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Electrochemical Studies of Corrosion Inhibitors

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TECHNICAL PAPER

ELECTROCHEMICAL STUDIES OF CORROSION INHIBITORS

I. INTRODUCTION

Although the mechanism of the action of inhibitors, when studied by electrochemical methods, may be different from that in weight-loss methods over a period of time, it is of interest to see how the methods compare in the evaluation of corrosion inhibitors. For example, the electrochemical method may not properly account for the incubation time, or for the period required for breakdown of any oxide film or formation of a protective layer on the specimen surface. This is particularly true in the case of aluminum. Electrochemical results, when based on a single determination after a very short exposure to the inhibitor solution, are subject to this effect. However, such shortcomings may be overcome with several measurements made over a period of days, provided that the proper method is employed in the electrochemical technique. The polarization resistance method is ideal for this purpose since it employs very low currents which have little effect on the sample surface, making repeated measurements possible. This electrochemical technique has been described [1,2].

The effectiveness of single salts as corrosion inhibitors in various media was determined in this work, with measurements being made on both steel and aluminum samples. The effectiveness of multicomponent mixtures was also investigated, and results are compared to those obtained by the weight-loss method. A study of molybdate-containing inhibitors for steel and aluminum was carried out, as well as a study of inhibitors consisting of other chemical mixtures and the effect of oxygen on corrosion rates was determined for type 1010 steel, copper, and 5052 aluminum alloy. A study was also made of the corrosion inhibition for steel using a mixture of borax ($Na_2B_4O_7$) and sodium nitrite ($NaNO_2$) (each 0.03M). These results are compared to those by the weight-loss method.

II. EXPERIMENTAL

The sample holder employed is shown in figure 1. Samples, which consisted of circular disks 1.43 cm (9/16 in) in diameter and approximately 0.16 cm (1/16 in) in thickness, were prepared for study by wet sanding on 400-grit silicon carbide paper and subsequent degreasing in boiling trichloroethylene. The samples were mounted in this holder and immersed in the appropriate medium for at least 1 hour before polarization resistance measurements were made. The EG&G-PARC model 350A corrosion measurement console was employed for the collection of data. Data were collected at 0.5 mV intervals at a scan rate of 0.1 mV/s. The measurement range for all determinations was from –20 mV to +20 mV with respect to E_{CORR}, the normal corrosion potential of the sample in a given medium. The data were stored on disk and then transferred to computer memory for calculation of I_{CORR}, from which corrosion rates are determined [1,2], using the program POLCURR [3]. Polarization resistance measurements were made first on a blank (no inhibitor present) and then on a sample immersed in the inhibitor-containing medium (sea water, salt water, corrosive water, etc.). The corrosive water contained 148-ppm sodium sulfate, 165-ppm sodium chloride, and 138-ppm sodium bicarbonate added to deionized water. The percent inhibition was determined by:

percent inhibition = (corrosion rate in blank − corrosion rate in inhibitor)/(corrosion rate in blank) × 100.

For determination of oxygen effects, corrosion cells were purged with air to produce an oxygen-rich environment or with dry nitrogen to produce an oxygen-free environment.

III. RESULTS AND DISCUSSION

A. Single Salts

The corrosion inhibitions exhibited by single salts for type 1010 steel in 3.5-percent salt water are shown in table 1. All salts investigated are good corrosion inhibitors for steel except borax ($Na_2B_4O_7$) and sodium nitrate ($NaNO_3$). The percent inhibition by $NaNO_3$ was actually negative.

Inhibitions for type 5052 aluminum in the same medium by the same salts are listed in table 2. In this case, sodium nitrite ($NaNO_2$), sodium chromate (Na_2CrO_4), and sodium nitrate ($NaNO_3$) give acceptable results, while sodium silicate (Na_2SiO_3), borax ($Na_2B_4O_7$), and sodium phosphate (Na_3PO_4) are unacceptable. Na_3PO_4 gave a negative value for the percent corrosion inhibition in this case. Thus, $NaNO_2$ and Na_2CrO_4 are excellent corrosion inhibitors for both steel and aluminum while $NaNO_3$ is acceptable for aluminum but not for steel. The reverse is true for Na_2SiO_3, which is acceptable for steel but not for aluminum.

