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Inhibition of Atmospheric Corrosion of Mild Steel by Sodium Benzoate Treatment

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The objective of this study was to evaluate the effectiveness of sodium benzoate as an inhibitor to slow down or prevent atmospheric corrosion/discoloration of the local mild steel during storage in the Arabian Gulf region. Test specimens were prepared from locally produced reinforcing steel products. The inhibitor solution was applied on steel specimens at a concentration of 100 mM for 1 day at room temperature. Wooden exposure racks were used to hold as-received and inhibitor-treated specimens during atmospheric exposure for different periods. Corrosion was evaluated through weight loss determination and electrochemical technique. As expected, the Arabian Gulf atmosphere was corrosive on the as-received local mild steel. On the other hand, treatment of steel with sodium benzoate lowered its corrosion rate during initial days of its exposure to atmosphere. However, atmospheric corrosion inhibition performance of sodium benzoate deteriorated with exposure time after 30 or more days of atmospheric exposure, and the corrosion rates of sodium benzoate-treated specimens reached that of the unprotected specimens at the end of 90 days of atmospheric exposure.

Keywords Arabian Gulf, atmospheric corrosion, inhibitors, sodium benzoate, steel

1. Introduction

The weather in the Arabian Gulf region is hot and humid, providing a corrosive environment for metallic structures. In Dhahran and Jubail, the relative humidity is above 50% during most of the year. In summer, air temperature may go up to 50 °C. The daily temperature fluctuations can be as high as 20 °C during hot seasons, whereas the fluctuations of relative humidity may range between 40 and 100% over a 24 h period.

Petroleum and petrochemical industrial areas and the proximity of the inhabited areas to the shores of the Gulf have caused a dramatic increase in atmospheric corrosion of the metallic structures. The atmospheric corrosion in the Gulf region is aggravated further by high salinity of Gulf water, resulting in the high rate of sea-salt deposition. The chloride and sulfate contents in the atmospheric air of the Gulf coast in Dhahran are 63.2×10^{-3} and 33.8×10^{-3} mg/m^3, respectively.[1]

Various inhibitors that can help in protection against metal corrosion in aqueous environments were reported in the literature. Among them are 3-(toluyl)-N-(1,1-dimethyl-2-hydroxyethyl)-alanine known as toluylalanine,[2] 3-(trimethoxysilyl) propanethiol-1,[3] cyclohexyl amine,[4] dicyclohexylamine nitrite,[5] benzoic acid,[6] sebacic acid,[2] ethanolamine,[7] thiophenol,[8,9] imidazole derivatives,[10] chromates,[11-13] fatty acid esters,[14] carboxylic acid,[15] benzoates,[2] sulfonates,[16] silicates,[12] phosphates,[12,17] nitrites,[2] nitrates,[18] and some commercial coolants.[19]

The role of inhibitors can be due to adsorption of phase layers on the metal surface or by the interaction with one of several corrosion products to form a new protective phase, rather than by adsorption on the metal surface. Inhibitors such as sodium benzoate adsorb on the metal surface and provide a barrier for the entry of aggressive ions such as chloride. The inhibitors may also passivate the metal by stabilization of the passivating oxide film and by decreasing its dissolution rate. Inhibitors can also interact with the oxide-covered metal surface to form insoluble compounds that plug pores in the oxide film and prevent oxygen reduction reaction at the cathodic sites in neutral solutions.[20]

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 the Arabian Gulf region (industrial marine environment). It should be noted that the inhibitor is not applied in the corrosive environment; instead, the inhibitor solution is first applied on steel, which is then taken out of the inhibitor solution and exposed to the atmosphere.

2. Experimental

2.1 Test Specimens

The test specimens were prepared from locally produced reinforcing steel products. Two groups of specimens were prepared. The first included 5 in. long specimens for weight loss determinations. The second included 1 in. long specimens for electrochemical measurements that 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 by using soap and water, followed by ultrasonic cleaning in acetone and methanol before drying.

