JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 11, Preprint 10 submitted 19 August 2008

Corrosion inhibitor formulations from coal-tar distillation products for acid cleaning of steel in HCl

A. A. El Hosary and N. A. Abdel Ghany*, R. M. Saleh

Electrochemistry and Corrosion Dept.,
National Research Centre, Dokki, Cairo, Egypt.

Abstract

The chemical cleaning of boilers, heat exchangers, vessels, reactors, piping and other equipments from deposits and scales are usually conducted in acid solutions. Effective corrosion inhibitors are adding to avoid the acid attack on metallic surface. The employed inhibitors in this field based mainly on organic molecules containing nitrogen, sulfur and/or phosphorus. In this paper, inhibitor formulations prepared from cool-tar distillation products were evaluated for application in acid cleaning processes using weight loss and polarization measurements. These industrial byproducts contain large number from the above needed molecules. Some of the prepared formulations could afford high inhibition action (about 98 %). The effect of immersion time and temperature revealed quite stability of the inhibitors. The polarization data indicate general adsorption of the additives, affecting both the anodic and cathodic reactions of the metal corrosion.

Key words: Corrosion inhibitor, acid cleaning, mild steel.

* Corresponding author Fax 00202 333 70931 Email: na_manakhly@yahoo.co.uk (N.A. Abdel Ghany)

1. Introduction

Equipments in power plants, chemical plants, steel mills, paper mills, sugar plants, pipelines, air conditions and many other industrial environments are subjected to scale and deposit formation either by circulating water or by process compounds. These include boilers, heat exchangers, vessels, reactors, piping and other equipments. These deposits may reduce heat transfer, cause tube overheating and failure. To prevent many difficulties, cleaning of the metal surfaces is required. Pre-operational cleaning is also necessary to remove pre-formed oxides, weld splatter and dirt accumulated during transportation and installation.

The cleaning processes are usually conducted by different acids, including hydrochloric, sulfuric, sulphamic, citric and other acids [1, 2]. To avoid the acid attack on the metal surface, effective corrosion inhibitors are used. Most of the acid inhibitors are organic compounds, with at least polar unit having, N, S, O, atoms and in some cases Se and P. More details on the acid corrosion inhibitors are given in a number of review papers [2-14].

In the present paper, Anthracene Oil (A.O.), one of the coal tar distillation products (C.T.D.P.) is used for the preparation of effective inhibitor formulations for acid cleaning. A number of C.T.D.P. have been previously investigated for acid cleaning, and gave appreciable efficiencies [15-18]. These products are characterized by having large number of constituents, including N-, S-, and O- containing molecules, predicting good inhibitive action via expected synergistic action.

2. Experimental

The Anthracene Oil (A.O) is supplied by El Nasr Co. for Coke and Chemicals, Egypt. It has been analyzed by a Gas Chromatography-Mass Spectral (GC/MS) using column coupled to type SSQ 7000 (Finnigan, Germany) running in the electro impact mode at 70 eV (MS/EI).

The GC/MS analysis is listed in Table 1. This table shows that this product is composed of a large number of O-, N- and S-containing compounds.

2.1. Preparation of Inhibitor Formulations

Stock solutions from Anthracene oil composed of 20% (by volume) from the oil dissolved in different solvents were prepared. Acceptable solubility of the oil has been attained in hydrochloric acid (5 %), acetic acid and phosphoric acids (20%) alone or mixed with equal volume from organic solvents. Table 2 shows the composition of prepared solutions.

2.2. Corrosion Inhibition Measurements

The prepared formulations have been evaluated for the inhibition of mild steel (composition in Table 3) in 5% w/v HCl mainly at 60°C using weight loss and polarization measurements. In each test two coupons (50 x 50 x 2 mm) were cleaned as previously described [19, 20], dried and immersed in 500 mL HCl solution for 2 hours. From the average weight loss in the absence (W_{free}) and presence of inhibitor (W_{inh}), the inhibition efficiency, I, of the additive was determined according to:

$$I, \% = 100\,(W_{free}-W_{inh.})/W_{free}$$

2.3. Electrochemical Polarization Measurements

Tafel polarization plots were performed using EG&G Potentiostat/Galvanostat (Applied Princeton Research) Model 273A driven by software M352/252 Corrosion Measurement System. Mild steel sheets (10 x 10 x 2 mm) precleaned as mentioned before [20] were used as working electrodes. A platinum wire sealed in a glass tube was used as a counter electrode. The potential was measured relative to a Saturated Calomel Electrode (SCE).