Caution must be exercised on inhibitor effects in the case of aluminum alloys. The samples were exposed to the medium for only 1 hour before determination of the corrosion rates. Often, several hours or several days are required for the inhibitor to have an effect. However, those inhibitors which show high effectiveness after only a short exposure can generally be accepted without too many reservations.

B. Molybdate-Containing Inhibitors

This work was undertaken to study the use of electrochemical techniques for evaluating low toxicity corrosion inhibitors for use in hot water systems. The basic inhibitor ingredient is sodium molybdate. Tests were made with four solutions having different sodium molybdate containing inhibitors, the composition of which are shown in table 3. All tests were made using corrosive water as the medium. Results for solutions 1 through 4 (table 3) are shown in table 4 for type 1010 steel. Studies were made at 30 and 60 °C. As shown in table 4, corrosion inhibition at both temperatures is excellent for all solutions.

Results for the inhibition of corrosion for type 5052 aluminum by sodium molybdate ($NaMoO_4$) containing solutions are listed in table 5. The percents inhibition for solutions 2 and 4 are both excellent and immediate at 30 and 60 °C. Both of these solutions contain sodium silicate. It is apparent that sodium silicate is necessary to form a protective layer on the aluminum surface at a rapid rate in order to reduce the corrosion rate quickly.

The corrosion rate for solution 1 shows a great increase over that for corrosive water, but declines with time, as shown by figure 1. The corrosion rate drops rapidly during the first 6 hours and decreases slowly thereafter, reaching a rate of 0.786 mils/year after a period of 24 hours. The rate eventually drops to about the rate observed for solutions 2 and 4. Thus, an incubation period is required to obtain effective inhibition.

The change in corrosion rate for solution 3 is shown in figure 2 as a function of time at 30 °C. The rate of corrosion in this case increases from 6.3 mils/year to 7.75 mils/year during the first 3 hours of sample immersion. The corrosion rate drops beyond that point, reaching a value of 2.2 mils/year after about 24 hours. The corrosion rate thus drops more slowly than that for solution 1 and yet does not approach the values obtained for solutions 2 and 4. It appears that the presence of $Na_2B_4O_7$ in solution 3 actually enhances the corrosion rate for a rather long period of time. However, when Na_2SiO_3 is added to this solution, the corrosion rate drops immediately, as evidenced by the result obtained for solution 4. Thus inhibitors 1, 2, and 4 are effective for 5052 aluminum alloy, with an induction period being required for inhibitor 1.

It was found in weight-loss methods [4], where multimetallic samples (1100 aluminum, type 1010 steel, and 321 stainless steel) in electrical contact were placed in hot water (82 °C) for a period of 1 year, that all inhibitor solutions were effective for type 1010 steel, in agreement with the electrochemical results. However, in the case of 1100 aluminum, only solutions 1 and 4 were effective in the multimetallic system, with solution 1 being the most effective. This is compared to the electrochemical results, which indicated that solutions 1 and 4 were effective, but also included solution 2. However, it must be remembered that the electrochemical determinations were made on 5052 aluminum only, while the weight-loss tests were made on electrically connected multimetallic systems.

C. Corrosion Inhibition by 0.03M $Na_2B_4O_7$ Plus 0.03M $NaNo_2$

This study was undertaken to supplement other tests carried out by conventional methods, wherein type 1010 steel samples were immersed in solutions containing the inhibitor for a period of 14 months and corrosion effects determined by the weight-loss method [5]. Electrochemical tests were made on type 1010 steel samples immersed in inhibitor solutions prepared using tap water, deionized water, or corrosive water. Results are shown in table 6. In all three cases, the effectiveness of the inhibitor in preventing corrosion is excellent. These results are in agreement with those from the weight-loss method, in which no corrosion was observed over the 14-month immersion period.

D. The Effect of Oxygen on Corrosion Inhibition

The effect of substitution of a nitrogen-purged for an air-purged system is quite dramatic. The corrosion rates in corrosive water (H_2O) for air-purged and nitrogen-purged systems are shown in table 7. The corrosion rates for 1010 steel and copper are decreased considerably in the nitrogen-purged system, while the corrosion rate for aluminum is greatly increased. These results indicate that the absence of oxygen has a favorable effect in inhibiting the corrosion rates of type 1010 steel and copper, but a negative effect in inhibiting the corrosion rate of 5052 aluminum alloy. This may be understood by considering the ways with which corrosion of aluminum can occur. Two mechanisms are thermodynamically possible.