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2.2 Inhibitor Application

The solution of the inhibitor (sodium benzoate) was prepared in distilled water in a concentration of 100 mM (as determined to be the most effective concentration by preliminary laboratory tests in a simulated environment of 2% NaCl and 1% Na_2SO_4[1]) by using 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 (5, 15, 30, 90, and 180 days) before corrosion measurements. The results were compared with 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 Atmospheric Corrosion by Weight Loss Determination

The weight losses of the exposed specimens were determined at the end of each exposure period to quantify their corrosion. The procedure given below was followed[1,21,22]:

- Before treatment of specimens and exposure:
  1) Specimens were cleaned by using acetone and distillate water and air-dried.
  2) Specimen lengths and diameters were measured to determine the surface areas of specimens.
  3) Initial weights of specimens were determined to the nearest 0.1 mg.
- After atmospheric exposure:
  4) Specimens were cleaned from corrosion products with 10% HCl, washed with acetone and distillate water, and air dried.
  5) Final weights of specimens were determined to the nearest 0.1 mg.
  6) Weight loss = initial weight – final weight.

The effect of HCl in weight loss determination was also considered as follows:

1) Initial weight of unexposed specimen was taken.
2) Unexposed specimen was cleaned with 10% HCl, washed, and dried.
3) Final weight of unexposed specimen was taken.
4) Weight loss of this specimen due to acid cleaning is subtracted from the weight loss of each exposed specimen to determine the net weight loss due to atmospheric corrosion.

The corrosion rate by weight loss determination is obtained by the following formula:

$$\text{Corrosion rate (mm/y)} = 87.6 \frac{W}{D\,A\,T}$$

where W is the weight loss in mg, D is the density of sample (7.87 g/cm^3), A is the area of sample in square centimeters, T is exposure time in hours, and 87.6 is the conversion factor.

2.5 Electrochemical Laboratory Tests Under Simulated Environment

The effect of inhibitors on the corrosion of steel specimens in a simulated environment was evaluated by the electrochemical technique in a standard test cell. The cell was a vessel containing the solution electrolyte and electrodes. The solution electrolyte was distillate water with dissolved salts. The salt solution contained 2% sodium chloride (NaCl) and 1% sodium sulfide (Na_2SO_4).[1] The steel specimens were the working electrodes in the electrochemical test cell. A direct current power supply supplied current to the working electrode through the auxiliary electrode (graphite) in the test cell. The corrosion current density (I_{corr}) and the polarization resistance (R_p) of the steel specimens were measured with respect to a reference electrode. The reference electrode was the saturated calomel electrode (SCE). A potentiostat (EG&G Model 273A) was connected to the electrochemical cell to give Tafel and polarization curves. All required data were given to the model through an external computer connected to the potentiostat and the output curves and results (Tafel constants, I_{corr}, R_p, corrosion rate) were also stored in the computer.

The Tafel test was performed only once for the inhibitor at 100 mM to obtain the Tafel constants β_{anode} and $\beta_{cathode}$. β_{anode} and $\beta_{cathode}$ were used in the polarization runs for corrosion rate determination. The input data for Tafel and polarization runs are given in Table 1.

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% Na_2SO_4 by the 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 Fig. 1 as corrosion rate relative to that of the untreated steel versus exposure time for untreated and sodium benzoate-treated steel specimens.

Table 1 Input Data for Tafel and Polarization Tests

	Input Data	
	Tafel	**Polarization**
Minimum potential	−25 mV	−10 mV
Maximum potential	+25 mV	+10 mV
Scanning rate	0.1 mV/s	0.1 mV/s
β_{anode}	—	From the Tafel test
$\beta_{cathode}$	—	From the Tafel test
Sample area	Depends on the sample	Depends on the sample
Sample density	7.87 g/cm^3	7.87 g/cm^3
Equivalent weight	27.89	27.89

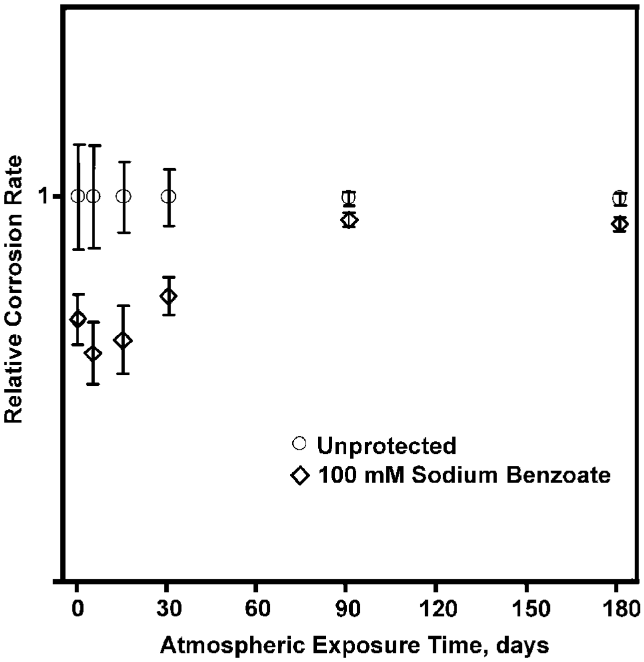

Fig. 1 Corrosion rates of untreated and inhibitor treated steel specimens in the simulated solution of 2% NaCl and 1% Na_2SO_4 vs duration of atmospheric exposure

Each value is an average of three tests. Standard deviations were also included in the plot.

