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

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A new and effective corrosion inhibitor namely ACIDEX-Q1, useful during acidization of petroleum well has been synthesized in the laboratory from indigenous and cost effective chemicals and its corrosion inhibiting action has been evaluated by weight loss and electrochemical techniques in 15% hydrochloric acid under boiling condition. The performance of the synthesized compound was compared with propargyl alcohol, a commercially available acidizing inhibitor. The synthesized compound ACIDEX-Q1 showed better performance than that of PA on mild steel and oil well steel.

Keywords: Synthesized corrosion inhibitor and oil well acidization

## INTRODUCTION

Acidization of petroleum oil well is one of the important stimulation techniques for enhancing oil production. Hydrochloric acid (15 to 28%) 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 casing materials [1] during acidization.

A survey of literature reveals that only few inhibitors are available that can withstand higher acid concentration and temperature. 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 remains [12].

Among various organic compounds available, acetylenic alcohols are widely used because of their commercial viability. However, they suffer from the following drawbacks. They are effective only in 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 new corrosion inhibitors have been prepared in the laboratory from 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  $380 \pm 2$  K. The composition of oil field steel is given in 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 decreased 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 centimeter was maintained at about 20 ml. The inhibitors ACIDEX-Q1 was prepared by reacting an equimolar mixture of a heloketone and thiourea and the resulting product was condensed with automatic aldehyde, and was characterized through its spectral data and its purity was confirmed by TLC.

For polarisation studies, specimens of 1 sq.cm. area were used. The specimens were polished with different grades of emery papers of 1/0-4/0 degreased with trichloro ethylene. 5 necked specially designed glass cell was used for the electrochemical studies. Mild steel and oil field steel were

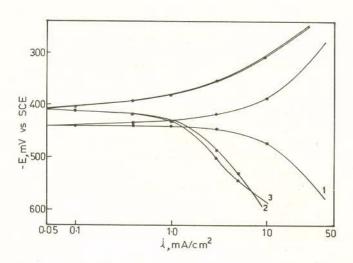


Fig.1: Potentiostatic polarisation curves for MS in 15% at 380 K 1. MS + 15% HCl 2. MS + 15% HCl + PA 3. MS + 15% HCl + ACIDEX-Q1

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 potentiostat (EG & 173) universal programmer (EG & G 175) 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 the absence and presence of inhibitors, under boiling hydrochloric acid conditions at  $380 \pm 2$  K at concentration of 0.25% each, are

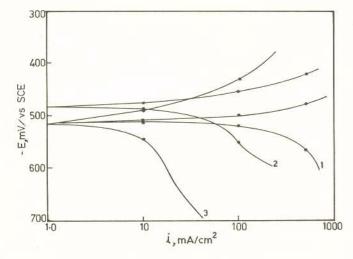


Fig.2: Potentiostatic polarisation curves for P-105 in 15% HCl at 380 K 1. P-105 + 15% HCl 2. P-105 + 15% HCl + PA 3. P-105 + 15% HCl + ACIDEX-Q1

TABLE I: Electrochemical corrosion parameters for P-105 in 15% HCl containing 0.25% inhibitors at 380K

Inh	E <sub>corr</sub> mV vs	Tafel slopes mV/decade		I <sub>corr</sub> mA/cm <sup>2</sup>	Corr.	I.E %
	SCE	be	ba		(mmpy)	- 1141
Blank 15% HCl	-460	120	130	5.0	57.00	_
ACIDEX-Q	-405	110	80	0.6	6.84	88
PA	-404	110	80	0.6	6.84	88

given in Table III. It is evident from the table that the synthesized compound gave better performance than PA propargyl alcohol.

The potentiostatic polarisation curves of mild steel and oil well tubular steel P-105 in absence and presence of 0.25% the 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 ACIDEX-Q1 & PA are of mixed type but predominantly control anodic reaction. The corrosion rate of mild steel in 15% HCl at 380 ± 2 K is 456 mmpv. ACIDEX-Q1 and PA reduce the corrosion rate to 6.72 and 43. These results show that the synthesized inhibitors is better than the PA inhibitor. There is a fairly good agreement between the inhibition efficiency values obtained by weight loss & electrochemical methods. The corrosion parameters obtained by the electrochemical technique on P-105 are shown in Table I. The results show that ACIDEX-Q1 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 in presence of PA is well documented in the literature [15-16]. The synthesized inhibitor ACIDEX-Q1 is a heterocyclic compound. It inhibits the corrosion of the steel in hydrochloric acid by getting adsorbed on the metal surface

TABLE II: Electrochemical corrosion parameters for mild steel in 15% HCl containing 0.25% inhibitors at 380K

Inh	E <sub>corr</sub> mV vs SCE	Tafel slopes mV/decade		I <sub>corr</sub> mA/cm <sup>2</sup>	Corr.	I.F.
		be	ba	•	(mmpy)	
Blank 15% HCl	-510	110	110	40.0	456.00	_
ACIDEX-Q	-515	140	64	0.6	6.72	98.5
PA	-480	138	66	3.8	43.23	90.5

TABLE III: Electrochemical corrosion parameters for MS in 15% HCl at 380 K (wt. loss method) containing 0.25% inhibitors

Inhibitors	Wt. loss (g/cm <sup>2</sup> )	Corrosion rate (mmpy)	I.E. (%)	
Blank 15 % HCl	0.8676	9969.0	700	
ACIDEX-Q1	0.0224	250.0	97.49	
PA	0.0250	278.0	97.20	

through its  $\pi$  electrons and lone pairs of electrons of the N and S atoms present in the heterocyclic ring.

## CONCLUSION

The synthesized compound ACIDEX-Q1 has been found to act as an effective corrosion inhibitor for mild steel and oil well tubular steel (P-105) in 15% boiling hydrochloric acid solutions. It showed better performance than propargyl alcohol for mild steel and was found to be as good as propargyl alcohol for oil well tubular steel.

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#### REFERENCES

- 1. G Schmitt, Brit Corros J, 19 (1984) 165
- F A Brindsi, T W Blecks and T E Sullivan, U S Pat, 430 (1981) 2246
- T M Muzyezko, S Share and J A Martin, U S Pat, 3 (1972) 106; 105 (1972) 106
- 4. B F Mago, U S Pat, 4 (1987) 263167
- I L Rosenfield, Corrosion inhibitors, Mcgraw-Hill, New York, (1981) 98
- W Frenier, F B Growcock and V R Lopp, Corrosion, 44 (1988) 590
- 7. W W Frenier, Eur Pat, (1992) 47400
- E B Grocock, W W Frenier and P A Andreozzi, Corrosion, 45 (1989) 1007
- 9. A Cizek, US Pat 4 (1991) 40; 997 (1991) 40
- 10. A E Woodson, U S Pat, (1976) 3982894
- K D Neemla, A Jayaraman, R C Saxena, A K Agarwal and R Krishna, Bull Electrochem Soc, 5 (1988) 250
- R F Monroe, C H Kucera, B D Oates, U S Pat, 300 (1963)
  454
- 13. D D N Singh and A K Dey, Corrosion, 49 (1993) 594
- Metals handbook 9th Edition (American Society for Metals)
  1 (1978) 319
- 15. G W Poling, J Electrochem Soc, 114 (1967) 1209
- 16. R J Tedeschi, Corrosion, 31 (1975) 130