

A STUDY OF CORROSION INHIBITORS ON OIL WELL STEEL AND MILD STEEL IN BOILING HYDROCHLORIC ACID

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Two heterocyclic compounds namely QJ-1 and QJ-2 have been synthesized in the laboratory from indigenous chemicals and their corrosion inhibiting action has been evaluated by weight loss method and electrochemical technique in 15% hydrochloric acid under boiling condition. The performance of synthesized compounds was compared with propargyl alcohol, a commercially available acidizing inhibitor. Both QJ-1 QJ-2 showed better performance than that of PA for mild steel. In case of oil field steel QJ-2 was found to be as effective as PA.

Keywords: Heterocyclic compounds, inhibitors and mild steel

INTRODUCTION

Acidization of petroleum oil well is one of the important stimulation techniques for enhancing oil production. Hydrochloric acid (15-20%) solutions are commonly used for this purpose. Because of the extremely aggressive nature of the acid solution, the practice of inhibition is commonly used to reduce the aggressive attack of the acid on tubing and causing materials [1] during acidization.

A survey of literature reveals that only a few inhibitors that can withstand higher acid concentration and temperature are available.

The effective acidizing inhibitors which are usually found in commercial formulations are acetylenic alcohols [2-5] Alkenyl phenones [6] Aromatic Aldehydes [7,8]. Nitrogen containing heterocyclics and their quaternary salts [9-11] condensation products of carbonyls and amines [12].

Among various organic compounds available, acetylenic alcohols are widely used because of their commercial viability. However they suffer from following drawbacks. They are effective only at high concentration and produce toxic vapours under acidizing process [13].

In view of the above mentioned factors there exists a need for development of new acidizing corrosion inhibitors.

In the present investigation we have prepared two heterocyclic corrosion inhibitors in the laboratory in the form of indigenous raw materials. The corrosion inhibiting action of these compounds has been evaluated by weight loss and electrochemical methods.

EXPERIMENTAL

The experiments were carried out using oilfield steel p-105 and cold rolled mild steel (0.2%) in 15% HCl at 380 ± 2 K. The composition of oil field steel is given in the literature [14]. The metal samples of size 3 cm x 2.5 cm were used for weight loss studies. The metal specimens were polished and degreased with trichloroethylene before use and weight loss experiments were performed in a specially designed glass cell consisting of 3 necks. The volume of test solution per square centimetre was maintained at about 20 ml. The inhibitor QJ-1 was prepared by reacting a equimolar mixture of a haloketone and thiourea, and the resulting product was condensed with aromatic aldehyde. Inhibitors QJ-2 prepared by refluxing thiocarbonylhydrazide in a aliphatic acid and the resulting product was condensed with an aromatic aldehyde. Both the compounds were characterized through their spectra data and their purity was confirmed by TLC.

For polarisation studies specimen of 1 cm² area was used. The specimens were polished with different grades of emery

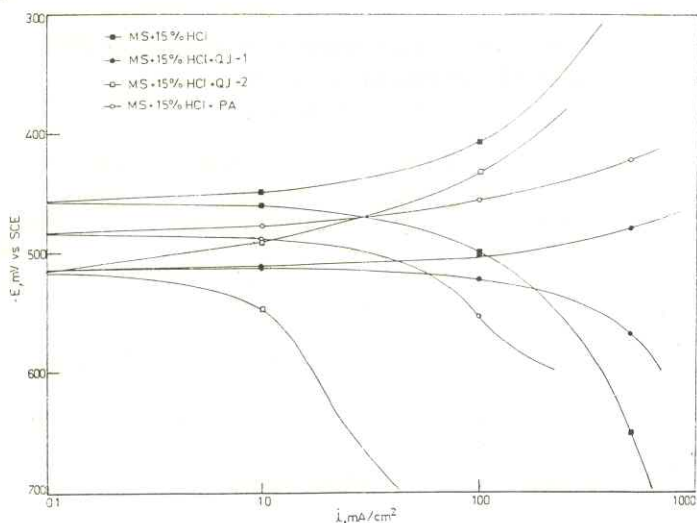


Fig. 1: Polarisation curves of mild steel with 25% concentration of each inhibitor in 15% HCl

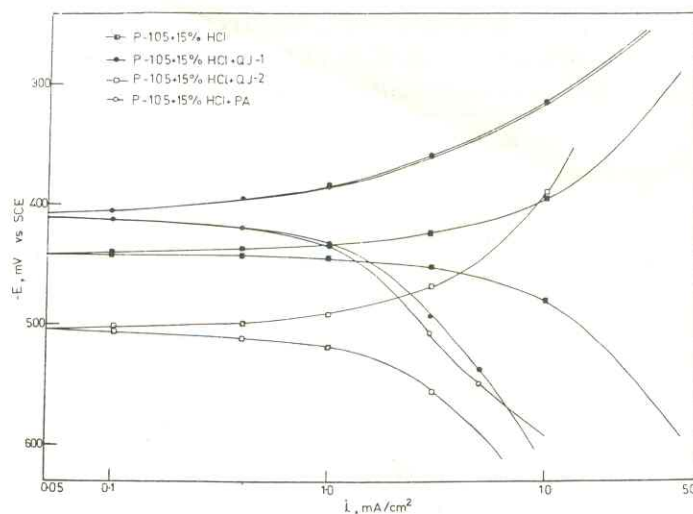


Fig. 2: Polarisation curves of oilwell tubular steel (P105) with 25% concentration of each inhibitor in 15% HCl

