APPENDIX

STRUCTURAL FORMULAE OF DYES INVESTIGATED AS INHIBITORS
**STRUCTURAL FORMULAE OF TRIPHENYL METHANE DYES**

<table>
<thead>
<tr>
<th><strong>1. MALACHITE GREEN</strong> ( (C_{23}H_{25}ClN_2) )</th>
<th>MW: 364.9</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Malachite Green Structural Formula" /></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>2. FAST GREEN</strong> ( (C_{27}H_{33}N_2Cl) )</th>
<th>MW: 420.5</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image2" alt="Fast Green Structural Formula" /></td>
<td></td>
</tr>
</tbody>
</table>
3. FUCHSINE BASE \((C_{20}H_{20}N_3Cl)\)

\[
\begin{align*}
\text{MW: } & 337.86 \\
\end{align*}
\]

4. METHYL VIOLET 6B \((C_{24}H_{28}N_3Cl)\)

\[
\begin{align*}
\text{MW: } & 393.96 \\
\end{align*}
\]
5. CRYSTAL VIOLET \((C_{25}H_{30}N_3Cl)\)
MW: 407.5

6. LIGHT GREEN \((C_{26}H_{33}Cl_2N_3)\)
MW: 458.48
7. VICTORIA BLUE \( \text{C}_{33}\text{H}_{32}\text{N}_3\text{Cl} \)

\[
\begin{align*}
\text{MW: } & 505.5 \\
\text{Formula: } & (\text{CH}_3)_2\text{N-} \text{C=}
\end{align*}
\]

8. FUCHSINE ACID \( \text{C}_{20}\text{H}_{17}\text{N}_3\text{O}_9\text{S}_3\text{Na}_2 \)

\[
\begin{align*}
\text{MW: } & 585 \\
\text{Formula: } & \text{H}_2\text{N-} \text{C=}
\end{align*}
\]
<table>
<thead>
<tr>
<th>Structural Formulae of Azo Dyes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Resorcine Yellow (C_{12}H_{9}N_{2}SO_{5}Na)</td>
</tr>
<tr>
<td>MW: 316</td>
</tr>
<tr>
<td><img src="image" alt="Resorcine Yellow Structure" /></td>
</tr>
<tr>
<td>2. Alizarin Yellow (C_{14}H_{12}N_{2}O_{4})</td>
</tr>
<tr>
<td>MW: 272</td>
</tr>
<tr>
<td><img src="image" alt="Alizarin Yellow Structure" /></td>
</tr>
<tr>
<td>3. Fast Garnet (C_{14}H_{15}N_{3})</td>
</tr>
<tr>
<td>MW: 225</td>
</tr>
<tr>
<td><img src="image" alt="Fast Garnet Structure" /></td>
</tr>
</tbody>
</table>
4. METHYL RED \((C_{15}H_{15}N_3O_2)\)

MW: 269.3

\[
\begin{align*}
\text{(CH}_3\text{)}_2\text{N} & - \left[ \begin{array}{c}
\text{H} \\
\text{N} \\
\text{N}=\text{N} \\
\end{array} \right] \\
\text{SO}_3\text{Na}
\end{align*}
\]

5. METANIL YELLOW \((C_{18}H_{14}N_3SO_3Na)\)

MW: 375

\[
\begin{align*}
\text{N} & - \left[ \begin{array}{c}
\text{N} \\
\text{N}=\text{N} \\
\text{SO}_3\text{Na}
\end{array} \right] \\
\end{align*}
\]

6. ERIOCHROME BLACK T \((C_{20}H_{12}N_3SO_7Na)\)

MW: 461.38

\[
\begin{align*}
\text{OH} & - \left[ \begin{array}{c}
\text{N}=\text{N} \\
\text{SO}_3\text{Na}
\end{array} \right] \\
\text{NO}_2
\end{align*}
\]
7. FAST SULPHON BLACK F
\[ (C_{30}H_{17}O_{11}N_{4}S_{3}Na_{3}) \]
MW: 774

8. NAPHTHOL BLUE BLACK
\[ (C_{22}H_{14}N_{6}S_{2}O_{9}Na_{2}) \]
MW: 616
DYES AS CORROSION INHIBITORS
PART II TRIPHENYL METHANE DYES AS INHIBITORS FOR ALUMINIUM — COPPER ALLOY IN PHOSPHORIC ACID

