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Conductance Measurements in Corrosion and Inhibition of Al and Al–Mn Alloy

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Studies were performed to determine the effect of 2-picoline, 3-picoline, 4-pyridinol, and 2-pyridinamine on the dissolution of untreated, anodized, and sealed aluminum and aluminum–manganese alloys at 30.0 and 40.0 °C. Conductance measurements were applied to evaluate the corrosion rate. A comparison was carried out between this newly suggested conductance method and other methods previously used to estimate the dissolution rate. This comparison shows of the reliability of this conductance method. A good correlation was observed between the basicity, structure, and the inhibition effect of all compounds investigated. The order of inhibition efficiency is increasing as: 2-pyridinamine>4-pyridinol>3-picoline>2-picoline. This order described above is consistent with the evidence that the oxidized specimens show higher inhibition in the presence of additives than sealed and untreated ones.

Several investigations have been carried out about the corrosion and inhibition of Al and its alloys in different media.[1—8] Many techniques were suggested for such investigations: e.g., Mylius thermometric, weight loss,[1—5] hydrogen evolution,[1—6] and polarization resistance technique.[2,5,7]

Antropov[9] concluded that the organic compounds should exhibit adsorbability at liquid–solid interfaces. Fink[10] suggested that corrosion inhibition caused by organic compounds could be attributed to the chemisorption of such compounds, which led to a significant increase in polarization of both anodes and cathodes, with consequent surface "equipotentialization" and diminshing corrosion. The inhibitive effects of pyridine, 2-picoline, 3-picoline, 8-quinolinol, and 2-pyridinamine were studied in acidic and alkaline media by Abou-El-Wafa.[11] He showed that these compounds are more effective in acidic media. A correlation is discussed between the basicity, structure and inhibition effect. We have investigated the effect of some Schiff bases on the dissolution rate of Al and Al–Mn alloy in 3 M HCl solution (1 M=1 mol dm^{-3}) using Mylius, hydrogen evolution and weight loss methods.[6] The rate of dissolution was found to be greatly inhibited. The compounds containing active centers are more adsorbable and consequently exhibit higher inhibition.

In the present work we compare the Mylius thermometric method, hydrogen evolution method, and a newly suggested conductance method. The conductance measurements were used to study the inhibition effect of some organic compounds on the untreated, anodized and sealed Al and Al–Mn alloys in HCL solution.

Experimental

Al (Mn=0.10%, Si=0.10%, and Fe=0.10%) and Al–Mn (Mn=2.00%, Si=0.10%, and Fe=0.10%) alloy sheets (of thickness 0.80 mm.) of surface area 1.0 cm×2.0 cm were degreased before each run using a solution containing Na_2CO_3 (25 g dm^{-3}), Na_3PO_4 (25 g dm^{-3}) and wetting agent (10 g dm^{-3}) for 5 min at 85.0 °C,[12] then washed with distilled water, and dipped in pickling solution (4 M HCl) for one minute followed by dippings in hot and cold distilled water.

An AC treatment of specimens was carried out in 90 ml of the 0.1 M anodizing acid solution (oxalic, phosphoric, or sulfuric acid) for 20 min at 30.0±1°C using a power supply connected with a transformer (0.0—250 V) under 50 V-ac. The advantages of the ac anodization process are that, by virtue of the rectification effect which takes place during the electrolytic treatment of Al and Al–Mn alloy, anodic films can grow at both electrodes during the anodic half-cycles without significant reduction during the intervening cathodic half-cycles. Consequently, both electrodes are anodized simultaneously and substantial thicknesses can be developed more rapidly than DC techniques.[13,14] Sealed specimens were prepared by boiling Al and Al–Mn sheets in 250 ml distilled water for 20 min.

Conductance measurements were carried out during the dissolution of specimens (untreated, sealed, or anodized specimens) in a special conductivity water jacket cell shown in Fig. 1. The two electrodes, which are of the same dimension and composition, were immersed in 20.0 ml solution of 3.00 M HCl and kept 2.0 cm apart. The temperature was adjusted at 30.0 °C by means of an ultra-thermostat. Conductance meter YSI Model 35 was used for these measurements.

All chemicals used were of Analar quality and were used

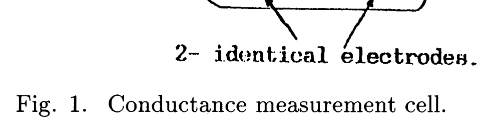

Fig. 1. Conductance measurement cell.

without further purification.

The Relations (T–τ), (V_H–τ), and (k–τ): An effective way to find whether there is any determinate error in the mean value of a set of experimental results or not is to compare the mean with the mean of some other experiment which has been determined at another time, with other equipment, by a different chemist or preferably by using a different procedure. In one test for consistency of experimental results, the two means are considered to be consistent (i.e., in agreement) if the difference between the means is less than the difference of standard deviations.[14,15] To evaluate the conductance method, the data obtained for each method were repeated twenty times in two series at different times (each series ten experiments). Figures 2, 3, and 4 show the relations T-τ (Mylius method) of untreated Al specimens in 3 M HCl, V_H–τ (hydrogen evolution method) of untreated Al specimens in 2 M HCl, and k–τ (conductance method) of untreated Al in 3 M HCl. A similar behavior was obtained for the sealed Al sample. The first look at these figures shows a distinct nonlinear behavior at first portion, then passing through a linear one after a certain activation period. The transition of the nonlinear into a linear character is mainly attributed to the leveling interaction of the different factors and the resultant compensating effect on the measured value (T, V_H, and k). The most probable factors are the HCl concentrations, the appearance and accumulation of Al^{3+}, the state of the surface and the temperature.