This study has been carried out in hydrochloric acid solutions because of its economical and ecological advantages, ability to dissolve hard deposits from water and to remove iron oxide containing scale [10].

3. Results and discussion

3.1. Corrosion Inhibition Measurements

The Anthracene Oil (A.O.) was found to have acceptable solubility in hydrochloric, acetic and phosphoric acids. The inhibition action of the formulations (No.1, 2 and 3 in Table 2) for the corrosion of mild steel in 5% HCl solutions at 60°C is given on Fig 1.

The results of Fig.1 show:

(i) Very high values of inhibition efficiencies, approaching 98% could be afforded. This performance could not be easily obtained by commercial inhibitors.

ii) Appreciable inhibition action could be attained at very small concentration from the additives.

To select the most effective formulation, on which further study will be carried out, the inhibition efficiency values recorded at some doses from the three formulations are compared in Table 4.

These data indicate that formulation (2) is the most effective; it could afford limiting high efficiency (98%) at lower doses (0.1 %).

3.2. Effect of organic solvents on the performance of formulation (2)

To achieve better solubility of A.O. and more economic formulation, A.O. has been dissolved in binary mixtures of acetic acid and other organic solvents. Formulations

(No. 4, 5 and 6) have been prepared and tested for inhibition of the corrosion of steel in 5% HCl at 60°C. The results are given on Fig.2. No significant effect of the tested organic solvents on the performance of the inhibitor could be seen.

From these results, formulation No. 5 (Ac. Ac.-Thinner) has been selected and subjected to more testing. To simulate the conditions in most cleaning process, the action of the cleaning period and temperature on the performance of this formulation has been examined. The results showed no significant change of the inhibition action for test periods extended to 10 hours at 60°C. Also, the efficiency increased from 90% at 25°C to 99% at 70°C. These results indicate stability of the formulation and strong adsorption of its inhibiting molecules to the metal surface.

3.3. Polarization measurements

The galvanostatic polarization curves of mild steel in 5 % HCl at 60°C in the absence and presence of formulation (5) are drawn on Fig.3. The polarization parameters are given in Table 5.

The results show that both anodic and cathodic currents decreased in presence of inhibitor, but the Tafel slopes are little changed. The corrosion potentials (Ec) are shifted to more positive values, by 25-50 mV. These findings are in agreement with previously reported data [21-23]. These observations suggest general adsorption of the inhibitive molecules on both anodic and cathodic sites, with more blocking effect on the anodic reaction [24].

Table 5 includes also the values of the corrosion current (Ic) in the absence and presence of different inhibitor concentrations. The inhibition efficiencies calculated from Ic are fairly compared with those obtained by weight loss.

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 11, Preprint 10 submitted 19 August 2008

4. Conclusions

Corrosion inhibitor formulations prepared from coal –tar distillation product have been tested for the inhibition of the steel in HCl solutions. The formulations contain large number of N-, S-, and O- containing organic molecules. The results of weight loss and polarization measurements revealed high inhibitive action (about 98 %) for formulation composed from 20 % Anthracene oil dissolved in acetic acid. This formulation is characterized by good thermal stability and strong adsorption on both anodic and cathodic areas of the steel surface. The results suggest application of this inhibitor formulation for the acid cleaning process of steel.

References

1. NACE Task Groups T-3M-4 (1982) "Industrial Cleaning Manul".1982 Houston, Texas: NACE Corros. Abs. 21:61,376-4.

2. Schmitt G (1994)"Inhibition in Acid Media", European Federation of Corrosion publications, A Working Party Report on Corrosion Inhibitors 11:64.

3. Hodgkiessa T, Al-Omarib KH, Bontemsa N, Lesiaka B (2005) Desalination 183 :209.

4. Machnikova EWhitmire, KH, Hackerman N (2008) Electrochimica Acta 53:6024.

5. Solmaz R, Kardaş G, Çulha M, Yazıcı B, Erbil M (2008) Electrochimica Acta 53: 5941.

6. NACE Task Group T-3A-15 (1993) "Reviews on Corrosion Inhibitors Science and Technology" II-20-1-II-20-22, Houston, Texas.

7. Robinson JS (1979) "Corrosion Inhibitors, Recent Developments" Noyes Data Corporation, New Jersey.

8. Collie MJ (1983)"Corrosion Inhibitors. Development since 1980" Noyes Data Corporation, New Jersey.

9. Maitra AN, Singh G, Bhattacharyya K (1980) Trans. SAEST 16:61.

10. Kuznetsov Yu I, Isaev V A, Rylkina MV, Garmanov ME (2001) Protection of Metals, 37:144–147.

11. Trabanelli G (1994) "Inhibitors for Chemical Cleaning Treatments", European Federation of Corrosion Publications, A Working Party Report on Corrosion Inhibitors 11:92.