J.D. Talati and J.M. Daraji
Shri U.P. Arts, Shri N.G. Panchal Science and Shri V.L. Shuk Commerce College,
PILVAI (382 850) INDIA

The inhibitive efficiency of triphenylmethylene dyes for B26S aluminium in phosphoric acid increases with inhibitor concentration but decrease with acid concentration. At 0.5% inhibitor concentration in 0.033M H₃PO₄, the efficiency increases in the order: Methyl violet 6B (15%) < crystal violet < fuchsin acid < fuchsin base (36%) < malachite green (68%) < light green < fuchsine base (88%). A rise in temperature decreases the efficiency, the energy of activation for the corrosion process being 14.7 Kcal/mole.

B26S aluminium in 0.033 M H₃PO₄ develops a corrosion potential of -755 mV vs SCE. The potentials are found to range from -740 (fuchsine acid) to -805 mV (crystal violet). In inhibited acid, galvanostatic polarisation curves show polaiisation of both, cathodes as well as anodes. The inhibitors appear to function through general adsorption following Langmuir isotherm.

Solutions of phosphoric acid are frequently employed for cleaning aluminium <1,2>, in commercial preplating anodic oxidation <3> and in chemical polishing <4,5> or etching of Aluminium. For electroplating <5,6> phosphoric acid baths containing thiourea <2>, ethylene glycol, glucose <5>, gelatin etc are used. These additives function as corrosion inhibitors and also as surface brighteners. Although dyes are used to give multi-coloured effects to anodised aluminium surfaces, data regarding their effect on the acid corrosion of aluminium is not much available. Talati and Gandhi have studied the effect of some dyes as corrosion inhibitors for B26S aluminium in hydrochloric acid <8>. The present work was undertaken to study the effect of some triphenylmethane dyes as corrosion inhibitors for B26S aluminium (Al-4% Cu alloy) in phosphoric acid.

EXPERIMENTAL

Rectangular specimens (50x40 mm) of B26S aluminium (supplied by Indian Aluminium Co Ltd., Bombay) were used for the determination of the corrosion rate. The alloy used and the experimental procedure followed was the same as that described by Talati and Gandhi <8>, with H₃PO₄ as the corroding medium. The ranges of concentrations studied were 0.0033M to 1.3M for the acid and 0.01 — 0.5% for the inhibitors.

For galvanostatic polarisation studies circular metal coupon, dia. 28.4 mm with a handle 32.2 x 4.8 mm, were used. The area exposed to the test solutions was 6.33 cm² while the applied c.d. was varied in the range 1.58 x 10⁻⁵ to 7.943 x 10⁻¹ A/cm².

RESULTS AND DISCUSSION

Observations

In inhibited acid, the specimens were covered with a loose film of the same colour as that of the dye and it could be easily removed by the cleaning solution. The surface of the corroded specimens on cleaning showed a dull metallic appearance.

Corrosion In Uninhibited Phosphoric Acid

Effect of Acid Concentration and Immersion Period

To study the effect of acid concentration and immersion period on corrosion, weight losses were determined in 0.033M to 0.667M plain phosphoric acid for immersion periods ranging from 1/2 to 3 days and are shown in Fig.1.

The decrease in corrosion rate at lower acid concentrations may be traced to a slight increase in the pH of the solution due to the depletion of the acid during
corrosion. This increase in pH may favour the formation of protective oxide film which is reported to be more stable in the pH range 3 - 10 <9,10>. Further as the solubilities of the various aluminium phosphates increase in the order : AlPO₄ < Al₁₆ (H₂PO₄)₁₂ < Al₂ (H₂PO₄)₁₃. There will not be any formation of the film of aluminium phosphate on the metal surface and hence aluminium will dissolve in higher concentrations of the acid with the formation of Al₂ (H₂PO₄)₃ leading to an increase in the corrosion rate.

