



EFFECT OF SODIUM BENZOATE APPLICATION ON ATMOSPHERIC CORROSION OF MILD STEEL

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ABSTRACT

The purpose of this study was to search for an inhibitor to slow down or prevent atmospheric corrosion/discoloration of the local mild steel during storage in the Arabian Gulf region. Various inhibitors were reported in the literature that can help in protection against atmospheric corrosion. In light of the results of some preliminary studies, sodium benzoate was selected for examination against atmospheric corrosion of steel to be applied at 10 and 100 mM concentrations for 1 day at room temperature. Test specimens were prepared from locally produced reinforcing steel products. Exposure racks were constructed from wood to hold specimens during atmospheric exposure for different periods. Corrosion was evaluated through weight loss determination and electrochemical technique. Corrosion rates of the inhibitor treated specimens were lower than that of the unprotected specimens for over a month of atmospheric exposure. However, further exposure to atmosphere caused deterioration in the inhibition performance of sodium benzoate and the corrosion rates of sodium benzoate treated specimens reached that of the unprotected specimens at the end of three months of atmospheric exposure.

Keywords: *Inhibitors, Atmospheric Corrosion, Arabian Gulf, Steel, Sodium Benzoate.*

1. INTRODUCTION

The atmospheric conditions in the Arabian Gulf region is corrosive to metallic structures due to high relative humidity, high ambient temperature, especially during summer, and high levels of contamination of the atmosphere with sea-salt and sulfur dioxide originating from the Gulf and industrial complexes in the region.

Various inhibitors were reported in the literature that can help in protection against metal corrosion in aqueous environments. Among them are Toluylalanine, cyclohexyl amine, dicyclohexylamine nitrite, methylcyclohexylamine, phenylthiourea, sodium benzoate, sebacic acid, sodium nitrite, calcium silicate, sodium phosphate and sodium nitrate.

[Saurbier, et al. 1994] compared 3-(Toluyl)-N-(1,1-dimethyl-2-hydroxyethyl)-alanine, known as Toluylalanine (TALA) $C_{15}H_{21}NO_4$, Sebacte (seba) $C_{10}H_{18}O_4$, i-Nonate (i-non) $C_9H_{18}O_2$, m-nitrobenzoate (m-nitro) $C_7H_5NO_4$, i-phthalate (i-phtha) $C_8H_6O_4$, Benzoate (Benz) $C_7H_6NO_2$ and nitrite as inhibitors of corrosion in wet atmosphere. The most effective inhibition was obtained in solution with the passivating TALA.

It has been recently reported that dicyclohexylamine nitrite (DICHAN) provided moderate protection for steel at 65-85% relative humidity [Bastidas and Mora, 1998]. The inhibition of 3-(trimethoxysilyl) propanethiol-1 (TMSPT) was reported to be effective against corrosion of steel in NaCl solutions [Beccaria, et al., 1994]. Some other inhibitors reported to be effective against corrosion are TPI-4 [Trufanova, et al., 1991], $NaNO_2$ water solution [Miglyachenko, 1992], five-membered polynitrogen heterocycles [Tsarenko, et al., 1995], amines such as cyclohexyl amine [Agres and Altisybeeva, 1990], ethanolamine [Andreev, et al., 1997], sulfonates and phosphorous-containing organic compounds [Sementsova, et al., 1998], Imidazole derivatives [Stupnisek-Lisac, et al., 1999] and fatty acid esters [Krauss and Nmai, 1996]. Some commercial coolants are also used as atmospheric corrosion inhibitors [Anderson and Devereux, 1993]. Chromates are effective as atmospheric inhibitors (for aerospace aluminum alloys), however they are identified to be carcinogen and their use therefore is not recommended [Jeffcoate, et al., 1998; Khobaib, et al., 1998]. Non-chromate inhibitor formulations such as borate, molybdate, phosphate and silicate were studied for aluminum aircraft [Khobaib, et al., 1998].

Thiophenol was reported to serve as a good inhibitor (studied at concentrations of 1 mM, 10 mM, 100 mM) for the corrosion of iron and mild steel in acidic solutions [Madhavan, et al., 1998; Bouayed, et al., 1999]. However, thiophenols have not been given much attention as inhibitors because of their obnoxious odour and low solubility in acidic solutions [Madhavan, et al., 1998].