Corrosion rates in the simulated solution before any atmospheric exposure were about 0.135 and 0.09 mm/y, for steel as received and steel treated with 100 mM sodium benzoate, respectively. Corrosion inhibition by sodium benzoate treatment is obvious in the simulated aqueous solution.

Corrosion rate of the specimens increased significantly with exposure time, probably because of the increase in corrosive atmospheric contamination on the exposed specimens with time. However, because 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.

Fifteen 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 corrosion rates of untreated and inhibitor treated steel specimens were determined by weight loss measurements and plotted against exposure duration in Fig. 2. Atmospheric corrosion rates of the inhibitor-treated specimens were lower than that of the unprotected specimens. As seen in the figure, after 15 days of exposure, the atmospheric corrosion rates determined are about 0.096 and 0.06 mm/y for untreated steel and steel-treated with 100 mM sodium benzoate, respectively. However, atmospheric corrosion inhibition performance of sodium benzoate deteriorated with exposure time. The corrosion rates of sodium benzoate-treated specimens were close to that of the untreated specimens after 30 or more days of atmospheric exposure.

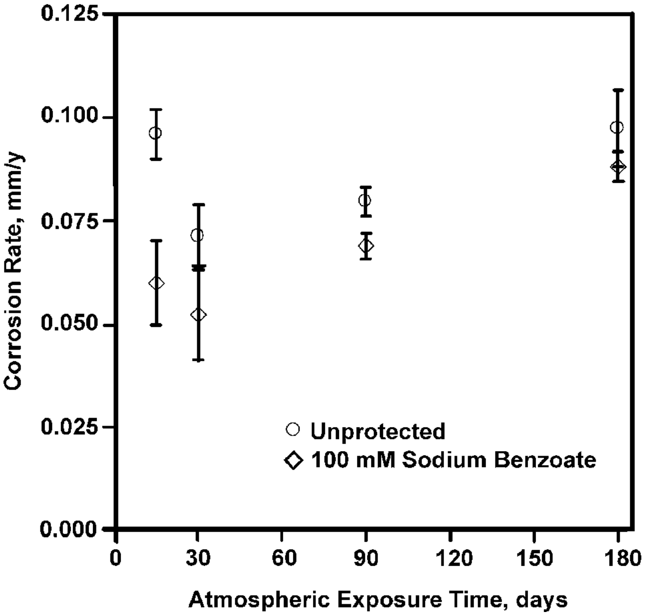

Fig. 2 Atmospheric corrosion rate of untreated and inhibitor treated steel vs atmospheric exposure period

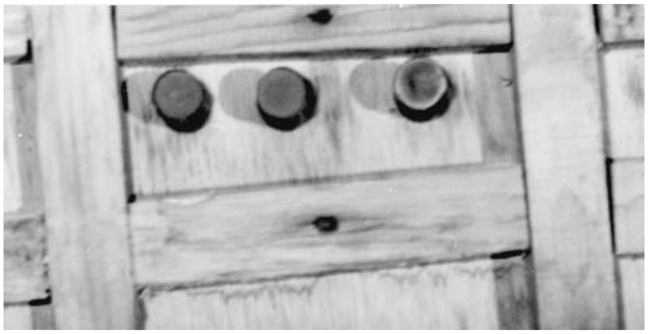

Fig. 3 Photograph of untreated steel specimens after a month of atmospheric exposure

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 (Fig. 4).