(1) $4Al + 3O_2 + 6H_2O = 4Al(OH)_3 \quad E^{o}_{Cell} = 2.06V$

(2) $2Al + 6H_2O = 6Al(OH)_3 + 3H_2 \quad E^{o}_{Cell} = 0.832V.$

The potential of the first reaction is greater than that for the second reaction, so that corrosion proceeds by that mechanism when oxygen is present. However, when the oxygen supply is depleted, the second reaction predominates. Reaction (2) proceeds at a much faster rate than reaction (1), so that the corrosion rate is increased in the absence of oxygen.

Inhibitor solution number 4 (table 3) was selected as the medium for investigating the effect of oxygen on the effectiveness of inhibitors. As table 7 shows, the corrosion rates for copper are by far the lowest in the nitrogen-purged inhibitor solution, and it would suggest that copper systems be kept as air-free as possible.

The percent inhibition in air-purged and nitrogen-purged solution 4 in corrosive H_2O is shown in table 8 and is based on the corrosion rates observed in air-purged and nitrogen-purged corrosive H_2O at the corresponding temperatures. Generally, the percent inhibition is comparable for the air-purged and nitrogen-purged systems, although the corrosion rates are effected considerably.

E. Corrosion Inhibition by Chemical Mixtures in Corrosive Water

The effect of four different chemical mixtures on the inhibition of corrosion was investigated for type 1010 steel and 5052 aluminum alloy. The chemical mixture compositions are listed in table 9. Results are tabulated in table 10. These results show that all inhibitors are effective for type 1010 steel, in agreement with weight-loss studies [6], wherein samples were studied for a period of 1 year. For 5052 aluminum alloy, the electrochemical study indicated that mixture 1 was best, also in agreement with the weight-loss study. However, the weight-loss study indicated that mixture 3 was also effective, in disagreement with the electrochemical result. A study was therefore made for this inhibitor by the electrochemical method, using 2219-T87 aluminum alloy, as a function of time [7]. The curve is shown in figure 4. The corrosion rate drops rapidly from a very high initial value to about 0.002 mils/year after 30 days of exposure, bringing the weight-loss and electrochemical methods into agreement. The caution which must be exercised in studying the inhibition of aluminum corrosion electrochemically is again illustrated.

IV. CONCLUSIONS

As the results show, corrosion rates may be considerably affected by single salts, the effects of which may be much different for type 1010 steel and 5052 aluminum alloy. Molybdate-containing inhibitors are very effective in the prevention of steel corrosion. For aluminum, the effects vary. For the molybdate-containing solutions, a rapid decrease in corrosion rate is noted when Na_2SiO_3 is present. Caution must be exercised in the study of corrosion inhibitors for aluminum. Frequently an incubation period, which may be several hours or several days, is required for an inhibitor to become effective.

However, if an immediate decrease of corrosion rate is observed, the inhibitor can generally be considered effective. If the observed percent inhibition is 50.0 or less, the inhibitor can usually be considered ineffective. Steel almost always exhibits an immediate response to the addition of inhibitor.

In oxygen-free solutions, corrosion rates are greatly decreased for type 1010 steel and copper, but are increased for 5052 aluminum alloy. This is attributed to the two possible mechanisms by which aluminum can oxidize. However, corrosion inhibition is generally comparable for oxygen-rich and oxygen-free inhibitor solutions.

In general, the results of this study show that the electrochemical method is an effective means for screening inhibitors. However, in many cases, long-term exposure is necessary to establish inhibitor effectiveness, especially in systems containing more than one metal in electrical contact where electrochemical methods cannot be employed.