The influence of the concentration of electrolyte anions on the efficiency of acid based inhibitors for steel in the neutral solution was studied using anodic and cathodic polarization at a rotating disk electrode. The N-ethyl-morpholine of a q-benzoyl alcanoic acid and benzoic acid were used

as inhibitors. Both inhibitors were found to inhibit the anodic partial reaction. The inhibition effect was more pronounced at low electrolyte concentration [Agarwal and Landolt, 1998].

The corrosion inhibiting performance of a tertiary amine possessing two carboxylic acid groups (N coco-amine-2-propionic acid) was studied on initially clean and pre-corroded mild steel. High levels of efficiency were found of the inhibitor at a concentration level of 10 ppm [Malik, 1999].

The passivity and pitting behavior of A56-70 carbon steel in chromate solutions were studied using electrochemical measurements. Chromate ions play a prominent role in the formation of passive film, but hardly affect the stability of the passive state [Cheng and Luo, 1999].

The influences of inhibitor concentrations for orthophosphate mixed with polyphosphate were studied on steel. The total concentration of two inhibitors was 15 mg/L. The corrosion rate which was 1.9 mpy at 0% of orthophosphate decreased to 0.3 mpy at 60 % of orthophosphate but then increased up to 1.8 mpy when orthophosphate concentration increased to 100% [Bofardi, 1993].

The objective of this study was to investigate experimentally the effectiveness of sodium benzoate treatment in preventing or decreasing the corrosion/discoloration of local mild steel products during storage under atmospheric conditions in Arabian Gulf region.

2. EXPERIMENTAL

2.1. Test Specimens

The test specimens were prepared from locally produced reinforcing steel products with a typical composition (in wt%) of C: 0.38, Si: 0.20, Mn: 1.53, P: 0.021, S: 0.017, Cu: 0.054, Cr: 0.020, Mo: 0.009, Ni: 0.011, Sn: 0.004, V: 0.004, Nb: 0.005, Fe: balance. The steel had been manufactured by continuous casting followed by quenching with water spray and air cooling. Two groups of specimens were prepared as 5-inch (12.7 cm) long specimens for weight loss determinations and 1-inch (2.54 cm) long specimens for electrochemical measurements. 5-inch long specimens were used as they are. 1-inch specimens were threaded at one cross sectional side to fit them in the working electrode rod of the electrochemical cell. All specimens were washed prior to the study using soap and water, followed by ultrasonic cleaning in acetone and methanol before drying.

2.2. Inhibitor Application

The solution of the inhibitor (sodium benzoate) was prepared in distilled water in concentrations of 10 and 100 mM (as determined to be effective concentrations by preliminary laboratory tests in a simulated environment of 2% NaCl and 1% Na₂SO₄ [Allam, et al., 1991]) utilizing magnetic mixing. Inhibitor application of specimens to be

protected was conducted by inserting the specimens in the inhibitor solution for 1 day at room temperature.

2.3. Atmospheric Exposure

The specimens were exposed to atmosphere in Dhahran (on the roof of the Research Institute of King Fahd University of Petroleum and Minerals) after treating them with the inhibitor. Specimens were exposed for different periods of time, for 5 days, 15 days, 30 days, 90 days, and 180 days, before corrosion measurements. The results were compared to that of unexposed specimens (control samples). During exposure, the specimens were visually inspected and any change that occurred in their appearance due to corrosion was recorded photographically.

2.4. Inhibitor Performance Analysis

The weight losses of the exposed specimens were determined at the end of each exposure period to quantify their corrosion. Also, the effect of inhibitors on the corrosion of steel specimens in a simulated laboratory environment of 2% NaCl and 1% Na₂SO₄ was evaluated by electrochemical technique in a standard corrosion cell [Al-Mathami, 2001]. Morphological changes of the specimens were examined by photography and scanning electron microscopy (SEM). The experimental system used for SEM analysis was JSM-840 Scanning Electron Microscope located at the Research Institute of King Fahd University of Petroleum & Minerals. Compositional analysis of selected surfaces was also done by the EDS (Energy Dispersive Spectrometry) technique available with the SEM system.