Extent of discoloration on the steel specimens increased with exposure period (Fig. 5 and 6). Three months of atmospheric exposure resulted in heavy corrosion on the untreated

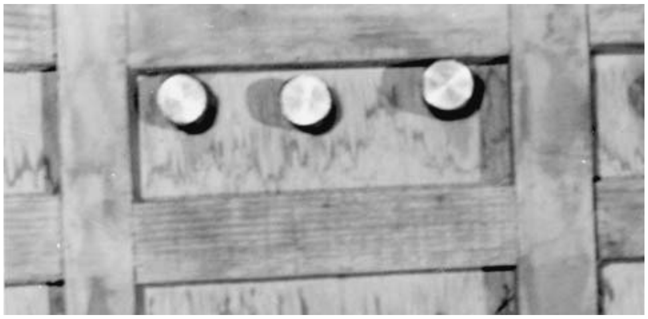

Fig. 4 Photograph of steel specimens exposed to atmosphere for a month after treatment with 100 mM sodium benzoate

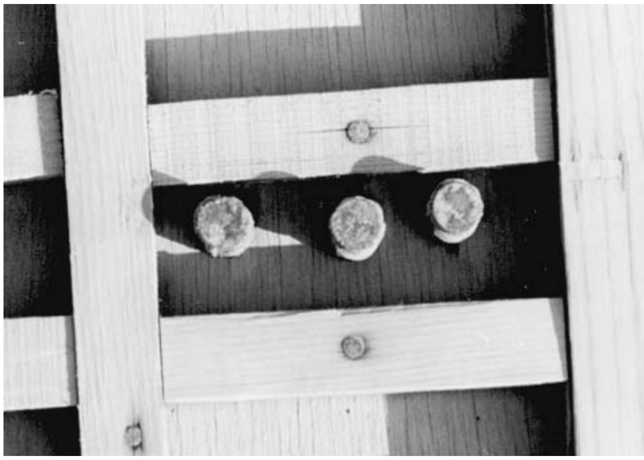

Fig. 5 Photograph of untreated steel specimens after 3 months of atmospheric exposure

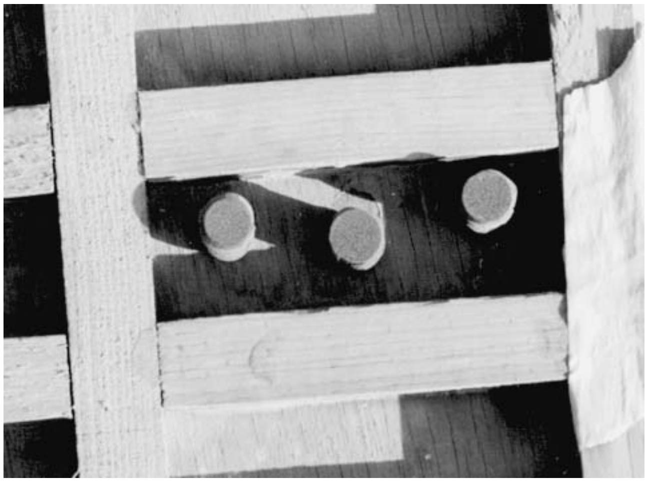

Fig. 6 Photograph of steel specimens exposed to atmosphere for 3 months after treatment with 100 mM sodium benzoate

specimens. On the other hand, discoloration was also extensive on sodium benzoate treated specimens at the end of 3 months of exposure to atmosphere.

4. Conclusions

As expected, the Arabian Gulf atmosphere was corrosive on the as-received local mild steel. Treatment of steel with sodium benzoate lowered its corrosion rate during initial days of its exposure to atmosphere. Atmospheric corrosion inhibition performance of sodium benzoate deteriorated with exposure time for longer exposure durations and the atmospheric corrosion rates of sodium benzoate-treated specimens reached that of the unprotected specimens at the end of 90 days of atmospheric exposure.