Regression Analysis and Statistical Treatment: All the data was statistically treated[14,15] and both series were compared within each method. The results obtained from each type of experiment were investigated based on the following relations:

(i) Linear regression: $x = A + By$ (1)

(ii) Logarithmic regression: $x = A + B \log y$ (2)

(iii) Power regression: $x = A\ y^B$ (3)

(iv) Exponential regression: $x = A\ 10^{By}$ (4)

where x is the time τ and y stands for ΔT, the rise in temperature in the Mylius method, V_H is the volume of evolved hydrogen in the hydrogen evolution method, and k is the value of conductance measured in the HCl solution based on the conductance method. The data obtained were treated using regression analysis for untreated Al and sealed Al specimens in corroding HCl medium using thermometric, hydrogen evolution and conductance methods. Tables 1 and 2 indicate examples for the data treatment of the first and second series of conductance measurements during the dissolution of untreated Al in 3 M HCl acid. In these tables are reported the values of A and B, the constants in Eqs. 1, 2, 3, and 4 together with r—the correlation coefficient, t—the student criterion (t test) and α—the level of significance. The correlation coefficient r is calculated from:

$$r = \frac{s_{x,y}}{s_x s_y}$$

$$r = \frac{n\sum xy - \sum x \sum y}{[\{n\sum x^2 - (\sum x)^2\}\{n\sum y^2 - (\sum y)^2\}]^{1/2}} \qquad (5)$$

where s- is the standard deviation and n is the number of x or y recorded through each experiment. For perfect positive or negative correlation $r=+1$ or -1 respectively. The student criterion t is estimated by using the following equation:[16)]

$$t = \left[\frac{r^2(n-2)}{(1-r^2)}\right]^{1/2} \qquad (6)$$

The level of significance α is obtained using tables of the percentage points of the t- distribution.[16)] It is quite clear from these tables that the conductance method can be expressed successively by a linear equation for the clear linear portion in the k–τ relationship and by a logarithmic equation for the first nonlinear portion. On the other hand, the power and exponential regressions give values of r and t which are unsatisfactory.

Statistical treatments were applied for the constants A and B in regression analysis of Eqs. 1 and 2 for data of both untreated and sealed Al, examined by the three methods. Two series of measurements in each method were concucted, and both series were compared within each method. For example, Tables 3 and 4 give the result of statistical treatment for untreated Al using the conductance method. In these two tables are given the values of a (the mean), s (standard deviation), s/a (the coefficient of variation), $s_{(\alpha1-\alpha2)}$ (the difference of the standard deviation) and $t_{(\alpha1-\alpha2)}$ (student criterion). $s_{(\alpha1-\alpha2)}$ and $t_{(\alpha1-\alpha2)}$ are determined as follows:

$$s_{(\alpha1-\alpha2)} = \left(s_{\alpha1}^2 + s_{\alpha2}^2\right)^{1/2} \qquad (7)$$

$$t_{(\alpha1-\alpha2)} = \frac{a_1 - a_2}{s_{(\alpha1+\alpha2)}}\left[\frac{n_1 n_2}{n_1 + n_2}\right]^{1/2} \qquad (8)$$

$$s_{(\alpha1+\alpha2)} = \left[\frac{\sum(x_1 - a_1)^2 + \sum(x_2 - a_2)^2}{n_1 + n_2 - 2}\right]^{1/2} \qquad (9)$$

where n_1 and n_2 are the number of experiments with the means a_1 and a_2 respectively. $s_{(\alpha1+\alpha2)}$ is the standard deviation of the combined experimental results, where x_1 and x_2 represent the individual experimental results of the first and second series given in Tables 3 and 4. From these tables it is obvious that the values of a, s, and s/a are in satisfactory agreement with each other in the two series in each method.

It is quite clear, from the regression analysis and the statistical treatment for the data obtained in these three methods, that there is an analogous behavior between them, and all the results are consistent. These results suggest the reliability of the newly suggested conductance method. This technique proved to be sufficiently accurate, sensitive and easy to perform.

Quantitative Treatment of Conductance Measurements Data: Conductance–time relation k,τ:

It was found from a regression analysis,[14,15] that the conductance–time (k,τ) relation could be expressed over a wide range of the clear nonlinear portion by the empirical formula

$$\tau = A + B \log k \qquad (10)$$

where A and B are constants, and k the measured conductance at time τ. A is the time needed for the conductance to reach $k=1.00$ milli mho, while B is the time required for raising the conductance from 1.00 to 10.0 milli mho. The constants A and B were replaced by a and b respectively in the conductance method. This replacement was necessitated by the nature of k itself, because at time $\tau=0.00$ k has a certain value k_o.

$$a = \tau(k_o + 1) = A + B \log(k_o + 1) \qquad (11)$$

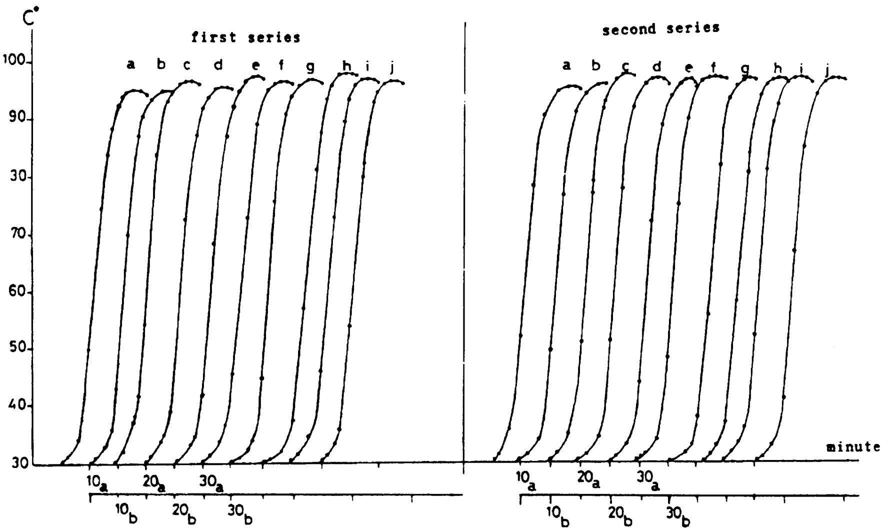

Fig. 2. T–τ curves for the two series of untreated Al in 3.00 M HCl at initial temperature t_0=30.0°C. Scale -a for the curve a, scale -b for the curve b...j.