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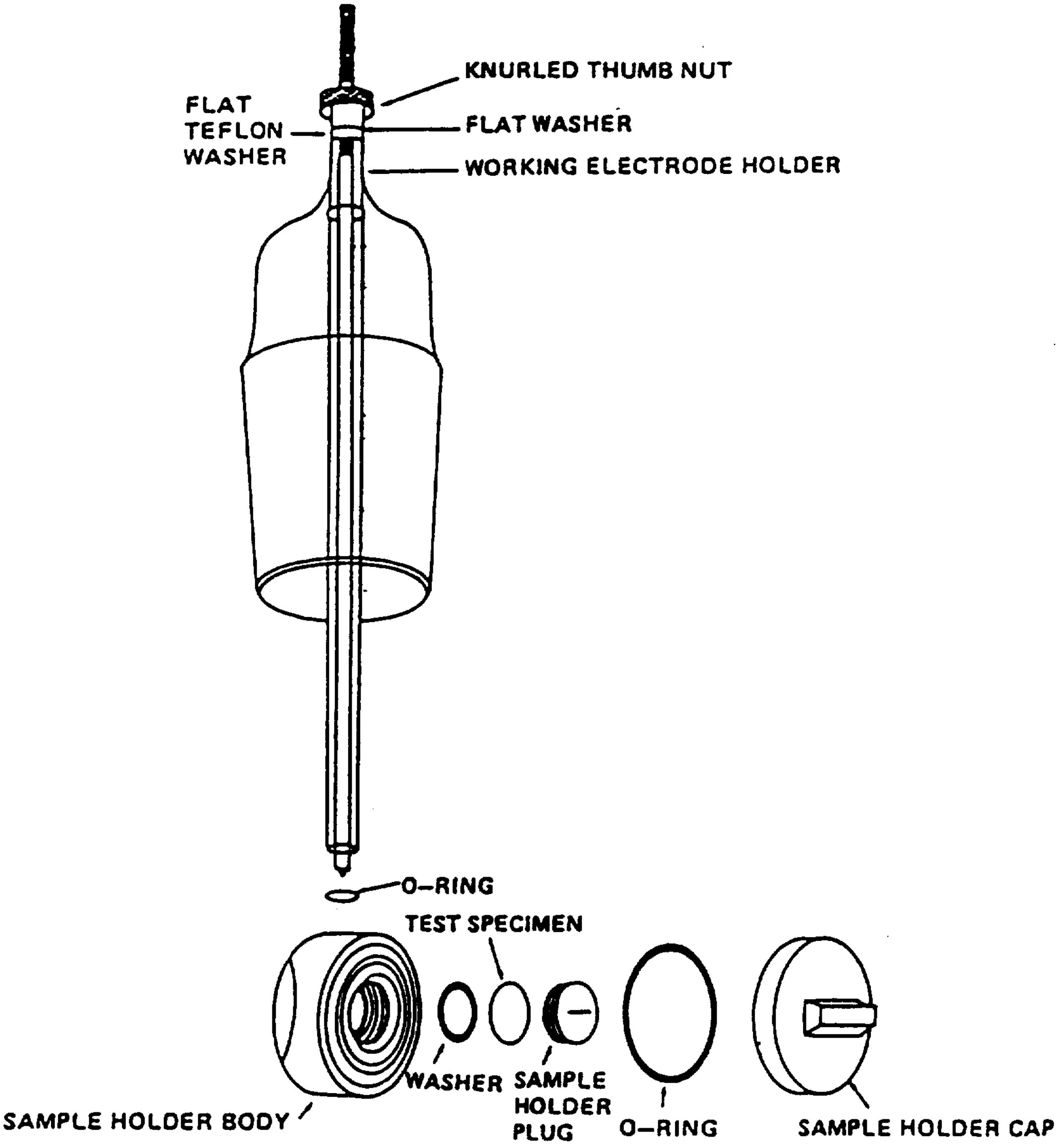

Figure 1. Exploded view of the sample holder.