3. RESULTS AND DISCUSSIONS

3.1. Electrochemical Tests

Corrosion rates of unprotected and inhibitor treated steel specimens were determined in the simulated solution of 2% NaCl and 1% Na₂SO₄ by electrochemical technique before and after exposing them in the atmosphere for specified durations. These measurements obviously do not give the rate of atmospheric corrosion, however they give an indication of the level of corrosion inhibition before and after atmospheric exposure. The results obtained are presented in Figure 1 as corrosion rate relative to that of the untreated steel vs exposure time for untreated and 10 and 100 mM sodium benzoate treated steel specimens. Each value is an average of three tests.

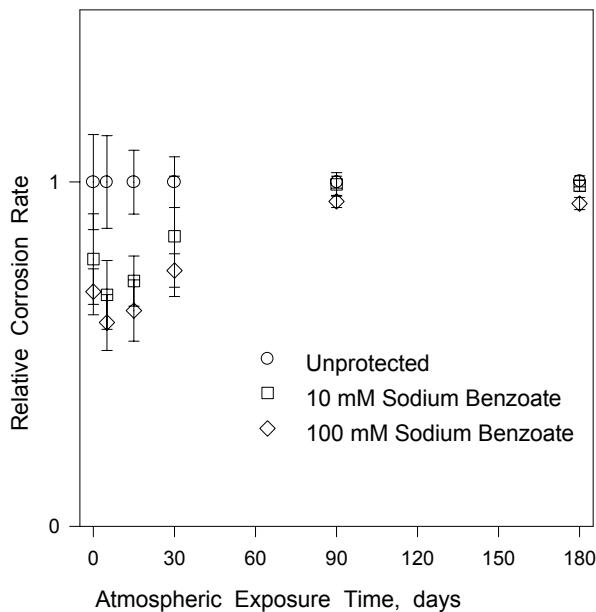


Figure 1. Corrosion rates of untreated and inhibitor treated steel specimens in the simulated solution of 2% NaCl and 1% Na₂SO₄ vs duration of atmospheric exposure.

Corrosion rates in the simulated solution before any atmospheric exposure were about 0.135, 0.10 and 0.09 mm/y for steel as received, steel treated with 10 mM sodium benzoate and steel treated with 100 mM sodium benzoate, respectively. 100 mM inhibitor concentration resulted in a better corrosion protection than 10 mM concentration, in general.

Corrosion rate of all specimens increased significantly with exposure time, probably due to the increase in corrosive atmospheric contamination on the exposed specimens with time. However, since the corrosion rates of the inhibitor treated specimens relative to that of the untreated ones were of concern and for a more clear presentation, relative corrosion rates were used in the plot.

15 days of atmospheric exposure did not cause deterioration in corrosion inhibition performance of sodium benzoate. However, a deterioration in the corrosion inhibition was observed for 30 or more days of atmospheric exposure. Corrosion rates of untreated and sodium benzoate treated specimens were similar in the simulated solution after 3 or more months of atmospheric exposure.

3.2. Study of Atmospheric Corrosion

Atmospheric rates of untreated and inhibitor treated steel specimens were determined by weight loss measurements and plotted against exposure duration in Figure 2. As seen in the figure, after 15 days of exposure, the atmospheric corrosion rates determined are about 0.096, 0.074 and

0.06 mm/y for untreated steel, steel treated with 10 mM sodium benzoate and steel treated with 100 mM sodium benzoate, respectively.

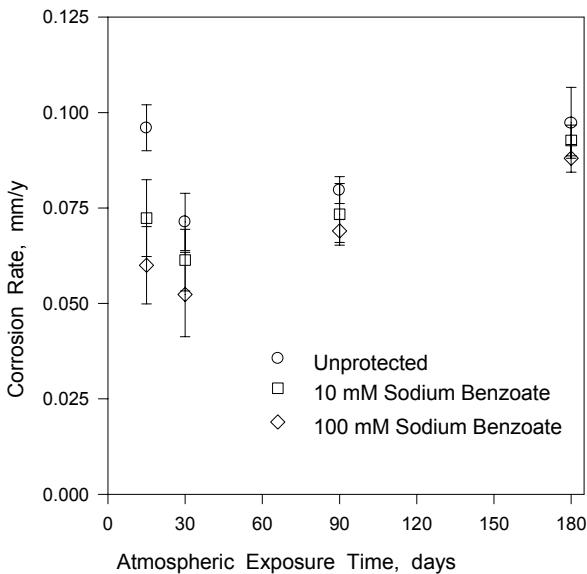


Figure 2. Atmospheric corrosion rate of untreated and inhibitor treated steel vs atmospheric exposure period.