12. Granese SL, Roscales BM (1990) Structural effects of the aromatic quaternary ammonium compounds on inhibition of steel in chloride containing media, Proc. 7th SEIC, Ann. Univ. Ferrara, N.S., Sez. V, Suppl. 9:73.

13. Stupnisek –Lisac E, Metikos-Hukovic M (1990) The influence of the composition and structure of substituted pyrroles on their inhibitory properties, Proc. 7th SEIC, Ann. Univ. Ferrara, N.S., Sez. V, Suppl. 9:203.

14. Hudson RM, Loony QL, Waring C J (1967) Br. Corrs. J. 2:81.

15. Saleh RM, El Hosary AA (1983) Coal-tar distillation products as corrosion inhibitors for the corrosion of mild steel in hydrochloric acid, Intern. Confer. On Corros. Inhibition, NACE, Dallas, Texas.

16. Saleh RM, El Hosary AA (1985) Coal-tar distillation products as corrosion inhibitors for the corrosion of mild steel in sulfuric acid, 6th European Symp. On Corros. Inhibitors, Ferrara, Italy.

17. El Hosary AA, Saleh RM (1990) Inhibition action of coal tar distillation products on the corrosion of mild steel in hydrochloric, citric and sulfuric acids, 11th Intern. Corros. Congr., Milano, Italy,.

18. Abdel Ghany NA, El Hosary AA, Saleh RM (2007) Corrosion inhibition in petroleum production: Formulation and evaluation of corrosion inhibitor from industrial byproducts Eurocorr, Freiburg, Germany.

19. Tayor W, El Hosary AA, Saleh RM, Abdel Ghany NA (1995) Ferric ion and corrosion inhibition in acid cleaning, 8th European Symp. on Corros. Inhibitors, Ferrara, Italy.

20. Saleh RM, El Hosary AA, Abdel Ghany NA (1997) Corrosion inhibitors from oil refinery by-products for acid cleaning processes: I-Inhibition of mild steel in HCl, Eurocorr, Trondheim, Norway.

21. Saleh RM, Ismail AA, El Hosary AA (1982) Br. Corros. J. 17:131.

22. Foroulis ZA (1966) J. Electrochem. Soc.113:532.

23. Felloni L, Corrs. Sci. (1968) 8:113.

24. Horvath T, Kalman E, Kutsan G, Rauscher A (1994) Br. Corros. J. 29:215.

Figure Captions

Fig.1. Corrosion inhibition of mild steel measured in 5 % HCl by formulations (1, 2, 3).

Fig.2. Corrosion inhibition of mild steel measured in 5 % HCl by formulations (4, 5, 6).

Fig.3. Tafel polarization curves of mild steel measured in 5 % HCl at 60°C in presence of different concentrations of formulation (5).

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 11, Preprint 10 submitted 19 August 2008

Table 1. GC/MS analysis of Anthracene-oil: major constituents.

Scan area	Constituents	Molecular Formula	Percent
3741	Anthracene, Pyrene, Fluoranthene and their derivatives.	C_6H_{10}, $C_{16}H_{12}$ $C_{16}H_{11}NO_2$	30 %
3125	Cyclopropen-diphenyl, dipheylethelyne, phenanthrene, Iminodiacetic acid, N-fluorenyloxy-carbonyl, and Hydroxymethyl phenyl oxadiazoline.	$C_{15}H_{10}O$, $C_{14}H_{10}$ $C_{21}H_{18}$,$C_{19}H_{17}NO_6$ $C_9H_{10}N_2O_2$	16 %
2394	Acenaphtene, naphthacene, Naphthalene carbonitrile, Chlorodiphenyl arsine and, Naphthalene iso cyano.	$C_{12}H_{10}$,$C_{12}H_{10}$ $C_{11}H_7N$, $C_{12}H_{10}Cl.As$ $C_{11}H_7N$	8 %
4211	Naphthacene, Triphenylene, Phenanthradicarbonitrile, and Thiazolo quinoline trimethyl	$C_{18}H_{12}$,$C_{16}H_8N_2$ $C_{13}H_{12}N_2S$	6 %
3638	Furobenzopyran hydroxyl, and Pyrimidine methoxy hydroxyphenyl	$C_{11}H_6O_4$ $C_{11}H_{10}N_2O_2$	4 %
2479	Dibenzofuran, beta-carboline, Pyrido-indole, naphthalene carbonitrile amino, propendinitrile phenylethyldiene, Quinoline carbonitrile methyl,	$C_{12}H_8O$, $C_{11}H_8N_2$ $C_9H_{16}N_2O$, $C_{13}H_{20}O_3$ $C_{16}H_{17}NCl$,	3.5 %