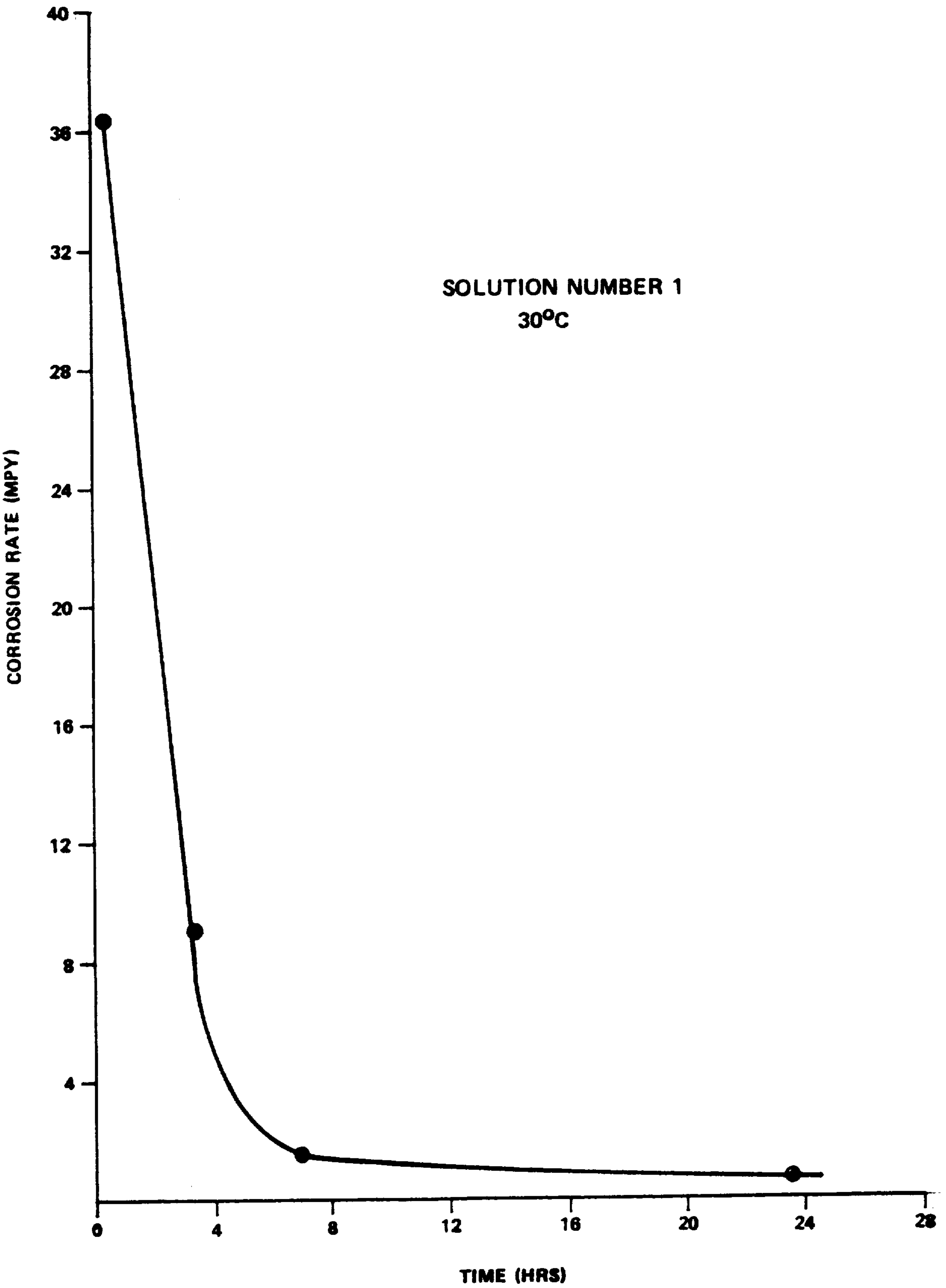

Figure 2. Corrosion rate as a function of time for solution number 1.