Atmospheric corrosion rates of the inhibitor treated specimens were lower than that of the unprotected specimens. 100 mM inhibitor concentration resulted again in better protection against atmospheric corrosion than 10 mM concentration.

Atmospheric corrosion inhibition performance of sodium benzoate deteriorated with exposure time. Atmospheric corrosion rates of sodium benzoate treated specimens were close to that of the untreated specimens after 30 or more days of atmospheric exposure.

3.3. Morphological Analysis of Corrosion Specimens

Steel specimens were observed by photography during their exposure to atmosphere. Figure 3 shows untreated specimens after a month of atmospheric exposure. Significant discoloration on the steel specimens can be seen. Specimens treated with sodium benzoate on the other hand, did not show such discoloration at the end of their exposure to atmosphere for 30 days (Figure 4).



Figure 3. Photograph of untreated steel specimens after a month of atmospheric exposure.



Figure 4. Photograph of steel specimens exposed to atmosphere for a month after treatment with 100 mM sodium benzoate.

SEM/EDS studies were performed on an as received steel specimen (control) and inhibitor treated and untreated specimens after atmospheric exposure of 5 days.

Figure 5 is an SEM micrograph taken on an as received steel specimen (control) after polishing. EDS analysis of the surface is presented in Table 1. As expected, no significant contamination but lots of polishing scratches were observed on the surface. The surface was composed of mostly iron with trace amounts of C, Al, Si, Cl, S, and Mn.

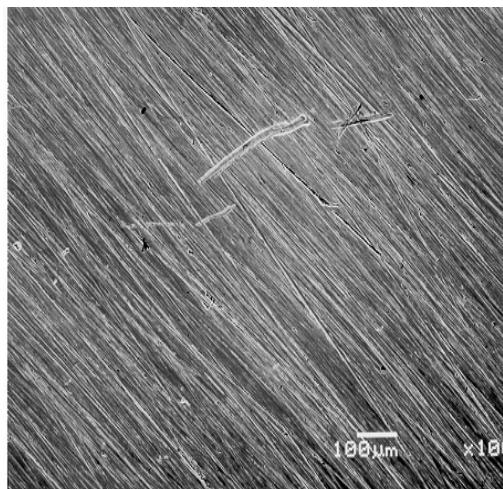


Figure 5. SEM micrograph of an as received steel specimen after polishing (control specimen).

Table 1. Elemental composition by EDS analysis of the as received steel (control specimen).

C, wt%	Al, wt%	Si, wt%	Cl, wt%	Mn, wt%	S, wt%	Fe, wt%
0.46	0.26	0.14	0.14	0.2	0.01	98.8

Figure 6 is an SEM micrograph of the surface of an untreated steel specimen at the end of 5 days of exposure to atmosphere. Table 2 presents the EDS analysis of that surface on three different points, one on the dark spot near the center, one on the bigger white spot at left and one at the center part away from the dark or white spots.

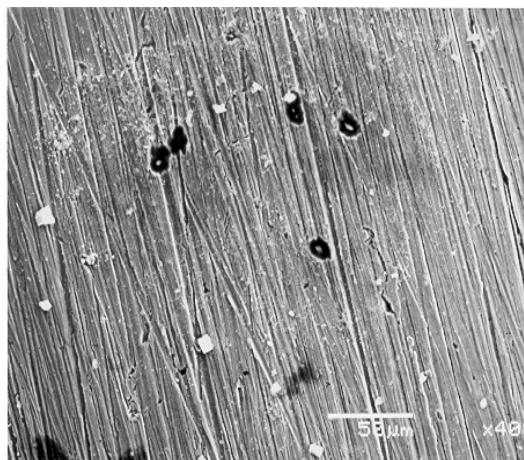


Figure 6. SEM micrograph of an untreated steel specimen after 5 days of atmospheric exposure.

