G.U. Journal of Science
19(3): 149-154 (2006)

www.gujs.org

Protection of Corrosion of Carbon Steel by Inhibitors in Chloride Containing Solutions

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Received: 10. 10. 2005 *Accepted: 31. 05. 2006*

ABSTRACT

In the first part of this study, the inhibitor effect of single, binary and ternary mixture of chromate, molybdate, nitrite, tetraborate, ortophosphate, benzoate, acetate, ascorbic acid on the corrosion of carbon steel was investigated. Experiments were carried out in neutral aqueous solution containing 100 ppm Cl^- at room temperature. The current-potential curves were obtained by potentiostatic (1mV/s) method and the corrosion rates were determined by the extrapolation of the Tafel slope of the cathodic polarization curves method and linear polarization method. In the second part, the inhibitor effect of some one component, binary and ternary inhibitor blends was investigated depending on the temperature (30, 40, 50 ^oC) and pH (5, 7, 9). The inhibitor effects were found to be %95 for solutions containing 50 ppm nitrite. Of all inhibitor systems tried, chromate-molibdate and chromate- nitrite- molibdate was found to be the most effective binary and ternary inhibitor blends, the effectiveness of which is equal to that of sodium chromate, sodium nitrite, sodium molibdate that alone and used at a high level.

Key Words: Corrosion, Inhibitor, Carbon Steel

1. INTRODUCTION

Metal use of countries increases with technologic and economic development. However, destruction of metals by environmental factors is the main problem for the industrial companies. Metal and alloys that come into contact with water are susceptible to corrosion because of their thermodynamic instability in the cooling system. The common way for corrosion protection is to use durable material. But this way is impossible owing to economic causes in the complex and wide process such as, the cooling system. The most common way is to use inhibitor to reduce corrosion in this condition. The most effective and widely used inhibitors (sodium nitrit, molibdat etc.) have disadvantages such as high cost [1-3]. Chromates are the oldest and one of the most effective inhibitors available and have been widely used both in heating and cooling systems. Since 1970 regulations for preventing water pollution have become very severe in most countries; for example the permissible dosage of chromate based inhibitors used in cooling systems have been sharply reduced. Therefore considerable work has been undertaken to find other additives with which to synergise so allowing lower levels to be effectively used [4,5]. be made investigations on the multicomponent inhibitor mixtures with its low level for reaching optimum inhibitor effects.

One of the major limitations of a high nitrite level to treat open recirculating cooling systems is its susceptibility to bacterial degradation. This problem has been overcome with the use of non oxidizing biocides. This treatment however is economically unacceptable and the trend has been to lower the nitrite level by blending it with other suitable chemicals. Ortophosphates are used as anodic inhibitors. High level of phosphates can form insoluble salts and can also act as nutrients for algal growth. Phosphate concentration could be reduced by blending it with sodium nitrite (6. Molybdates [7-9] are now being increasingly used as anodic inhibitors especially because of their low order of toxicity. Besides its environmental acceptability, moliybdate gives

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multimetal protection, and is effective under more diverse water conditions, and is both thermally and chemically stable. Due to the high cost of molybdates, they are not used alone, but synergized with other inhibitors. From the review of the literature, it can be seen that the influence of multicomponent inhibitor mixtures has been somewhat more extensively investigated in the case of ferrous metals .The inhibitor effect of components was investigated depending on the temperature and pH [10]. From the review of the literature, it can be seen that the many specific, and blended, chemical inhibitors are commonly utilized in cooling water treatment programs for control of corrosion [11].

2. EXPERIMENTAL METHOD

Working electrodes were prepared from carbon steel having % 0.18 C, % 0.04 S, % 0.03 Si, % 0.05 Mn, % 0.15 Ni and % 0.05 Mo. The rods were cut into slices 20 mm in length. Copper wires were threaded to the back of the specimens after the wire was enclosed in a glass sleeve and the specimen was completely embedded in an epoxy resin cured at 70 ^{0}C. Boundaries between metal surface and epoxy resin were carefully shielded with a resin paint. The exposed surface area was a circle of about 0.785 cm^2. Prior to each experiment specimens were ground with alumina. They were degreased with acetone and washed in water. A conventional three electrode system using platinum counter electrode and saturated calomel reference electrode (SCE) were employed. All potentials are referred to the (SCE). The oxygen content of the solutions was limited to that from natural aeration. A heating magnetic stirrer was used for agitation and controlling the temperature at 25 ^{0}C with a thermistor probe in conjunction with it. NaOH was used to adjust the pH of the solutions prepared with distilled water and reagent grade chemicals. All the experiments were repeated to verify their reproducibility.

Potentiostatic polarization measurements were obtained using EG&G Model 362 Scanning Potentiostat. A Servagor 120 X-Y recorder was used for simultaneous measurement of potential and current. After open-circuit stand, electrodes were polarized with a scan rate of 1mV/s. The cathodic curves from the potentiodynamic polarization experiments were used to identify the action of the individual and mixed components of the inhibitor blends.