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References

1. M. Allam, J.S. Arlow, and H. Saricimen: "Initial Stages of Atmospheric Corrosion of Steel in the Arabian Gulf," *Corros. Sci.,* 1991, *32,* pp. 417-32.
2. K. Saurbier, J.W. Schultz, and J. Geke: "Temporary Inhibitors of Corrosion in Wet Atmosphere: Electrochemical Investigations of the Mechanism and Efficiency," *Electrochem. Acta,* 1994, *39,* pp. 1171-78.
3. A.M. Beccaria, M. Ghiaazza, and G. Poggi: "The Effect of Change of pH on the Inhibitory Action of 3-(trimethoxysilyt) propanethiol-1 on Corrosion Behavior of Carbon Steel in NaCl Solutions," *Corros. Sci.,* 1994, *36,* pp. 1381-93.
4. E.M. Agres, and A.I. Altsybeeva: "One Method of Determination of the Volatility of Atmospheric Corrosion Inhibitors," *Protection of Metals,* 1990, *25,* pp. 822-25.
5. J.M. Bastidas, and E.M. Mora: "Laboratory Study of Mild Steel Vapor Phase Corrosion and Its Inhibition by Dicyclohexylamine Nitrite," *Can. Metall. Q.,* 1998, *37,* pp. 57-65.
6. P. Agarwal, and D. Landolt: "Effect of Anions on the Efficiency of Aromatic Carboxylic Acid Corrosion Inhibitors in Near Neutral Media: Experimental Investigation and Theoretical Modeling," *Corros. Sci.,* 1998, *40,* pp. 673-91.
7. N.N. Andreev, N.P. Andreeva, R.S. Vartapetyan, Y.I. Kuznetsov, and T.V. Fedotova: "Volatile Corrosion Inhibitors Based on Ethanolamines," *Zashchita Metallov,* 1997, *33,* pp. 521-27.
8. K. Madhavan, S. Muralidharan, and S. Venkatakrishna: "Thiophenol As an Inhibitor for the Corrosion and Hydrogen Permeation Through Mild Steel in Acidic Solutions," *Anti-Corrosion Meth. and Mater.,* 1998, *45,* pp. 227-32.
9. M. Bouayed, H. Rabaa, A. Srhiri, J.-Y. Saillard, A. Ben Bachir, and A. Le Beuze: "Experimental and Theoretical Study of Organic Corrosion Inhibitors on Iron in Acidic Medium," *Corros. Sci.,* 1999, *41,* pp. 501-17.
10. E. Stupnisek-Lisac, V. Cinotti, and D. Reichenbach: "Atmospheric Corrosion Inhibitors for Copper in the Electronics Industry," *J. Appl. Electrochem.,* 1999, *29*(1), pp. 117-22.
11. C.S. Jeffcoate, N.N. Voevodin, M. Khobaib, L.B. Reynolds, W.K. Kuhn, and M.S. Donley: "Future Trends in Non-chromate Corrosion Inhibitors," *43rd International SAMPE Symposium and Exhibition (Proceedings),* 1998, SAMPE, *43*(2), pp. 2113-22.
12. M. Khobaib, N. Schehl, G.A. Hartman, and M.S. Donley: "Effects of Environmentally Compliant Corrosion Inhibitors on Crack Growth Behavior of Aerospace Aluminum Alloys," *International SAMPE Symposium and Exhibition (Proceedings),* 1998, SAMPE, *43*(2), pp. 2102-12.
13. Y.F. Cheng, and J.L. Luo: "Passiving and Pitting of Carbon Steel in Chromate Solutions," *Electrochem. Acta,* 1999 *44,* pp. 4795-4804.
14. P.D. Krauss, and C.K. Nmai: "Preliminary Corrosion Investigation of Prestressed Concrete Piles in a Marine Environment: Deerfield Beach Fishing Pier," *Proceedings of the 1994 Symposium on Techniques to*

Assess the Corrosion Activity of Steel Reinforced Concrete, October 1996, MRS, SAE Special Publications, *1276,* pp. 161-72.

15. H. Malik: "Corrosion Inhibition by N Coco-amine-2-proprionic Acid on Mild Steel in CO_2 Saturated 5% NaCl at pH 6.5," *Anti-Corrosion Meth. and Mater.,* 1999, *46,* pp. 434-38.
16. V.M. Sementsova, I.V. Filippov, A.N. Klimushkin, V.I. Tevs, and A.N. Kalenkova: "New Composition of the Slushing Oil for Stock Protection Against Atmospheric Corrosion," *Stal*', 1998, *8,* pp. 35-36.
17. B.P. Bofardi: "Influence of Polyphosphate/PO_4 Ratio on Steel Corrosion," *Corrosion Inhibitor Sci. and Technol.,* 1993, *4,* pp. 70-75.
18. V.P. Miglyachenko: "Inhibiting Properties of $NaNO_2$ Water Solutions in Soils," *Zashchita Metallov,* 1992, *3,* pp. 507-8.
19. W.D. Anderson, and O.F. Devereux: "Corrosion Inhibitor Degradation in Grinding Coolants," *Lubrication Eng.,* 1993, *49,* pp. 901-7.
20. G. Fontana: *Mars, Corrosion Engineering,* McGraw-Hill, Inc. New York, 1986.
21. ASTM Designation 61-88, *Annual Book of ASTM Standards,* Vol. 3.02, ASTM, Philadelphia, PA, 1988, p. 61.
22. NACE Standard TM-01-69 (1976 Revision), *Laboratory Corrosion Testing of Metals for Process Industries,* NACE, Houston, 1976.