Table 2. EDS analysis of the surface shown in Figure 6 (untreated steel specimen after 5 days of atmospheric exposure). Elemental composition of the control specimen is also included for comparison purposes.

	C, wt%	O, wt%	Na, wt%	Al, wt%	Si, wt%	Cl, wt%	Mn, wt%	S, wt%	K, wt%	Fe, wt%
Dark spot near the center	1.1	2.93	-	2.69	0.23	0.12	1.76	0.43	-	90.7
Big white spot at left	0.61	3.41	-	4.14	2.9	0.05	0.57	-	0.22	88.1
Center part away from dark or white spots	0.94	3.21	-	2.82	0.3	0.07	0.76	-	-	91.9
Control	0.46	-	-	0.26	0.14	0.14	0.2	0.01	-	98.8

Compositions of the three points were not that different from each other. Higher Mn content in the dark spot might indicate that dark spots are steel interior points. Higher Si content in the white spot indicates that it might be sand contamination. Higher oxygen content in all points might be a result of minor corrosion of the specimen during 5 days of atmospheric exposure. Aluminum on the surfaces was probably left during polishing with Alumina solutions.

SEM micrographs were also taken on steel specimens treated with 100 mM sodium benzoate. A small white layer was observed on part of the surface. Figure 7 is an SEM micrograph taken at a part away from that layer. EDS analysis of the surface is given in Table 3. SEM micrograph and EDS analysis on the white layer of the surface are also presented in Figure 8 and Table 3, respectively.

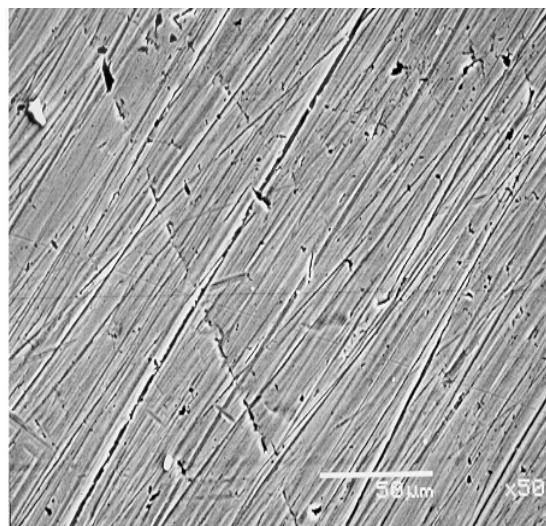


Figure 7. SEM micrograph taken on an unexposed steel specimen treated with 100 mM sodium benzoate (at a part away from the white layer on the surface).

Table 3. EDS analysis of the surface of an unexposed steel specimen treated with 100 mM sodium benzoate.

	C, wt%	O, wt%	Na, wt%	Mg, Wt%	Al, wt%	Si, wt%	Cl, wt%	Ca, wt%	Mn, wt%	Fe, wt%
Away from the white layer on the surface	0.7	-	-	-	0.41	0.24	0.17	0.1	0.68	97.7
White layer on the surface	7.37	2.19	4.05	0.18	0.37	0.27	0.07	0.08	0.81	84.6
Control	0.46	-	-	-	0.26	0.14	0.14	-	0.2	98.8



Figure 8. SEM micrograph taken on the white layer of the unexposed steel specimen treated with 100 mM sodium benzoate.

Higher Na, O, and C content on the white layer indicates that it is a thicker but loose film of the inhibitor, sodium benzoate, (which comes out easily by washing with water). The elemental composition of the rest of the surface (away from the white layer) was not significantly different than that of the control indicating that the inhibitor film must be very thin which might not contribute much in the EDS analysis.

SEM and EDS analyses were also performed on a sodium benzoate treated specimen after 5 days of atmospheric exposure. Figure 9 is a micrograph taken at a part away from white layers which were present on the surface. An SEM micrograph was also taken on a white layer on the surface and shown in Figure 10. EDS analyses of the surfaces are given in Table 4.