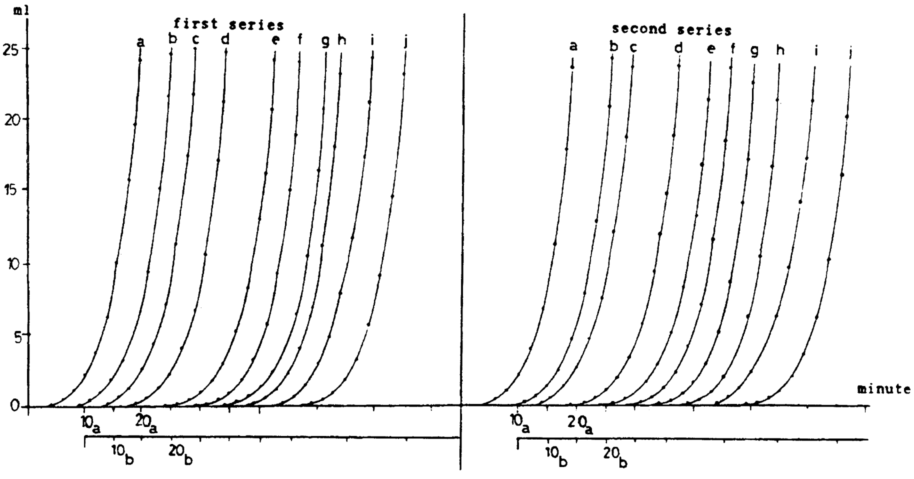

Fig. 3. V_H–τ curves for the two series of untreated Al in 2.00 M HCl at 30.0 °C. Scale -a for the curve a, scale -b for the curve b...j.

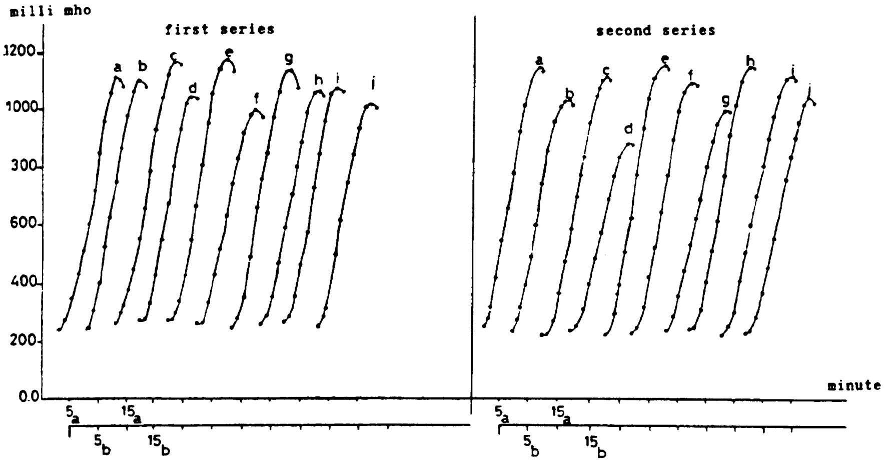

Fig. 4. k–τ curves for the two series of untreated Al in 3.00 M HCl at 30.0 °C. Scale -a for the curve a, scale -b for the curve b...j.

Table 1. Values of A, B, r, t, and α for Conductance Method Measurements during the Dissolution of Untreated Al of the First Series in 20.0 ml, 3.00 M HCl at 30.0 °C

No.		Power regression $\tau=A\,k^{B}$	Exponential regression $\tau=A\,10^{Bk}$	Logarithmic regression $\tau=A+B\,\log k$	Linear regression $\tau=A+B\,k$
	A	0.00759	2.10	−23.3	2.27
	B	1.11	0.00107	11.1	0.0092
1	r	0.986	0.751	0.998	0.998
	t	8.36	1.61	22.3	35.3
	α	0.01—0.02	0.10—0.25	0.002—0.01	0.00—0.001
	A	0.00134	0.921	−23.5	1.44
	B	1.38	0.00188	11.0	0.00878
2	r	0.888	0.870	0.941	0.999
	t	2.73	2.50	3.93	44.7
	α	0.01—0.25	0.10—0.25	0.05—0.10	0.00—0.001
	A	0.00392	1.33	−26.2	2.08
	B	1.21	0.00151	12.2	0.00868
3	r	0.981	0.968	0.994	0.996
	t	7.15	5.46	12.8	24.9
	α	0.01—0.02	0.02—0.05	0.002—0.01	0.00—0.001
	A	0.000207	0.696	−29.5	1.46
	B	0.168	0.00207	13.2	0.00822
4	r	0.875	0.859	0.930	0.999
	t	2.56	2.37	3.58	44.7
	α	0.10—0.25	0.10—0.25	0.05—0.10	0.00—0.001
	A	0.00606	1.32	−21.5	1.67
	B	1.11	0.00137	10.1	0.00786
5	r	0.988	0.977	0.997	0.999
	t	6.40	4.58	12.9	44.7
	α	0.05—0.10	0.10—0.25	0.02—0.05	0.00—0.001
	A	0.00000652	0.311	−36.6	0.669
	B	2.31	0.00344	16.2	0.00101
6	r	0.831	0.829	0.881	0.999
	t	1.49	1.48	1.86	50.0
	α	0.25—0.50	0.25—0.50	0.25—0.50	0.00—0.001
	A	0.00356	1.19	−23.8	1.73
	B	1.24	0.00176	11.3	0.00855
7	r	0.966	0.952	0.982	0.996
	t	3.74	3.11	5.20	24.9
	α	0.10—0.25	0.10—0.25	0.10—0.25	0.00—0.001
	A	0.000758	0.910	−29.2	1.39
	B	1.51	0.00215	13.8	0.00966
8	r	0.969	0.958	0.984	0.998
	t	3.92	3.34	5.52	38.7
	α	0.10—0.25	0.10—0.25	0.10—0.25	0.00—0.001
	A	0.0000139	0.367	−33.5	1.16
	B	2.15	0.00298	14.8	0.00821
9	r	0.912	0.902	0.948	0.999
	t	2.22	2.09	2.89	44.7
	α	0.25—0.50	0.25—0.50	0.10—0.25	0.00—0.001
	A	0.00691	1.31	−20.9	1.32
	B	1.11	0.00151	10.0	0.00923
10	r	0.993	0.983	0.999	0.999
	t	8.41	5.35	22.3	50.0
	α	0.05—0.10	0.10—0.25	0.02—0.05	0.00—0.001
$\bar{r}$		0.939	0.905	0.965	0.998