Corrosion in Inhibited Acid

Effect of Inhibitor Concentration

To assess their effect as corrosion inhibitors, various triphenylmethane dyes were added in concentrations ranging from 0.01 -0.5% in 0.33 M phosphoric acid and the weight losses were determined in these solutions at 30 ± 0.5°C for 1 day immersion period. The results are given in Fig. 2. From the results, it may be generalised that in almost all the cases, the inhibitive efficiency increases with inhibitor concentration. Thus at an inhibitor concentration of 0.01%, the efficiency of the various inhibitors is found to increase in the order: Methyl violet 6B (1.6%) < fuchsine base (0.1%); crystal violet (6.5%) < malachite green (7.1%) < fuchsine acid (8.3%) < Victoria blue (13.6%) < fast green (17.2%) < light green (28.0%).

At 0.5% concentration the efficiency increases in the order: Methyl violet 6B (15.1%) < crystal violet (25.8%) < fuchsine acid (30.6%) < fuchsine base (36.4%) < malachite green (68.0%) < victoria blue (74.8%) < light green (75.5%) < fast green (88.0%).

It is apparent from the results that of the eight compounds studied malachite green, victoria blue, fast green and light green show better efficiency (> 50%) at concentrations ranging from 0.1 - 0.5%.

Effect of Acid Concentration on Inhibitive Efficiency

To determine the effect of acid concentration on inhibitive efficiency, weight losses were determined in different concentrations of acid (0.167M to 1.33M) containing a constant inhibitor concentration of 0.1%. From the results given in Fig. 3, it may be generalised that the efficiency of almost all the inhibitors decreases with increase in acid concentration. Thus in 0.167 M acid, the efficiency
TABLE 1

| Dyes as corrosion inhibitors - Talati & Daraji |

Effect of chloride ion on inhibitive efficiency of tripbenylmethane dyes for B26S aluminium in H₃PO₄.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>0.033 M</th>
<th>0.033 H₃PO₄</th>
<th>0.1 M NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loss, mg</td>
<td>XI.</td>
<td>Loss, mg</td>
<td>XI.</td>
</tr>
<tr>
<td>Nil</td>
<td>33.7</td>
<td>26.6</td>
<td>21.0</td>
</tr>
<tr>
<td>Victoria blue</td>
<td>16.5</td>
<td>22.8</td>
<td>32.5</td>
</tr>
<tr>
<td>Fast green</td>
<td>14.6</td>
<td>18.8</td>
<td>44.2</td>
</tr>
<tr>
<td>Light green</td>
<td>16.2</td>
<td>24.6</td>
<td>34.5</td>
</tr>
<tr>
<td>Fuchsin base</td>
<td>27.5</td>
<td>18.4</td>
<td>44.5</td>
</tr>
<tr>
<td>Fuchsin acid</td>
<td>26.9</td>
<td>20.2</td>
<td>34.6</td>
</tr>
<tr>
<td>Crystal violet</td>
<td>27.1</td>
<td>19.6</td>
<td>33.5</td>
</tr>
<tr>
<td>Methyl violet</td>
<td>31.5</td>
<td>22.0</td>
<td>23.1</td>
</tr>
</tbody>
</table>

ACID CONCENTRATION (M)

Fig. 3 Effect of concentration of H₃PO₄ on inhibitive efficiency of tripbenylmethane dyes for B26S aluminium (30°C)

Increases in the order: Fuchsin acid (25.2%) < Fuchsin base (27.3%) < Victoria blue (28.6%) < Light green (32.5%) < Crystal violet (36.7%) < Methyl violet 6B (38.9%) < Malachite green (43.6%) < Fast green (44.6%). In 1.33 M acid, the various dyes studied conferred only 9.4% (Fuchsin acid) to 24.9% (Fast green) protection.

The behaviour of the inhibitors in phosphoric acid is thus quite different from that in hydrochloric acid (<8,11>, wherein the efficiency was found to increase with acid concentration.

The presence of chloride ions was suspected to be the cause of this anomalous behaviour and therefore weight losses were determined in 0.167 M H₃PO₄ containing 0.1% inhibitor and 0.1 M sodium chloride (Table 1). It was found that the inhibitive efficiency of malachite green, fuchsin base, fuchsin acid, crystal violet and methyl violet 6B increased by 4 - 26% in the presence of chloride ions. Thus the chloride ions seem to augment the inhibitive behaviour of the dyes, perhaps by the in situ formation of compounds like (inhibitor) Al₃C₁₅H₂O on the metal surface (<12,17>, which may account for an increase in efficiency with increase in acid concentration in the case of hydrochloric acid.