3. RESULT AND DISCUSSION

Single Component System

In order to examine the influence of foreign ions on the corrosion rate of carbon steel, sodium moliybdate (SM), sodium chromate (SC), sodium nitrite (SN), sodium tetraborate (STB), sodium orthophosphate (SOP), ascorbic acid (AA), sodium benzoate (SB), calcium acetate (CA) were added to the 100 ppm sodium chloride solution in the range 10 ppm-100 ppm.

Although the corrosion currents were obtained both by extrapolation of the Tafel slope of cathodic polarization curve to the corresponding corrosion potential and linear polarization method, the values obtained by Tafel slope of cathodic polarization method were given in all the tables. Table 1 summarize the results obtained from polarization runs in the solutions of pH 7. It was found that the addition of inhibitors decreases the corrosion current with respect to the uninhibited case.

The inhibition efficiency (*I*) is represented in the usual manner as a percentage:

$$\%I = \frac{i_0 - i}{i_0} x100$$

where i_0 and i are the uninhibited and inhibited corrosion currents, respectively.

For the one component inhibitor studies, the best inhibitor effects were found to be % 93 for solution containing 10 ppm chromate, % 95 for 50 ppm nitrite and % 90 for solution with 50 ppm molybdate.

The relative effectiveness of the inhibitors is:

SN $\geq$ SC> SM> SB> CA> AA> SOP> STB

From the Table 1, it can be seen that the efficiency of nitrite and chromate are approximately the same but the amount of nitrite is 5 times that of chromate.

Nitrite concentration levels of 500-1000 ppm are commonly cited in the literature for cooling systems which have a total aggressive ion concentration of about 200 ppm. The present study indicates that lower levels of nitrite (50 ppm for 100 ppm NaCl) are required for carbon steel. Molybdate is efficiency as nitrite and chromate in the literature [12]. In this study it was observed that the efficiency of molybdate approaches to that of sodium nitrite.

Two Component Systems

Table 2 shows the corrosion currents in 100 ppm NaCl solution at pH=7 with different concentration ratios of the given inhibitors at a constant total inhibitor concentration of 10 ppm. As can be seen from this table, the degree of inhibition varies depending upon the type and the components in the mixture. From the binary inhibitor studies, it was found that the inhibitor effects were %95 for solution with 8 ppm nitrite+2 ppm ascorbic acid, % 97 with 1 ppm chromate+9 ppm molybdate.

Table 1. Inhibition efficiencies in solutions containing 100 ppm NaCl and inhibitor at 25^{0}C and pH=7.

Inhibitor	**Concentration (ppm)**	**Corrosion Potential**	**Corrosion Rates**	**Inhibitor Efficiency**
		(mV_{SCE})	(μA) / c m^2	(%)
No added	0	-300	19.1	-
SM	50	-282	1.9	90
SC	10	-282	1.4	93
SN	50	-190	1.0	95
STB	10	-249	8.3	57
SB	100	-265	3.7	81
CA	100	-278	4.5	77
SOP	10	-283	6.0	67
AA	5	-272	5.7	70

Table 2. Effect of binary inhibitor mixtures at total amount of 10 ppm on corrosion of Carbon steel in 100 ppm NaCl solutions at 25 ^{O}C and pH=7.

Inhibitor Compositions	**Ratio of Components**	**Corrosion Potential**	**Corrosion Rates**	**Inhibitor Efficiency**
		(mV_{SCE})	(μA) / c m^2	(%)
SC+SM	1:9	-240	0.6	97
	5:5	-264	1.9	90
SC+CA	5:5	-304	1.3	93
	1:9	-299	1.9	90
SC+SB	8:2	-306	1.0	95
	5:5	-276	1.3	93
	1:9	-275	1.9	90
SN+SB	5:5	-194	1.3	93
	1:9	-220	2.5	87
	8:2	-215	0.9	95
SN+SOP	8:2	-263	2.9	89
	5:5	-260	2.5	87
	1:9	-285	3.6	81
SOP+AA	8:2	-270	3.8	80
	2:8	-287	5.1	73
	5:5	-274	5.7	70
SN+AA	8:2	-222	1.0	95
	5:5	-235	2.0	89
	2:8	-266	3.2	83
SN+SM	8:2	-231	1.7	91
	5:5	-193	1.9	90
	1:9	-222	1.7	91
SM+SB	2:8	-256	2.5	87
	8:2	-230	1.9	90

In practice, inhibitor mixtures are used frequently to take the advantage of available synergism and to protect systems containing several metals. Molybdate is almost always used with one or more synergists for improved efficiency and cost-effectiveness. Molybdate-nitrite is reported to provide effective inhibition for steel and aluminum alloys. This pair of anodic inhibitors has been used in automotive antifreeze, cooling systems and coal-water slurries. A study of this combination [8] in an aggressive cooling tower water indicated that at least 2.5 mg/L oxygen is needed to be present for the synergism to be operative. Use of SN&SM to gather improves the individual efficiency of these two substances. Mixture of 10 ppm concentration produces the same effect as 50 ppm SN. Chromate, a strongly oxidizing anodic passivator, is also synergistic with molybdate in inhibiting ferrous and nonferrous metal corrosion [13,14]. The result of this study indicates also that the chromate enhances the efficiency of molybdate in chloride containing solutions. The effectiveness of these solutions in all ratios are higher than that of the solution containing molybdate alone.