(A) Constant term. (B) Regression coefficient. (r) Correlation coefficient. (t) Student criterion. (α) Level of significance.

Table 2. Values of A, B, r, t, and α for Conductance Method Measurements during the Dissolution of Untreated Al of the Second Series in 20.0 ml, 3.00 M HCl at 30.0 °C The meaning of each symbol is same as that in Table 1.

No.		Power regression $\tau=A\ k^B$	Exponential regression $\tau=A\ 10^{Bk}$	Logarithmic regression $\tau=A+B\ \log k$	Linear regression $\tau=A+B\ k$
1	A	0.00118	0.765	−19.6	0.558
	B	1.35	0.00176	9.04	0.00821
	r	0.988	0.974	0.998	0.999
	t	6.40	4.31	15.5	44.7
	α	0.05—0.10	0.10—0.25	0.02—0.05	0.00—0.001
2	A	0.000804	0.680	−20.5	0.868
	B	1.43	0.00203	9.48	0.00835
	r	0.998	0.992	0.999	0.999
	t	15.8	7.86	22.3	38.7
	α	0.02—0.05	0.05—0.10	0.02—0.05	0.00—0.001
3	A	0.0000021	0.236	−40.1	1.78
	B	2.58	0.00454	18.1	0.00873
	r	0.825	0.824	0.876	0.999
	t	1.46	1.45	1.82	50.0
	α	0.25—0.50	0.25—0.50	0.25—0.50	0.00—0.001
4	A	0.928	0.401	−31.1	0.702
	B	2.06	0.00322	14.1	0.0108
	r	0.928	0.917	0.959	0.999
	t	2.49	2.3	3.38	44.7
	α	0.10—0.25	0.25—0.50	0.10—0.25	0.00—0.001
5	A	0.0238	1.60	−16.0	2.17
	B	0.897	0.00128	8.09	0.00752
	r	0.997	0.987	0.999	0.998
	t	12.9	6.14	22.3	31.6
	α	0.02—0.05	0.10—0.25	0.02—0.05	0.00—0.001
6	A	0.000112	0.507	−27.2	1.36
	B	1.82	0.00284	12.5	0.00866
	r	0.924	0.911	0.957	0.998
	t	2.42	2.21	3.30	31.6
	α	0.05—0.10	0.05—0.10	0.02—0.05	0.00—0.001
7	A	0.00407	1.17	−23.1	0.960
	B	1.21	0.00179	11.0	0.0114
	r	0.992	0.986	0.999	0.999
	t	7.86	5.91	22.3	44.7
	α	0.05—0.10	0.10—0.25	0.02—0.05	0.00—0.001
8	A	0.0000101	0.305	−35.1	1.67
	B	2.25	0.00368	15.7	0.00823
	r	0.848	0.860	0.896	0.996
	t	1.60	1.69	2.02	22.3
	α	0.25—0.50	0.25—0.50	0.25—0.50	0.00—0.001
9	A	0.00272	1.11	−24.8	1.65
	B	1.30	0.00203	11.9	0.011
	r	0.974	0.962	0.988	0.999
	t	4.30	3.52	6.40	50.0
	α	0.10—0.25	0.10—0.25	0.05—0.10	0.00—0.001
10	A	0.000165	0.276	−21.2	1.03
	B	1.79	0.00403	10.2	0.0106
	r	0.813	0.831	0.998	0.999
	t	1.40	1.49	15.8	50.0
	α	0.25—0.50	0.25—0.50	0.02—0.05	0.00—0.001
$\bar{r}$		0.929	0.924	0.967	0.998

Table 3. Values of a, s, s/a, $s_{(\alpha_1-\alpha_2)}$, and $t_{(\alpha_1-\alpha_2)}$ of the Two Series Obtained from Statistical Treatment of A and B the Constants in the Logarithmic Regression Eq. 2 for Untreated Al Using Conductance Method Measurements
See the text for the meaning of each symbol.

No.	A		B	
	First series	Second series	First series	Second series
1	−23.3	−19.6	11.1	9.04
2	−23.5	−20.5	11.0	9.48
3	−26.2	−40.1	12.2	18.1
4	−29.5	−31.1	13.2	14.1
5	−21.5	−16.0	10.1	8.09
6	−36.6	−27.2	16.2	12.5
7	−23.8	−23.1	11.3	11.0
8	−29.9	−35.1	13.8	15.7
9	−33.5	−24.8	14.8	11.9
10	−20.9	−21.2	10.0	10.2
	$a_1=-26.9$	$a_2=-25.9$	$a_1=12.4$	$a_2=12.0$
	$s_1=5.30$	$s_2=7.55$	$s_1=2.08$	$s_2=3.17$
	$s_1/a_1=0.197$	$s_2/a_2=0.292$	$s_1/a_1=0.168$	$s_2/a_2=0.316$
	%=19.7%	%=29.2%	%=16.8%	%=31.6%
	$a_1-a_2=1.00$		$a_1-a_2=0.400$	
	$s_{(\alpha_1-\alpha_2)}=9.22$		$s_{(\alpha_1-\alpha_2)}=3.79$	
	$\therefore (a_1-a_2)<s_{(\alpha_1-\alpha_2)}$		$\therefore (a_1-a_2)<s_{(\alpha_1-\alpha_2)}$	
	$t_{(\alpha_1-\alpha_2)}=0.343$		$t_{(\alpha_1-\alpha_2)}=0.334$	

Table 4. Values of a, s, s/a, $s_{(\alpha_1-\alpha_2)}$, and $t_{(\alpha_1-\alpha_2)}$ of the Two Series Obtained from Statistical Treatment of A and B the Constants in the Linear Regression Eq. 1 for Untreated Al Using Conductance Method Measurements
See the text for the meaning of each symbol.