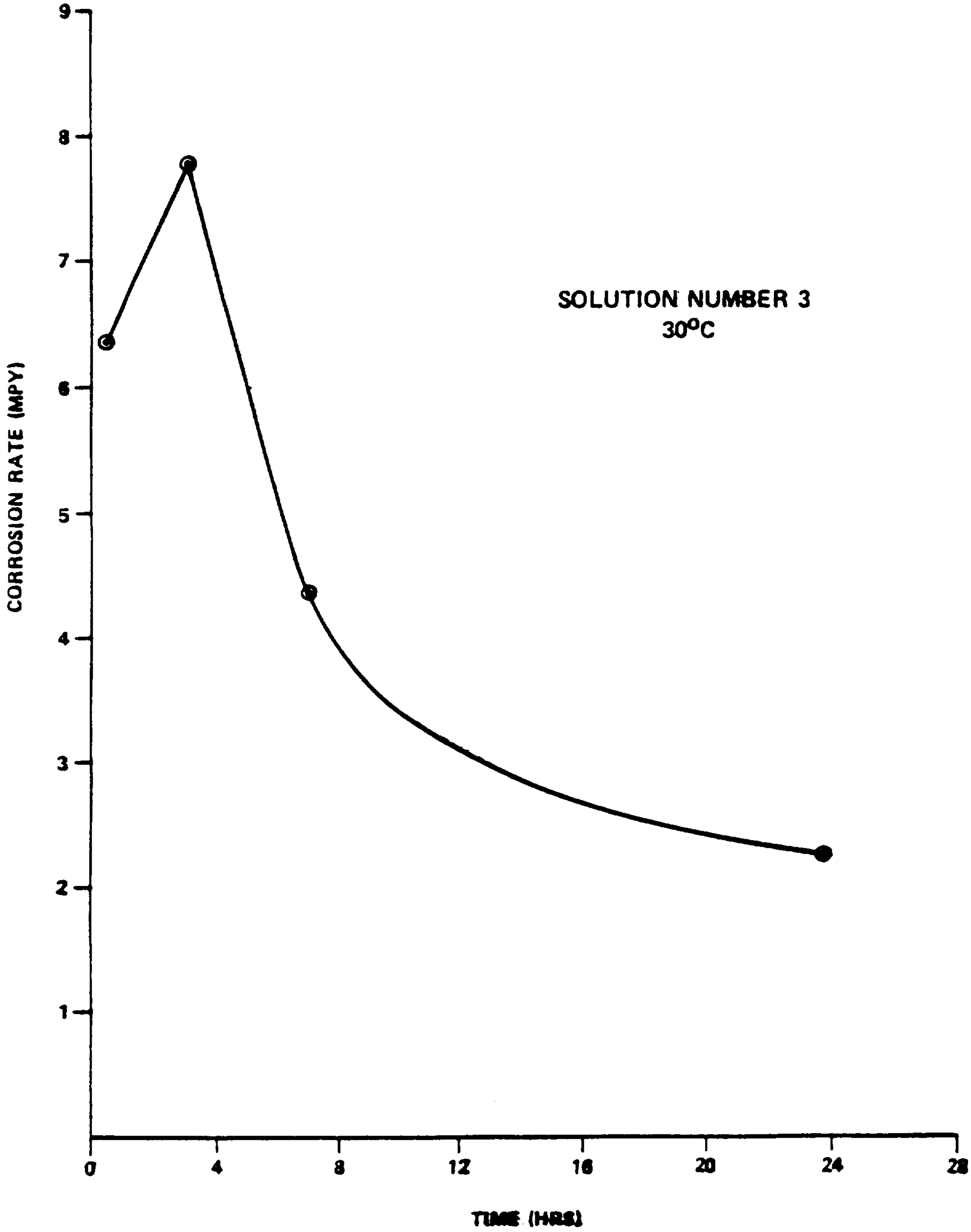

Figure 3. Corrosion rate as a function of time for solution number 3.