Effect of Temperature

To study the effect of temperature on inhibitive efficiency, weight losses were determined in 0.167 M H₃PO₄ containing 0.1% inhibitor at solution temperature of 30°C, 40°C, 50°C and 60°C. The results are given in Table 2. From the results it is evident that in inhibited as well as in uninhibited acid, the extent of corrosion increases and the inhibitive efficiency decreases with a rise in temperature. The decrease in efficiency is maximum with fast green and malachite green which happen to be better inhibitors at ordinary temperatures. At 60°C, the inhibitive efficiencies were quite lower and ranged from 6.0 (fuchsin acid) to 22.5% (fast green).

The values of the energy of activation, E, were calculated from the slopes of the Arrhenius plots of log corrosion rate (mg/dm²) vs. 1/T, (Fig 4). The E values are given in Table 3. A comparison of the E values in the presence and absence of inhibitors indicates that the values for inhibited acid are almost the same (within ± 2 kcal/mole) as that in uninhibited acid. According to Putilova et al., the behaviour of such inhibitors resembles that of stable poison in heterogeneous catalysis which do not effect the temperature coefficient of the reaction (<18>.

The values of heat of adsorption, Q₁ were calculated from the equation:

TABLE 2

EFFECT OF TEMPERATURE ON INHIBITIVE EFFICIENCY OF TRIPHENYL METHANE DYES FOR B26S ALUMINIUM IN 0.167 M H₃PO₄.

(Inhibitor concentration, 0.1X; exposure period, 5 hrs; surface area of specimen, 40 cm²).

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>% Inhibition at temperature of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
</tr>
<tr>
<td>Nil</td>
<td>(23.4)*</td>
</tr>
<tr>
<td>Victoria blue</td>
<td>28.6</td>
</tr>
<tr>
<td>Fast green</td>
<td>46.6</td>
</tr>
<tr>
<td>Light green</td>
<td>32.5</td>
</tr>
<tr>
<td>Malachite green</td>
<td>43.6</td>
</tr>
<tr>
<td>Fuchsine base</td>
<td>27.3</td>
</tr>
<tr>
<td>Fuchsine acid</td>
<td>25.2</td>
</tr>
<tr>
<td>Crystal violet</td>
<td>36.7</td>
</tr>
<tr>
<td>Methyl violet 6B</td>
<td>38.9</td>
</tr>
</tbody>
</table>

* The value in the parentheses indicates the weight loss in plain 0.167 M H₃PO₄.

TABLE 3

ENERGY OF ACTIVATION, (E), HEAT OF ADSORPTION, (Q), AND FREE ENERGY OF ADSORPTION, (ΔGₐ), OF TRIPHENYL METHANE DYES DURING CORROSION OF B26S ALUMINIUM IN 0.167 M H₃PO₄.

(Inhibitor concentration, 0.1X; Exposure period, 5 hrs; surface area of specimen, 40 cm²).

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>% Θ at 30°C kcal/mole</th>
<th>Q, kcal/mole, for the range</th>
<th>ΔGₐ kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30-40°C</td>
<td>40-50°C</td>
<td>50-60°C</td>
</tr>
<tr>
<td>Nil</td>
<td>14.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Victoria blue</td>
<td>28.6</td>
<td>-11.3</td>
<td>-2.5</td>
</tr>
<tr>
<td>Fast green</td>
<td>46.6</td>
<td>-12.1</td>
<td>-4.2</td>
</tr>
<tr>
<td>Light green</td>
<td>32.5</td>
<td>-10.9</td>
<td>-5.1</td>
</tr>
<tr>
<td>Malachite green</td>
<td>43.6</td>
<td>-5.4</td>
<td>-2.5</td>
</tr>
<tr>
<td>Fuchsine base</td>
<td>27.3</td>
<td>-11.5</td>
<td>-10.6</td>
</tr>
<tr>
<td>Fuchsine acid</td>
<td>25.2</td>
<td>-11.2</td>
<td>-18.1</td>
</tr>
<tr>
<td>Crystal violet</td>
<td>36.7</td>
<td>-10.4</td>
<td>-4.9</td>
</tr>
<tr>
<td>Methyl violet 6B</td>
<td>38.9</td>
<td>-4.4</td>
<td>-7.8</td>
</tr>
</tbody>
</table>