No.	A		B	
	First series	Second series	First series	Second series
1	2.27	0.558	0.00920	0.00821
2	1.44	0.868	0.00878	0.00835
3	2.08	1.78	0.00868	0.00873
4	1.46	0.702	0.00822	0.0108
5	1.67	2.17	0.00786	0.00752
6	0.669	1.36	0.0101	0.00866
7	1.73	0.960	0.00855	0.0114
8	1.39	1.67	0.00966	0.00823
9	1.16	1.65	0.00821	0.0110
10	1.32	1.03	0.00923	0.0106
	$a_1=1.52$	$a_2=1.28$	$a_1=0.00885$	$a_2=0.00935$
	$s_1=0.455$	$s_2=0.530$	$s_1=0.000699$	$s_2=0.00143$
	$s_1/a_1=0.299$	$s_2/a_2=0.414$	$s_1/a_1=0.0790$	$s_2/a_2=0.153$
	%=29.9%	%=41.4%	%=7.90%	%=15.3%
	$a_1-a_2=0.240$		$a_1-a_2=0.000500$	
	$s_{(\alpha_1-\alpha_2)}=0.698$		$s_{(\alpha_1-\alpha_2)}=0.000159$	
	$\therefore (a_1-a_2)<s_{(\alpha_1-\alpha_2)}$		$\therefore (a_1-a_2)<s_{(\alpha_1-\alpha_2)}$	
	$t_{(\alpha_1-\alpha_2)}=1.09$		$t_{(\alpha_1-\alpha_2)}=0.998$	

$$b = \tau(k_o + 10) - a = [A + B \log(k_o + 10)] - a \tag{12}$$

The value of a represents the time needed for raising the true measured conductance from k_o at the start moment to $k_o+1.00$ milli mho, while b is the time needed for raising the conductance from k_o+1 to k_o+10 milli mho.

At the same time, the k–τ relation can be expressed satisfactorily for the clear linear portion by the empirical formula:

$$\tau = A^* + B^*k \tag{13}$$

where A^* and B^* are constants, A^* is the time at intersection of the extended linear portion, while B^* is the time needed for raising the conductance by one milli mho during the linear portion.

The value of $1/a$ can be considered as a function of the dissolution rate of the outer most layer (the first stage of dissolution) of the oxide film. The inhibition efficiency I_1 of the inhibitor in the first stage of dissolution, is given by the equation:

$$I_1 = \frac{1/a - 1/\overline{a}}{1/a} \times 100$$

$$I_1 = (1 - a/\overline{a}) \times 100 \qquad (14)$$

where a and $\overline{a}$ are the constants given by Eq. 11 in absence and presence of additive respectively. At any time $\tau = A + B \log k$, so at $(k+x)$, where x is a small fraction of milli mho, e.g. 0.10 milli mho.

$$\tau_{\mathrm{at}(k+x)} = A + B \log(k + x) \qquad (15)$$

$$\tau_{\mathrm{at}(k-x)} = A + B \log(k - x) \qquad (16)$$

$$S_{\mathrm{o}} \frac{\mathrm{d}k}{\mathrm{d}\tau} = \frac{2x}{\tau_{(k+x)} - \tau_{(k-x)}} \qquad (17)$$

or

$$\frac{\mathrm{d}k}{\mathrm{d}\tau} = \frac{2x}{A + B \log(k+x) - A - B \log(k-x)} = \frac{2x}{B \log\left(\frac{k+x}{k-x}\right)} \qquad (18)$$

at the same value of k and using the same fraction x, the value of $\frac{2x}{\log\left(\frac{k+x}{k-x}\right)}$ becomes constant thus

$$\left(\frac{\mathrm{d}k}{\mathrm{d}\tau}\right) = 1/B \cdot K \qquad (19)$$

Hence $1/B$ represents a function of the dissolution rate, so the value $1/b$ represents a function of the subsurface layers of the oxide film, and the inhibition efficiency (I_2) of the inhibitor on the subsurface can thus be given as:

$$I_2 = \frac{1/b - 1/\overline{b}}{1/b} \times 100$$

$$I_2 = (1 - b/\overline{b}) \times 100 \qquad (20)$$

where b and $\overline{b}$ are the constants given by the Eq. 12 in the absence and presence of inhibitors respectively.

On the other hand, the value of $1/B^*$ can be considered as a function of the dissolution rate of the most internal layers (beginning with the clear linear portion) of the oxide film. The inhibition efficiency I_3 of the inhibitor on this layer can thus be given as:

$$I_3 = \frac{1/B^* - 1/\overline{B}^*}{1/\overline{B}^*} \times 100$$

$$= (1 - B^*/\overline{B}^*) \times 100 \qquad (21)$$

where B^* and $\overline{B}^*$ are the constants in Eq. 13 in the absence and presence of inhibitors respectively.

