

4. Conclusion

The effect of the three organic compounds on the corrosion of mild steel was examined in hydrochloric acid solutions through the hydrogen-evolution measurement and the surface observation for corroded specimens. The results are summarized as follows;

- 1) The evolution-rate of hydrogen was kept constant in the acid solution with thiourea as well as in 1.0~5.0% HCl solution. In contrast, the evolution-rate reduced with time in the solution with hexamethylenetetramine or N, N'-dicyclohexylthiourea.
- 2) The inhibitor concentration at which the inhibitor efficiency

was over 90% was 500ppm for thiourea and only 50ppm for the other inhibitors.

- 3) The surface of the corroded specimens was much smoother in the acid solution with hexamethylenetetramine than in the solution with thiourea, regardless of their corrosion-rate.

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