	Dipheneethylamine dichloro, and Pyridium iodide dimethyl phenyl	$C_{13}H_{14}N$	
2645	Fluorene Carboxylic acid and Fluorene bromo and other derivatives, and Ethanone daizodiphenyl	$C_{14}H_{10}O_2$, $C_{13}H_9Br$ $C_{13}H_{10}N_2$, $C_{14}H_{12}O$ $C_{14}H_{10}N_2O$	3 %
3871	Benzocarbazole, propanamine-dibenzo-cylohepten-ylidene-N,N-dimethyl, and Indeno quinoline	$C_{16}H_{11}N$, $C_{20}H_{21}N$ $C_{16}H_{11}N$	2.5 %
1668	Naphthalene, Benzenedicarbonitrile, Hydroxymethyl beta chloro ethylthiazole, and Quinoline Iodo-	$C_{10}H_8$, $C_8H_4N_2$ C_6H_8NOSCl, $C_8H_4N_2$ C_9H_6NI	2 %

Table 2. Anthracene Oil Prepared formulations.

Form-ulation No.	**A.O. (20%) in:**	**Form-ulation No.**	**A.O. (20%) in:**
(1)	Hydrochloric Acid (5%)	(4)	Acetic Acid (20%) + Methanol
(2)	Acetic Acid	(6)	Acetic Acid (20%) + Thinner
(3)	Phosphoric Acid (20%)	(5)	Acetic Acid (20%) + Kerosene

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 11, Preprint 10 submitted 19 August 2008

Table 3. Composition of mild steel.

Element	C	Mn	Si	P	S	Cu	Cr	Ni	Ti	Al	Mo	Sn
Amount,%	0.047	0.289	0.037	0.017	0.013	0.054	0.049	0.057	0.02	0.003	0.002	0.02

Table 4. Inhibition efficiencies of corrosion inhibitor formulations.

Formulation	**Inh.Eff., % , at:**			
	0.1	0.2	0.5	1 % vol./vol.
(1): A.O.-HCl	53.5	82	96.5	98
(2): A.O.-Ac.Ac.	98	98	99	99
(3): A.O.-Phos. Ac.	94.5	96	97	97.5

Table 5. Polarization parameters for steel in 5 % HCL at 60°C.

Inhibitor Conc., Vol %	**Ec, mV**	**Tafel Slope, mV/Decade**		**Ic, mA/cm2**	**Inhib. Eff., % from**	
		Anodic	**Cathodic**		**Ic**	**Wt. loss**
Blank	-520	70	100	630	----	-----
0.1	-475	65	85	35	94.5	98
0.2	-485	60	90	32	95	98
0.5	-485	60	100	36	94.3	99
0.7	-470	60	100	38	94	99

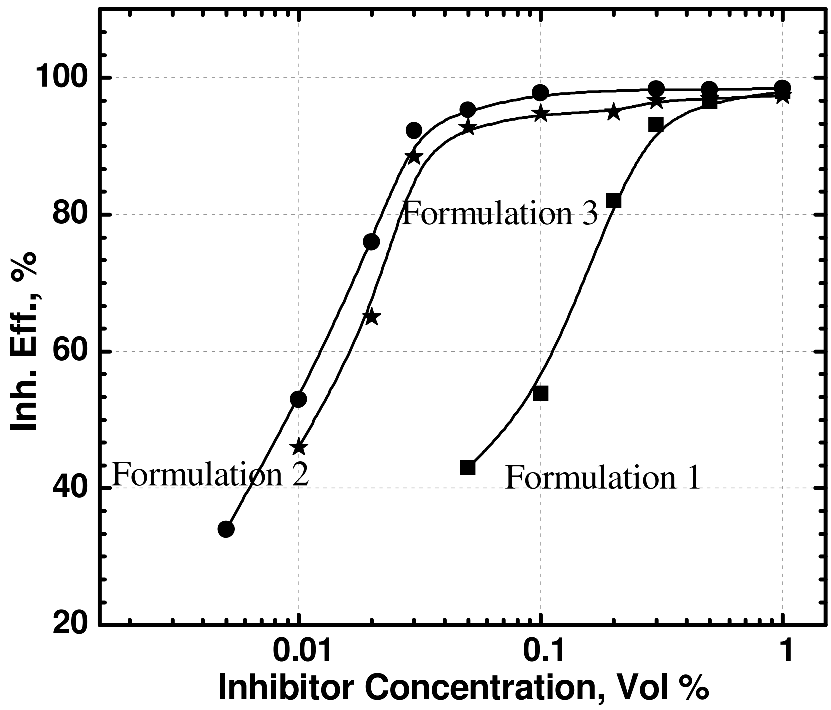

Figure.1.