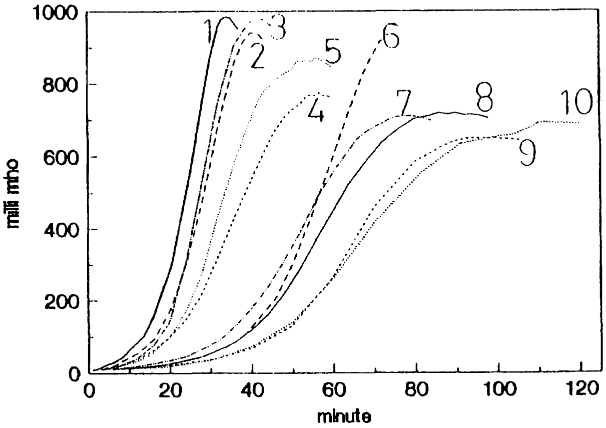

Fig. 5. k–τ curves for Al, anodized in 0.100 M oxalic acid at 50 V ac for 20.0 min at 30.0 °C, in 20.0 ml 3.00 M HCl (in presence and absence of 0.100 M of different inhibitors) at 30.0 and 40.0 °C. 1- Free at 40.0 °C. 2- 2-picoline at 40.0 °C. 3- 3-picoline at 40.0 °C. 4- 4-pyridinol at 40.0 °C. 5- 2-pyridinamine at 40.0 °C. 6- Free at 30.0 °C. 7- 2-picoline at 30.0 °C. 8- 3-picoline at 30.0 °C. 9- 4-pyridinol at 30.0 °C. 10- 2-pyridinamine at 30.0 °C.

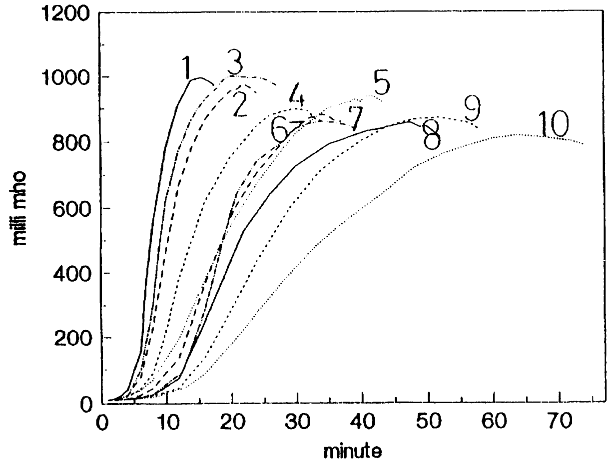

Fig. 6. k–τ curves for Al–Mn, anodized in 0.100 M oxalic acid at 50 V ac for 20.0 min at 30.0 °C, in 20.0 ml 3.00 M HCl (in presence and absence of 0.100 M of different inhibitors) at 30.0 and 40.0 °C. Notations 1—10 are given in Fig. 5.

Results and Discussion

In Figs. 5 and 6 are given representative milli mho–time curves of Al and Al–Mn alloy, anodized in 0.1 M oxalic acid, during their dissolution in 3 M HCl solution at 30.0 and 40.0 °C in absence and presence of the additives. Similar curves are obtained for the oxidized specimens in phosphoric, sulfuric acid, sealed and untreated Al and Al–Mn specimens. It is obvious that the dissolution resistance decreases with increasing temperature. This may be due to the increase of surface activity during the interaction between Al or Al–Mn alloy and HCl solution. Also, the increase of temperature accelerates the diffusion and convection transport in the corroding media. Moreover, the adsorption rate of the additives decreases with increasing temperature, as reported before.[17)]

On the other hand, it was found generally that the efficiency of the inhibition varies with the types of the additives as given below: 2-pyridinamine>4-pyridinol>3-picoline>2-picoline, in which 2-pyridinamine has the highest inhibition while 2-picoline is the lowest one. The only exception was observed for Al–Mn alloy oxidized in phosphoric acid, where the order among 3-picoline and 4-pyridinol is inverted.

Table 5. a, b, and B^* Constants and Inhibition Efficiency "I" for Different Inhibitors where: 1*, 2* Untreated Al. 3*, 4* Untreated Al–Mn.
[All values of a, b and B^* become $\overline{a}$, $\overline{b}$, and $\overline{B}^*$ in the presence of inhibitors.] See the text for the meaning of each symbol.

Type of specimens	Type of inhibitor	Free	2-Picoline	3-Picoline	4-Pyridinol	2-Pyridinamine
1* at 30.0 °C	a	3.13	6.52	6.70	8.27	11.0
	I_1	—	52.0	53.3	62.2	71.5
	b	0.213	0.226	0.191	0.428	0.846
	I_2	—	5.75	—	50.2	74.8
	B^*	0.00957	0.014	0.0141	0.0194	0.0264
	I_3	—	31.6	32.1	50.7	63.8
2* at 40.0 °C	a	1.56	1.81	1.79	3.43	4.48
	I_1	—	13.8	12.8	54.5	65.2
	b	0.0884	0.126	0.129	0.154	0.216
	I_2	—	29.8	31.5	42.6	59.1
	B^*	0.00372	0.00594	0.00725	0.00770	0.00915
	I_3	—	37.4	48.7	51.7	59.3
3* at 30.0 °C	a	1.78	2.04	1.55	3.37	4.21
	I_1	—	12.7	—	47.2	57.7
	b	0.170	0.142	0.196	0.236	0.271
	I_2	—	—	13.3	28.0	37.3
	B^*	0.00567	0.00997	0.00896	0.0143	0.0192
	I_3	—	43.1	36.7	60.0	70.5
4* at 40.0 °C	a	—	0.541	0.691	1.71	1.86
	I_1	—	—	—	—	—
	b	—	0.119	0.0818	0.152	0.136
	I_2	—	—	—	—	—
	B^*	0.00234	0.00317	0.00395	0.00844	0.0127
	I_3	—	26.2	40.8	72.3	81.6