* From Fig. 6.

\[ \frac{\log C}{1-\Theta} = \frac{\log B}{\Theta} \quad (i) \]

\[ \log B = -1.74 - \frac{\Delta G_a}{2.303 RT} \quad (ii) \]

where 0 and G2 are the fractions of the metal surface covered by the inhibitor at temperatures T1 and T2 (°K) respectively. The 0 values are given in Table 3. From the table, it is evident that in all the cases the 0 values are negative and range from -2.4 to -18.1 kcal/mole. The negative 0 values show that the adsorption and hence the inhibitive efficiency decreases with a rise in temperature.

The values of the free energy of adsorption, ΔGₐ, are calculated with the help of the equation

\[ \log B = \log \frac{\Theta}{1-\Theta} \quad (iii) \]

where C is the inhibitor concentration. These are given in Table 3. A comparison of the values of inhibitive efficiency and the free energy of adsorption shows that...
those compounds which show better efficiency give more negative free energy of adsorption.

**Polarisation Behaviour**

A specimen of B26S aluminium, when immersed in 0.0033 M H₃PO₄, develops a corrosion potential of −690 mV vs SCE. As the acid concentration is increased, the open circuit potential becomes more and more negative, it being −755 mV and −785 mV in 0.033 M and 0.33 M H₃PO₄ respectively. (Fig. 5).

In inhibited 0.033 M acid, the potentials are found to range from −740 (fuchsine acid) to −805 mV (crystal violet) (Table 4). The anodic and cathodic galvanostatic polarisation curves for B26S aluminium in 0.033 M H₃PO₄ alone and containing 0.002 M concentration of the various inhibitors (i.e., the same number of molecules of each inhibitor) are shown in Fig. 6. The curves show polarisation of both, the cathodes as well as the anodes, the anode being polarised to a greater extent than the cathode. The predominant polarisation of local anodes under the influence of an anodic current suggests that the inhibitors, may be useful when anodic protection of aluminium in phosphoric acid is desired.

Inhibitive efficiency calculated from corrosion currents obtained by extrapolation of the cathodic and anodic Tafel lines to the open circuit potentials are also given in Table 4. In almost all the cases, the Tafel plot efficiencies agree well (within ±7%) with the values obtained from weight loss data.

**Mechanism of Inhibition**

All the inhibitors discussed are triphenylmethane dyes having a general structure of

\[
\text{X} - \text{C} = \text{N} \text{R}_2 \text{Cl}
\]

Where X = −H, −NH₂, −N(CH₃)₂, −N\(^{(1)}\) (CH₃) Cl⁻ and R = −H, −CH₃, −C₂H₅

In addition, fuchsine acid, fuchsine base and victoria blue contain some more substituent groups.

The dyes investigated do not have much effect on the pH of the corroding solution as is evident from the pH values of the inhibited acid (Table 4). Further, both aluminium hydroxide and aluminium phosphate are insoluble in near neutral solutions and, therefore, in cases where, due to the corrosion process, the acid becomes depleted of a certain amount of hydrogen ions, there is every possibility that a film of oxide (or hydroxide) or phosphate may be deposited in situ. This would lead to a diminution of attack. On the other hand, if the inhibitor molecule contains one or more polar units having atoms of nitrogen, sulphur, oxygen etc., the inhibi-
TABLE 4

TAFEL PARAMETERS AND INHIBITOR EFFICIENCIES OF THE DYES FOR B26S ALUMINIUM IN 0.033 M H₃PO₄
(Inhibitor 0.002 M; Temperature, 30 ± 0.5°C; Surface area of the specimen, 6.33 cm²).