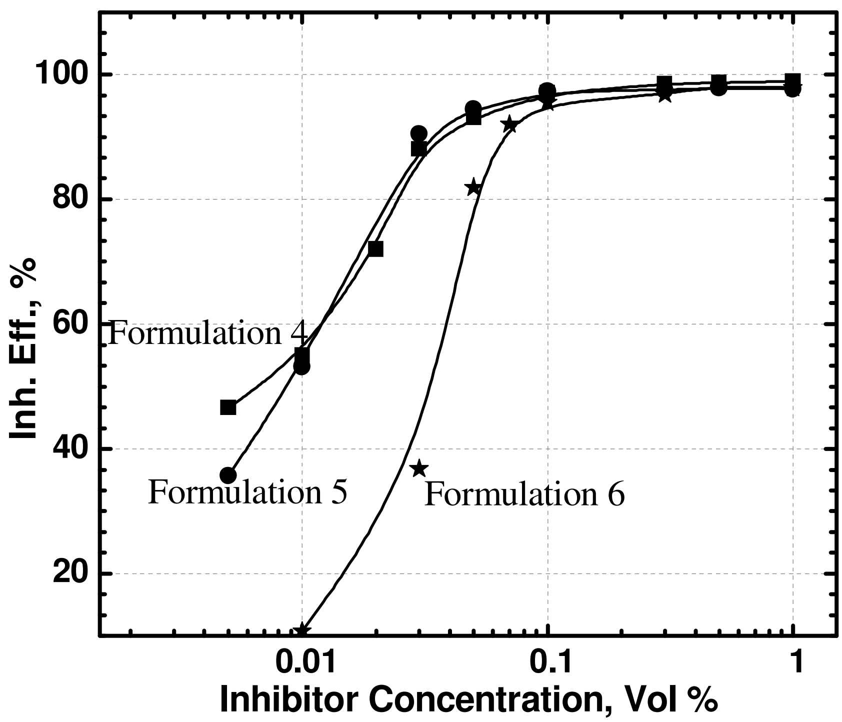

Figure 2

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 11, Preprint 10 submitted 19 August 2008

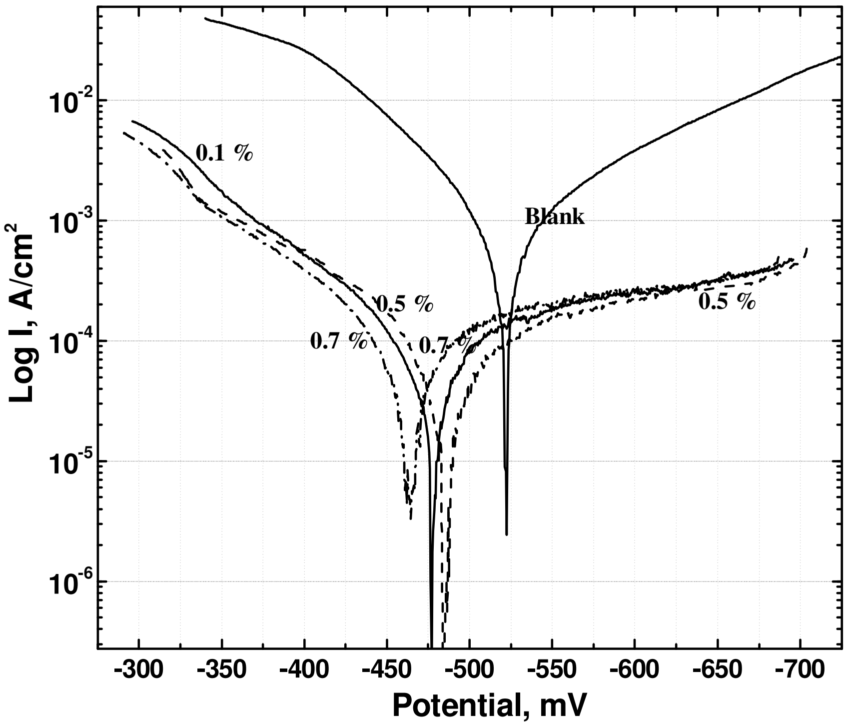

Figure 3