The observed high efficiency of the compounds studied[11] in acidic media may be attributed to the cationic nature of the additive in this media. The dissolution potential of Al in 3 M HCl solution is more negative than the zero charge point (z.c.p.).[18] This makes the adsorption of the cationic surfactants more effective than non-ionic or anionic species. Moreover, the observed inhibition may also be due to the easiness of adsorption at metal surfaces through the active centers of the organic compounds. All the compounds used have nitrogen as key atom for the adsorption process in addition to the delocalized π-electrons on the ring which makes the molecule more planer and which as a result makes a new center of adsorption easy to introduce. A good correlation was observed between both the basicity and the structure of the compounds investigated and this inhibition effect. The compound 2-pyridinamine with $\mathrm{p}K_\mathrm{b}=6.82$[19] has two nitrogen atoms as donor centers (bidentate) in addition to the aromatic ring, which increases the electron density on the sites of the specimens. Consequently, a strong attraction between the additive and the cathodic and anodic sites should be expected; this suggests that pyridine and its ring substituted are inhibitors of mixed types.[20] The compound 4-pyridinol is amphoteric, which causes the precipitation of Al^{3+} which replaces the hydrogen atom in the hydroxyl group and also forms coordination bonds with nitrogen atom (i.e. uninegative bidentate). The observed high inhibitive effect may be due to the formation of highly stable species. The order of efficiency of inhibition among 2- and 3-picoline is inconsistent with their basicities 6.00 and 5.70 respectively,[19] as in some cases. This behavior may be attributed to the steric hindrance of methyl group in *o*-position, which decreases the adsorption of 2-picoline. Each compound has one nitrogen atom as electron donor (monodentate) with aromatic ring. The presence of a methyl group in position 2 or 3 as an electron-releasing substituent may increase the basicity of the pyridine and consequently increase the adsorption, which it still less than the adsorption of bidentate and uninegative bidentate compound. At high temperature, the inhibitory order of 3- and 2-picoline, for Al and Al–Mn oxidized in oxalic acid together with Al–Mn oxidized in sulfuric acid, is reversed. The sealed Al shows the previously mentioned order. Present experiments also indicated that the inhibitive effect of the compounds studied on the dissolution of oxidized Al and Al–Mn alloy (in three acids) is more than that observed in the cases of sealed or untreated specimens, in the following order: oxidized in oxalic acid>oxidized in phosphoric acid>oxidized in sulfuric acid>sealed>untreated.

The values of inhibition efficiencies, I_1, I_2, and I_3, for the different inhibitors used are reported in Tables 5, 6, 7, 8, and 9 in cases of Al and Al–Mn dissolution (untreated, sealed, and oxidized) at 30.0 and

Table 6. a, b, and B^* Constants and Inhibition Efficiency "I" for Different Inhibitors where: 1*, 2* Sealed Al. 3*, 4* Sealed Al–Mn.
[All values of a, b, and B^* become $\overline{a}$, $\overline{b}$, and $\overline{B}^*$ in the presence of inhibitors.] See the text for the meaning of each symbol.

Type of specimens	Type of inhibitor	Free	2-Picoline	3-Picoline	4-Pyridinol	2-Pyridinamine
1* at 30.0 °C	a	3.51	3.97	4.04	5.53	3.70
	I_1	—	11.6	13.1	36.5	5.14
	b	0.521	0.699	0.732	1.25	1.16
	I_2	—	25.5	28.8	58.3	55.1
	B^*	0.0167	0.0229	0.0340	0.0407	0.0453
	I_3	—	27.1	50.9	59.0	63.1
2* at 40.0 °C	a	1.72	1.80	1.87	2.75	2.44
	I_1	—	4.44	8.02	37.4	29.5
	b	0.216	0.334	0.282	0.774	0.726
	I_2	—	35.3	23.4	72.1	70.2
	B^*	0.00817	0.0115	0.0108	0.0198	0.0213
	I_3	—	29.0	24.4	58.7	61.6
3* at 30.0 °C	a	—	—	—	—	—
	I_1	—	—	—	—	—
	b	—	—	—	—	—
	I_2	—	—	—	—	—
	B^*	0.00694	0.00937	0.0102	0.0212	0.0257
	I_3	—	25.9	32.0	67.3	73.0
4* at 40.0 °C	a	—	—	—	—	—
	I_1	—	—	—	—	—
	b	—	—	—	—	—
	I_2	—	—	—	—	—
	B^*	0.00355	0.00512	0.00504	0.00885	0.0118
	I_3	—	30.7	29.6	59.9	69.9

Table 7. a, b, and B^* Constants and Inhibition Efficiency "I" for Different Inhibitors where: 1*, 2* Al anodized in sulfuric acid. 3*, 4* Al–Mn anodized in sulfuric acid.
[All values of a, b, and B^* become $\overline{a}$, $\overline{b}$, and $\overline{B}^*$ in the presence of inhibitors.] See the text for the meaning of each symbol.

Type of specimens	Type of inhibitor	Free	2-Picoline	3-Picoline	4-Pyridinol	2-Pyridinamine
1* at 30.0 °C	a	2.52	1.00	0.625	3.02	1.08
	I_1	—	—	—	16.6	—
	b	1.35	2.32	2.50	2.72	2.94
	I_2	—	41.8	46.0	50.4	54.1
	B^*	0.0146	0.0188	0.0196	0.0204	0.0253
	I_3	—	22.3	25.5	28.4	42.3
2* at 40.0 °C	a	0.730	0.615	0.881	0.908	2.60
	I_1	—	—	17.1	19.6	71.9
	b	0.709	0.983	1.04	1.41	0.978
	I_2	—	27.9	31.8	49.7	27.5
	B^*	0.00572	0.00793	0.00742	0.00742	0.0101
	I_3	—	27.9	22.9	38.0	43.4
3* at 30.0 °C	a	—	—	—	—	0.381
	I_1	—	—	—	—	—
	b	—	—	—	—	0.779
	I_2	—	—	—	—	—
	B^*	0.0128	0.0135	0.0129	0.0171	0.0181
	I_3	—	5.18	0.775	25.1	29.3
4* at 40.0 °C	a	—	—	—	0.460	0.423
	I_1	—	—	—	—	—
	b	—	—	—	0.479	0.420
	I_2	—	—	—	—	—
	B^*	0.00126	0.00521	0.00517	0.00722	0.00697
	I_3	—	—	—	15.2	12.2

Table 8. a, b, and B^* Constants and Inhibition Efficiency "I" for Different Inhibitors where: 1*, 2* Al anodized in phosphoric acid. 3*, 4* Al–Mn anodized in phosphoric acid. [All values of a, b, and B^* become $\overline{a}$, $\overline{b}$, and $\overline{B}^*$ in the presence of inhibitors.] See the text for the meaning of each symbol.