<table>
<thead>
<tr>
<th>Inhibitor pH of</th>
<th>Open Tafel slope</th>
<th>Energy</th>
<th>I Corr</th>
<th>Inhibitor efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.033 M H₃PO₄</td>
<td>Circuit V/decade</td>
<td>transform (A/cm² x 10⁵)</td>
<td>X from extrapolation of</td>
<td>Catho- Anodic Weight</td>
</tr>
<tr>
<td>containing 0.1% Cathodic Anodic coef-</td>
<td>Cathodic</td>
<td>Anodic</td>
<td>Catho- Anodic</td>
<td></td>
</tr>
<tr>
<td>inhibitor.</td>
<td>coefficient</td>
<td>coefficient</td>
<td>Anodic weight</td>
<td></td>
</tr>
<tr>
<td>Nil</td>
<td>1.8</td>
<td>-755</td>
<td>0.78</td>
<td>0.12</td>
</tr>
<tr>
<td>Victoria blue</td>
<td>1.80</td>
<td>-785</td>
<td>0.053</td>
<td>0.064</td>
</tr>
<tr>
<td>Fast green</td>
<td>1.80</td>
<td>-785</td>
<td>0.24</td>
<td>0.32</td>
</tr>
<tr>
<td>Light green</td>
<td>1.85</td>
<td>-775</td>
<td>0.064</td>
<td>0.19</td>
</tr>
<tr>
<td>Malachite green</td>
<td>1.85</td>
<td>-795</td>
<td>0.12</td>
<td>0.27</td>
</tr>
<tr>
<td>Fuchshine base</td>
<td>1.85</td>
<td>-745</td>
<td>0.102</td>
<td>0.21</td>
</tr>
<tr>
<td>Fuchshine acid</td>
<td>1.30</td>
<td>-740</td>
<td>0.13</td>
<td>0.26</td>
</tr>
<tr>
<td>Crystal violet</td>
<td>1.35</td>
<td>-805</td>
<td>0.096</td>
<td>0.11</td>
</tr>
<tr>
<td>Methyl violet 6B</td>
<td>1.30</td>
<td>-775</td>
<td>0.066</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Fig. 6 Effect of current density on cathode and anode potentials of 326S aluminium in 0.033 M H₃PO₄ containing 0.002 M inhibitor.

Fig. 7 Langmuir adsorption isotherms for corrosion of 26S aluminium in 0.033 M H₃PO₄ containing various inhibitors.
Dyes as corrosion inhibitors - Talati & Daraji

bitor would get adsorbed on the metal surface through the polar unit and thus decrease the attack.

The steady state corrosion potentials in inhibited acid were found to be slightly more negative than that in uninhibited acid in almost all the cases, except fuchsine acid and fuchsine base, suggesting that there is preferential polarisation of the local cathodes. However, with an applied current, the anode becomes more polarised than the cathode. When log \( \theta/(1-\theta) \) is plotted against log inhibitor concentration, straight lines are obtained in the case of methyl violet 6B, fuchsine base, fuchsine acid, fast green, victoria blue and light green (Fig. 7). In some cases straight lines are obtained for limited ranges of concentrations. This suggests that the inhibitor covers both the anodic and cathodic regions following Langmuir isotherm.

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REFERENCES

THE JOURNAL

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Dyes as Corrosion Inhibitors for Aluminium Alloys in Acid Media Part-3. Triphenylmethane Dyes as Inhibitors for Aluminium-Copper Alloy in Sulphuric Acid

J. D. TALATI* and I. M. DARAJI
Chemistry Department, Shri K. B. Arts, Smt. M. S, Panvel Science and Shri V. J. Shah Commerce College, Panvel-382 905

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The corrosion of Al-4% Cu alloy in sulphuric acid increases with acid concentration and immersion period, the plots of $l$ (weight loss) vs $c$ (conc.) being parabolic in nature following the equation, $l = c^n$, where $n = 4.4$ and $k = 6.5 \times 10^{-6}$. At constant acid concentration, the inhibitive efficiency of the triphenylmethane dyes increases with inhibitor concentration whereas at constant inhibitor concentration the efficiency first decreases with the increase in acid concentration up to 1.0 M and then decreases; the increase in efficiency in 4 M acid being in the order: methyl violet < fuchsin base < victoria blue < fuchsin acid < light green < crystal violet < malachite green < fast green. The B26S aluminium alloy in 0.25 M H$_2$SO$_4$ develops a corrosion potential of $-755$ mV vs SCE and the potential remains unaffected on addition of inhibitors. Galvanostatic polarisation curves show polarisation of both, the cathodes as well as the anodes. The inhibitors appear to function through general adsorption following Langmuir adsorption isotherm.