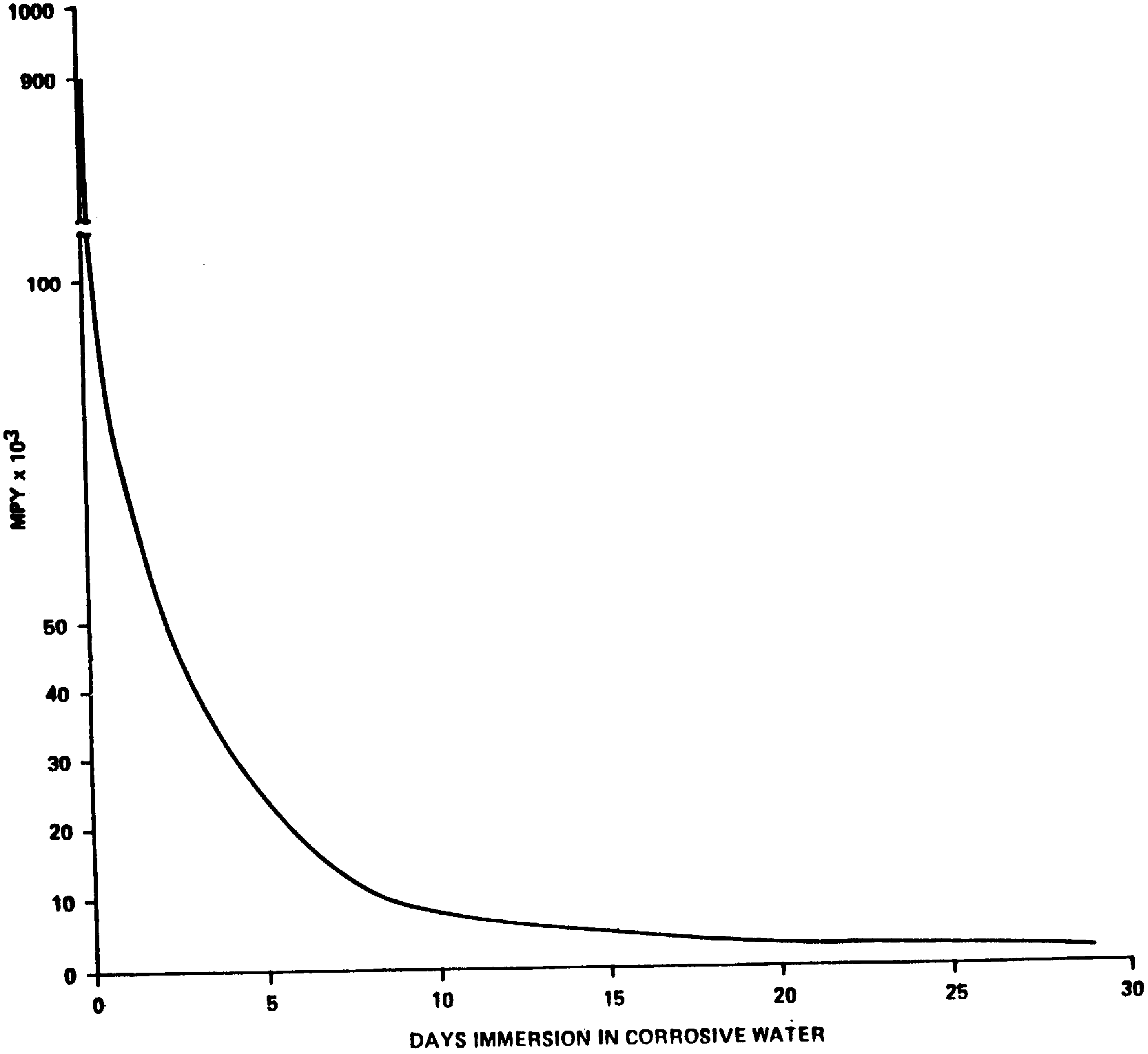

Figure 4. Corrosion rate of 2219-T87 aluminum with Mobay inhibitor in mils/year (MPY).

Table 1. Corrosion inhibition by single salts for type 1010 steel in 3.5% sodium chloride (NaCl).

Chemical*	Corrosion Rate mils/year	Percent Inhibition
$NaNO_2$	1.950	96.4
Na_2CrO_4	0.275	97.6
Na_2SiO_3	2.575	95.3
$Na_2B_4O_7$	26.12	52.1
Na_3PO_4	3.734	93.1
$NaNO_3$	112.7	--

* All solutions contain 1 percent salt.

Table 2. Corrosion inhibition by single salts for 5052 aluminum alloy in 3.5% NaCl.

Chemical*	Corrosion Rate mils/year	Percent Inhibition
$NaNO_2$	0.302	97.4
Na_2CrO_4	0.275	97.6
Na_2SiO_3	5.26	55.0
$Na_2B_4O_7$	7.648	34.6
Na_3PO_4	175.2	--
$NaNO_3$	0.324	97.2

*All solutions contain 1 percent salt.

Table 3. Composition of chemical inhibitors (gm/liter).

1. 1.2 $Na_2MoO_4 \cdot 2H_2O$, 1.0 $NaNO_3$, 2.0 NaMBT*, 2.3 $Na_3PO_4 \cdot 12H_2O$.

2. Number 1 plus 2.3 $Na_2SiO_3 \cdot 9H_2O$.

3. Number 1 plus 1.9 $Na_2B_4O_7 \cdot 10H_2O$.

4. Number 1 plus 2.3 $Na_2SiO_3 \cdot 9H_2O$ plus 1.9 $Na_2B_4O_7 \cdot 10H_2O$.

* Sodium Mercaptobenzothiazole.

Table 4. Inhibition of corrosion for type 1010 steel by sodium molybdate ($NaMoO_4$) containing solutions.

Solution	Corrosion Rate mils/year	Percent Inhibition
	A. 30°C	
Corrosive H_2O	21.24	--
1	0.128	99.4
2	0.102	99.5
3	0.313	98.5
4	0.108	99.5
	B. 60°C	
Corrosive H_2O	53.89	--
1	0.155	99.7
2	0.105	99.8
3	0.284	99.5
4	0.109	99.8

Table 5. Inhibition of corrosion for 5052 aluminum alloy by $NaMoO_4$ containing solutions.