papers of 1/0 to 4/0 degraded with trichloroethylene. Five necked specially designed glass cell was used for electrochemical studies. Mild steel and oil field steel were used as working electrode. Platinum was used as auxiliary electrode. Saturated calomel electrode was used as reference electrode. Potentiostatic polarisation studies were carried out using the potentiostat (EG&G 173) universal programmer (EG&G 175) and the X-Y recorder (Rikadenki Z01T) at a sweep rate of 1 mV/sec.

RESULTS AND DISCUSSION

Various corrosion parameters obtained from weight loss method for mild steel in 15% HCl in absence and presence of inhibitors under boiling hydrochloric acid conditions at $380 \pm 2K$ at concentration of 0.25% each, are given in Table III. It is evident from the Table that all the compounds examined are very good inhibitors. They give more than 95% inhibitor efficiency. The order of inhibitor efficiency has been found as follows:

$$QJ - 2 > QJ - 1 \geq PA$$

The potentiostatic polarisation curves of mild steel and oil well tubular steel P-105 in absence and presence of 0.25% concentration of each inhibitor in 15% HCl are shown in Figs. 1 and 2 and various electrochemical parameters are given in Tables I and II respectively. The results clearly bring out the facts that QJ-2 is a mixed inhibitor but predominately controls the cathodic reaction, while QJ-1 & PA are of mixed type but predominantly control anodic reaction. The corrosion rate of mild steel in 15% HCl at $380 \pm 2K$ is 456 mmpy. It is significantly reduced to 6.72 mmpy in presence of QJ-2, while QJ- 1 and PA reduce the corrosion rate to 22

& 43 mmpy respectively. Thus according to the effectiveness of the synthesized inhibitor and commercial inhibitor PA, they can be graded as follows:

$$QJ - 2 > QJ - 1 > PA$$

The results obtained by weight loss method and electrochemical technique are in well agreement.

The corrosion parameters obtained by electrochemical technique on P-105 are shown in Table I. The results show that QJ-1 and PA are predominantly anodic inhibitors and they individually reduce the corrosion rate of P-105 from 57 mmpy to 6.84 mmpy.

The mechanism of inhibition of steel corrosion is well documented in the literature [15-16]. Since synthesized inhibitors QJ-1 and QJ-2 are hetrocyclic compounds, they inhibit corrosion of the steel in hydrochloric acid by getting adsorbed on the metal surface through their π -electrons.

TABLE I: Corrosion parameters for tubular steel (electrochemical method) in 15% HCl containing 0.25% inhibitors under boiling condition (temp. 350 K)

Inhibitor	E_{corr} mV vs SCE	Tafel slopes mV/decade		I_{corr} mA/cm ²	Corrosion rate (mpy)	I.E. %
		bc	ba			
Blank 15%						
HCl	-460	120	130	5.2	57.00	—
QJ-1	-405	110	80	0.6	6.84	88
QJ-2	-502	134	62	1.2	13.64	76
PA	-404	110	80	0.6	6.84	88

TABLE II: Corrosion parameters for mild steel (electrochemical method) in 15% HCl containing 0.25% inhibitors under boiling condition (temp. 380 K)

Inhibitor	E_{corr} mV vs SCE	mV/decade		I_{corr} mA/cm ²	Corrosion rate (mpy)	I.E. %
		bc	ba			
Blank 15%						
HCl	-460	110	110	40.0	456.00	—
QJ-1	-445	100	70	2.0	22.40	96.0
QJ-2	-510	140	64	0.6	6.72	98.5
PA	-480	138	66	3.8	43.23	90.0

CONCLUSIONS

Both the synthesized compound QJ-1 and QJ-2 have been found to act as effective corrosion inhibitors of mild steel and oil well tubular steel (P-105) in 15% boiling hydrochloric acid solutions. They showed better performance than propargyl alcohol for mild steel and are found to be as good as propargyl alcohol for oil well tubular steel.

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TABLE III: Corrosion parameters for MS in 15% HCl at 380 K (wt loss method) in presence of inhibitor (0.25% each)

Inhibitor	Wt. loss (g/cm ²)	Corrosion rate (mpy)	I.E. %
Blank 15% HCl	0.8676	9969.0	—
QJ-1	0.1033	367.8	96.31
QJ-2	0.0224	250.0	97.49
PA	0.0250	278.6	97.20

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