SOLUTIONS of sulphuric acid (8-35% by weight) are used for anodising aluminium, while dyes are used to give multicoloured effects to the anodised metal. For electropolishing of aluminium, 20-70% (vol %) sulphuric acid containing 75-15% phosphoric acid is employed. Although the corrosion of aluminium in acid media and its inhibition has been studied by a number of workers, data regarding the inhibition of corrosion of aluminium in sulphuric acid are not adequate. The present communication, in continuation to the earlier ones, reports the use of some triphenylmethane (TPM) dyes in inhibiting the corrosion of B26S aluminium alloy in sulphuric acid.

Experimental

Rectangular specimens of B26S aluminium (Indian Aluminium Co. Ltd.) were used for the determination of the corrosion rates. The composition of the alloy was found to be: Cu, 3.88; Mn, 0.87; Si, 0.59; Fe, 0.43; Mg, $\leq$ 0.32%; Al remainder. The specimens (50 x 40 x 0.9 mm) were polished and the weight-loss data collected according to the method described earlier. The test specimens were exposed to sulphuric acid solutions in the concentration range 0.005-4.0 M containing up to 0.5% of TPM dyes.

For galvanostatic polarisation studies, circular metal coupons (dia. 28.4 mm with a handle 32.2 x 4.8 mm) were used. The area exposed to the test solution was 6.33 cm$^2$ while the polarising current density was varied in the range $1.58 \times 10^{-8}$ to $3.95 \times 10^{-8}$ A/cm$^2$. The potentials were recorded with an accuracy of $\pm 5$ mV by a Philips D.C. microvoltmeter.

Results and Discussion

The results are given in Figs. 1-8 and Tables 1 and 2. Inhibitor efficiency, expressed as percent inhibition (P.I.) is defined as

$$P.I. = \frac{W_a - W_i}{W_a} \times 100$$

where $W_i$ is weight loss (mg) of metal in inhibited acid and $W_a$ is weight loss (mg) in uninhibited solution.

Corrosion of B26S aluminium in plain sulphuric acid:

Effect of acid concentration and exposure period: The effect of acid concentration and exposure period on the weight-loss of B26S aluminium in sulphuric acid is shown in Figs. 1-2. Fig. 2 shows that the increase in corrosion with time is greater the higher the acid concentration, as is evident from an increase in the slope of the linear portion of the plots. The slightly lower corrosion for 12 h immersion period may be due to the induction period required to start the corrosion reaction after dissolving the oxide film from the metal surface. A similar behaviour has also been observed for aluminium in hydrochloric acid by Elawady and Ahmed.

Variation of pH, specific conductivity and relative corrosivity with acid concentration: The variation of the solution pH, specific conductivity and relative
The results show that when pH of the solution decreases, the specific conductivity and the rate of corrosion (mg/dm²/day) increase with the increase in acid concentration. Here also the increase in corrosion as well as the conductivity is not in the same proportion as that in acid concentration. This is evident from the values of relative corrosivity which decreases with the increase in acid concentration. The weight-loss data when plotted against the concentration of acid, give a parabolic curve (Fig. 3). From the data it may be generalised that the extent of corrosion ($\xi$) varies with acid concentration ($C$) following the parabolic equation of the type $\xi = KC^n$,

where $\xi$ is weight loss (mg dm$^{-2}$) of the specimen, $C$ is molarity of acid, and $n$ and $k$ are constants with $n = 4.4$ and $k = 6.8 \times 10^{-8}$.

**Corrosion in presence of inhibitors:**

To assess their protective value, TPM dyes like victoria blue, fast green, light green, malachite green, fuchsin acid, fuchsin base, crystal violet and methyl violet 6B were added to solutions of sulphuric acid. The pH values of 0.1% aqueous solutions of inhibitors lie in the range 3.1 (fast green) to 6.8 (light green) and are non-corrosive to aluminium. A 0.25 $M$ H$_2$SO$_4$ solution shows a pH of 0.35 while the pH values of inhibited acid (0.25 $M$ H$_2$SO$_4 + 0.1%$ inhibitor) lie in the range 0.30 (fast green and malachite green) to 0.32, i.e. the inhibitors do not have much effect on pH of the acid.