Type of specimens	Type of inhibitor	Free	2-Picoline	3-Picoline	4-Pyridinol	2-Pyridinamine
1* at 30.0 °C	a	4.88	3.82	4.24	7.21	5.81
	I_1	—	—	13.1	32.3	16.0
	b	5.50	5.76	4.50	5.22	7.79
	I_2	—	4.51	—	—	29.4
	B^*	0.0461	0.0859	0.106	0.102	0.0993
	I_3	—	46.3	56.5	54.8	53.6
2* at 40.0 °C	a	0.63	1.84	1.36	1.79	2.25
	I_1	—	65.8	53.7	64.8	72.0
	b	2.09	2.65	2.86	3.38	3.47
	I_2	—	21.1	26.9	38.2	39.8
	B^*	0.0209	0.0371	0.0420	0.0383	0.0438
	I_3	—	43.7	50.2	45.4	52.3
3* at 30.0 °C	a	0.770	0.629	0.861	1.09	1.84
	I_1	—	—	10.6	29.4	58.2
	b	1.23	2.00	2.16	2.20	2.22
	I_2	—	38.5	43.1	44.1	44.6
	B^*	0.0212	0.0238	0.0395	0.0334	0.0395
	I_3	—	10.9	46.3	36.5	46.3
4* at 40.0 °C	a	0.540	0.729	0.684	0.887	0.483
	I_1	—	25.9	21.1	39.1	—
	b	0.521	0.855	0.782	1.22	1.41
	I_2	—	39.1	33.4	57.3	63.0
	B^*	0.00787	0.00999	0.0117	0.0133	0.0171
	I_3	—	21.2	32.7	40.8	54.0

Table 9. a, b, and B^* Constants and Inhibition Efficiency "I" for Different Inhibitors where: 1*, 2* Al anodized in oxalic acid. 3*, 4* Al–Mn anodized in oxalic acid. [All values of a, b, and B^* become $\overline{a}$, $\overline{b}$, and $\overline{B}^*$ in the presence of inhibitors.] See the text for the meaning of each symbol.

Type of specimens	Type of inhibitor	Free	2-Picoline	3-Picoline	4-Pyridinol	2-Pyridinamine
1* at 30.0 °C	a	7.93	7.91	10.6	11.8	12.7
	I_1	—	—	25.2	32.8	37.6
	b	8.36	6.36	7.11	8.84	8.30
	I_2	—	—	15.0	5.43	—
	B^*	0.0343	0.0497	0.0548	0.0637	0.0744
	I_3	—	31.0	37.4	46.2	53.9
2* at 40.0 °C	a	0.90	2.95	4.63	4.64	5.30
	I_1	—	69.5	80.6	80.6	83.0
	b	3.37	3.52	3.27	3.88	3.71
	I_2	—	4.26	—	13.1	9.16
	B^*	0.0172	0.0213	0.0181	0.0389	0.0262
	I_3	—	19.2	4.97	55.8	34.4
3* at 30.0 °C	a	2.84	3.92	4.87	5.38	5.49
	I_1	—	27.6	41.7	47.2	48.3
	b	2.20	2.35	2.23	2.39	2.93
	I_2	—	6.38	1.34	7.95	24.9
	B^*	0.0185	0.0136	0.0219	0.0281	0.0441
	I_3	—	—	15.5	34.2	58.0
4* at 40.0 °C	a	1.50	2.42	2.52	2.66	2.54
	I_1	—	38.0	40.5	43.6	40.9
	b	1.03	1.03	0.923	1.38	1.66
	I_2	—	—	—	25.4	38.0
	B^*	0.00504	0.00923	0.00611	0.0150	0.0228
	I_3	—	45.4	17.5	66.4	77.9

40.0 °C, along with the constants a, b, and B^*. These data indicated that in some cases the logarithmic nonlinear behavior was not observed at all, as in the cases of untreated Al–Mn at 40.0 °C, sealed Al–Mn in absence and presence of the inhibitors at 30.0 and 40.0 °C and oxidized Al–Mn (in sulfuric acid) in absence and presence of 2-picoline at 30.0 and 40.0 °C and in presence of 4-pyridinol at 30.0 °C. For these cases, it is impossible to compute the inhibition efficiencies I_1 and I_2 at the first stage of dissolution because k–τ is linear from the start point. The inhibition efficiency, thus, is the same all over the linear part at the value which is exhibited from the first moment of contact between the specimens and HCl. From the data recorded we may conclude that the variations in the values of I between the different inhibitors are generally less for anodized Al and Al–Mn. On the other hand, for untreated Al and Al–Mn alloys, more considerable differences were observed between values of I in case of different inhibitors. This difference may be attributed to the leveling effect of the oxide layer in the adsorption process of anodized Al and Al–Mn. Tables 5, 6, 7, 8, and 9 also show that 2-pyridinamine has the highest effect on the dissolution of most specimens. The inhibition efficiency is greater for Al dissolution than that for Al–Mn. The inhibition effect is strongly dependent on the adsorption of the inhibitors and in this way the inhibitor 2-pyridinamine is more effective than the other studied inhibitors.

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