Addition of sodium chromate and sodim nitrite to other inhibitors tried improved the individual efficiency of the latter components (Table 2).

Three Component System

Multi component inhibitor systems were formulated to see if there was a synergistic effect between the selected inhibitors. The inhibitor mixtures and the ratios of the components are given in Table 3. For all three component mixtures the total inhibitor concentration was kept constant at 10 ppm. In these formulations, the amount of sodium chromate and sodium nitrite was kept at low levels because of environmental contamination.

In conclusion, ternary inhibitor blends that alternate single and two component system were investigated. The best inhibitor effect (%97) was blends of 1 ppm chromate + 6 ppm nitrite + 3 ppm molybdate. This combination is more economic than the single and two component systems that used high level of molybdate. The system that 1 ppm chromate + 3 ppm acetate+6ppm molybdate and 1 ppm nitrite + 8 ppm molybdate + 1 ppm orthophosphate appear also to be alternatives to single and two component systems that used high levels of nitrite and chromate.

Table 3. Effect of ternary inhibitor mixtures at total amount of 10 ppm on corrosion of Carbon steel in 100 ppm NaCl solutions at 25 ^{o}C and pH=7.

Inhibitor Compositions	Ratio of Components	Corrosion Potential	Corrosion Rates	Inhibitor Efficiency
		(mV_{SCE})	$(\mu A)/cm^2$	(%)
SC+SOP+AA	1:8:1 1:1:8	-247 -258	1.9 2.5	90 87
SC+SM+SOP	1:3:6 1:6:3	-238 -244	1.1 0.9	94 95
SC+SOP+STB	1:3:6 1:6:3	-291 -272	3.8 3.2	80 83
SN+SM+CA	2:4:4 2:2:6 2:6:2	-224 -227 -308	1.3 2.5 1.1	94 88 95
SN+CA+SOP	2:2:6 2:6:2	-263 -266	1.9 2.5	91 88
SC+CA+SM	1:4:5 1:6:3 1:3:6	-300 -250 -270	0.9 1.5 0.8	95 92 96
SC+SN+SM	1:3:6 1:6:3	-250 -248	0.6 0.5	97 97
SN+SM+SOP	2:6:2 1:8:1	-239 -240	2.0 1.5	89 92

Effect of Temperature and pH

The inhibitor effect of some one component, binary and ternary inhibitor blends was investigated depending on the temperature and pH (Table 4). The inhibitor effect decreased by increasing temperature. For pH 7& pH 9, efficiencies of the inhibitors are approximately the same. For almost all the inhibitor compositions with those values for pH 7 & pH 9.

Table 4. The inhibitor effect of binary and ternary inhibitor blends was investigated depending on the temperature and pH.

Inhibitor Compositions		Corrosion Potential (mV_{SCE})	Corrosion Rates $(\mu A)/cm^2$	Inhibitor Efficiency (%)
SM (50 ppm)	T=30 °C	-250	2.4	88
	T=40 °C	-262	3.9	84
	T=50 °C	-268	5.2	83
	pH=5	-254	3.0	86
	pH=7	-282	1.9	90
	pH=9	-224	1.0	93
SN (8 ppm) + SB (2 ppm)	T=30 °C	-270	1.6	92
	T=40 °C	-285	2.9	88
	T=50 °C	-282	4.7	84
	pH=5	-230	4.7	78
	pH=7	-215	0.9	95
	pH=9	-225	1.0	93
SN (2 ppm) + SM (6 ppm) + CA (2 ppm)	T=30 °C	-267	3.2	84
	T=40 °C	-290	4.4	83
	T=50 °C	-305	5.9	81
	pH=5	-280	5.1	76
	pH=7	-308	1.1	95
	pH=9	-265	0.9	94

4. CONCLUSION

In conclusion, for one component inhibitor studies, the best inhibitor effects were found to be % 93 for solution containing 10 ppm chromate, % 95 for 50 ppm nitrite and % 90 for solution with 50 ppm molybdate. At the binary inhibitor studies, it was found that the inhibitor effects were %95 for solution with 8 ppm nitrite+2 ppm ascorbic acid, % 97 with 1 ppm chromate+9 ppm molybdate. For 3 component mixtures, the best inhibitor effect (%97) was for blends of 1ppm chromate +6ppm nitrite+3 ppm molybdate. This combination is more economic than the single and two component systems that used high level molybdate. The mixture composed of 1ppm chromate +3ppm acetate+6ppm molybdate and 1ppm nitrite +8ppm molybdate +1ppm ortopophate appear also as attractive alternatives to single and two component systems that used high level nitrite and chromate. The inhibitor effect decreased by increasing temperature. Inhibitor efficiency in both neutral and basic environment are the same but it decreased in acidic medium. The use of sodium chromate or sodium nitrite increased the efficiency of individual components.

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