Solution	Corrosion Rate mils/year	Percent Inhibition
	A. 30°C	
Corrosive H_2O	0.303	--
1	36.41	--
2	0.087	71.3
3	6.348	--
4	0.083	72.6
	B. 60°C	
Corrosive H_2O	7.948	--
1	81.27	--
2	0.071	99.1
3	67.92	--
4	0.052	99.3

Table 6. Corrosion rates and percents inhibition for type 1010 steel in inhibitor solutions containing 0.03M $Na_2B_4O_7$ plus 0.03M $NaNO_2$.

Solution	Corrosion Rate mils/year	Percent Inhibition
1. (a) Deionized H_2O	0.551	
(b) With Inhibitor	0.014	97.5
2. (a) Tap Water	3.948	
(b) With Inhibitor	0.091	97.7
3. (a) Corrosive H_2O	5.339	
(b) With Inhibitor	0.131	97.5

Table 7. Corrosion rates in air-purged and nitrogen-purged inhibitor solution number 4 for type 1010 steel, 5052 aluminum alloy, and copper.

Material	Air-Purge mils/year	Nitrogen-Purge mils/year
	A. 30°C	
1010 Steel	0.108	0.071
5052 Aluminum	0.083	0.159
Copper	0.162	0.029
	B. 60°C	
1010 Steel	0.109	0.095
5052 Aluminum	0.052	0.438
Copper	0.141	0.074

Table 8. Inhibition of corrosion in air-purged and nitrogen-purged inhibitor solution 4 for type 1010 steel, 5052 aluminum alloy, and copper.

Material	Percent Inhibition Air-Purge	Percent Inhibition Nitrogen-Purge
	A. 30°C	
1010 Steel	99.7	88.4
5052 Aluminum	81.6	95.0
Copper	93.5	83.0
	B. 60°C	
1010 Steel	99.8	75.9
5052 Aluminum	94.5	98.2
Copper	74.0	73.9

Table 9. Composition of chemical inhibitors in corrosive water (gm/liter).

1. 1.0 $NaNO_3$, 2.0 $Na_3PO_4 \cdot 12H_2O$, 2.5 NaMBT*, 3.0 $Na_2B_4O_7$, 1.0 $Na_2SiO_3 \cdot 9H_2O$, 1.0 NaOH (formulated by General Motors).

2. 1.5 $NaNO_3$, 2.0 $Na_3PO_4 \cdot 12H_2O$, 2.5 NaMBT*, 4.0 $Na_2B_4O_7$.

3. 20.0 Mobay Product OC2002-sodium benzoate base.

4. 3.7 $NaNO_2$, 1.9 Na_2HPO_4, 1.9 NaH_2PO_4.

* Sodium mercaptobenzothiazole.

Table 10. Corrosion rates and percents inhibition for type 1010 steel and 5052 aluminum alloy for corrosion inhibition by chemical mixtures.

Inhibitor Number	Corrosion Rate mils/year	Percent Inhibition
	A. 1010 Steel	
1	0.153	99.2
2	0.239	98.7
3	0.273	98.2
4	1.218	93.3
	B. 5052 Aluminum	
1	0.157	81.8
2	3.157	--
3	0.811	5.8
4	0.460	46.6

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16. Abstract

The effect of single salts, as well as multicomponent mixtures, on corrosion inhibition has been studied for type 1010 steel; for 5052, 1100, and 2219-T87 aluminum alloys; and for copper. Molybdate-containing inhibitors exhibit an immediate, positive effect for steel corrosion, but an incubation period may be required for aluminum before the effect of a given inhibitor can be determined. The absence of oxygen was found to provide a positive effect (smaller corrosion rate) for steel and copper, but a negative effect for aluminum. This is attributed to the two possible mechanisms by which aluminum can oxidize. Corrosion inhibition is generally similar for oxygen-rich and oxygen-free environments. The results of this study show that the electrochemical method is an effective means of screening inhibitors for the corrosion of single metals, with caution to be exercised in the case of aluminum.

17. Key Words (Suggested by Author(s))

Corrosion inhibitors, electrochemical methods,
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