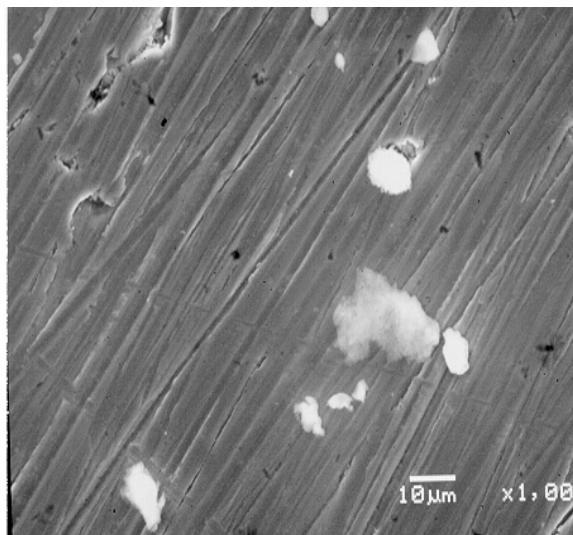


Figure 9. SEM micrograph taken on a sodium benzoate treated specimen after 5 days of atmospheric exposure (at a part away from the white layers on the surface).

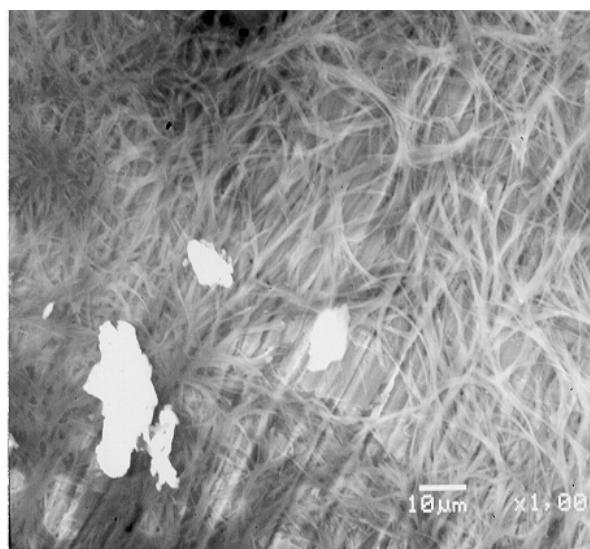


Figure 10. SEM micrograph taken on a sodium benzoate treated specimen after 5 days of atmospheric exposure (on a white layer which was present on the surface).

Table 4. EDS analysis on a specimen exposed to atmosphere for 5 days after treatment with 100 mM sodium benzoate (SEM micrographs taken on that specimen are given in Figures 9 and 10).

	C, wt%	O, wt%	Na, wt%	Mg, wt%	Al, wt%	Si, wt%	Cl, wt%	Ca, wt%	Mn, wt%	Fe, wt%
Away from white spots in Figure 9	0.9	-	-	-	0.52	0.2	0.2	0.09	0.7	97.4
White spot in Figure 9	1.95	9.18	-	0.16	2.31	4.34	0.29	0.78	0.69	80.3
Away from white spots in Figure 10	7.62	2.83	3.32	0.07	0.82	0.18	0.16	-	0.63	84.38
White spots in Figure 10	13.47	7.25	7.23	0.5	2.24	1.89	0.6	0.83	0.86	65.12
Control	0.46	-	-	-	0.26	0.14	0.14	-	0.2	98.8

Not much corrosion but lots of polishing scratches were observed on the specimen. White loose parts on Figure 9 are contamination, probably sand with higher contents of Ca, Si, and O (Table 4). The rest of the surface in Figure 9 is mostly Fe (the inhibitor film is probably too thin to contribute in the EDS analysis in Table 4). The fibrous structure in Figure 10 is a film of the inhibitor sodium benzoate with similar composition to that of the unexposed specimen treated with sodium benzoate (Figure 8 and Table 3). The white spots of Figure 10 are probably contamination with higher contents of Si, O, Na and Cl.

4. CONCLUSIONS

Treatment of steel with sodium benzoate inhibited the corrosion of steel significantly during the first month of its exposure to atmosphere. A deterioration in inhibition performance of sodium benzoate was observed with further atmospheric exposure. In general, 100 mM inhibitor concentration resulted in a better corrosion protection than 10 mM concentration.

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