As many of the results on inhibitor efficiency mentioned in the present work were obtained with experiments in 0.25 $M$ H$_2$SO$_4$, it was considered necessary to determine the mean weight-loss in this concentration of the acid. From 43 replicate measurements the average weight-loss was found to be 20.0 ± 0.4 mg. The standard deviation was calculated to be 0.723 ± 0.7 mg.

**Effect of inhibitor concentration:** From Fig. 4 it is evident that the inhibitive efficiency of various dyes in 0.25 $M$ sulphuric acid at 30°C increases with inhibitor concentration. The general order of efficiency of the different dyes in the concentration range studied has been found to be, methyl violet 6B < fuchsin base < fuchsin acid < crystal violet < victoria blue < light green < malachite green < fast green.

**Effect of acid concentration:** Fig. 5 shows that in all the cases, the inhibitive efficiency first decreases with the increase in acid concentration up to 1 $M$ and then increases up to 4 $M$. At 0.1% inhibitor concentration in 0.25 $M$ H$_2$SO$_4$, the efficiency of different dyes is found to increase in the order, methyl violet 6B (27%) < fuchsin base < fuchsin acid < crystal violet < victoria blue (38%) < light green < malachite green < fast green (66%). In 4 $M$ acid, the order of increase in efficiency is methyl violet 6B (25%) < fuchsin base < victoria blue < fuchsin acid < light green (41%) < crystal...


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AGIO CONCENTRATION

B 2SS

H2SO4

Fast green

X— K Malachite green

Art Fuchsine base

Methyl violet 6B

Fig. 4. Effect of inhibitor concn. on inhibitive efficiency of some triphenylmethane dyes for B2SS aluminium in 0.31 M H2SO4 at 80° for 1 day.

\[ \log \theta = \log A - E/RT \]  

(i)

This is further related to the concentration, steric effect, metal characteristics, etc.

If it is assumed that the inhibitor is adsorbed on the metal surface in the form of a monomolecular film, covering at any instant a fraction of the total surface in uniform or random manner, then the heat of adsorption of the inhibitor can be calculated from the equation:

\[ Q = 2.303 \times R \log \frac{\theta_a}{1 - \theta_a} - \log \frac{\theta_a}{1 - \theta_a} \left( \frac{T_1 \times T_2}{T_0^2} - 1 \right) \]  

(ii)

where \( \theta_a \) and \( \theta_b \) are the fractions of the metal surface covered by the inhibitor ((\( W_a \) - \( W_b \))/\( W_a \)) at temperatures \( T_1 \) and \( T_0 \) (K), respectively, and \( Q \) is the heat of adsorption. From Table 1 it is evident inhibitors thus belong to a class of compounds which can be considered for providing corrosion inhibition at elevated temperatures. Such substances are supposed to be firmly held on the metal surface either by forces of specific adsorption or chemisorption. In general, in the range 30–60°, the efficiency of the inhibitors increases in the order, crystal violet < fuchsine acid < methyl violet 6B < light green < victoria blue < fuchsine base < fast green < malachite green.

The values of energy of activation (E) were calculated from the slopes of the Arrhenius plots of log (f°/T) and are given in Table 1. The energy of activation has a value of ~ 64 kJ mol\(^{-1}\). In inhibited acid also the values are almost the same. The almost similar values of E in inhibited as well as uninhibited acid indicate that the behaviour of inhibitors is like that of the stable poisons in heterogeneous catalysis which do not affect the temperature coefficient of the reaction. The almost identical values of E for all the inhibitors suggest that the inhibitors are similar in their mechanism of action and the order of efficiency may be related to the pre-exponential factor A by the equation,

\[ \log \xi = \log A - E/RT \]

This is further related to the concentration, steric effect, metal characteristics, etc.

If it is assumed that the inhibitor is adsorbed on the metal surface in the form of a monomolecular film, covering at any instant a fraction of the total surface in uniform or random manner, then the heat of adsorption of the inhibitor can be calculated from the equation,

\[ Q = 2.303 \times R \log \frac{\theta_a}{1 - \theta_a} - \log \frac{\theta_a}{1 - \theta_a} \left( \frac{T_1 \times T_2}{T_0^2} - 1 \right) \]  

(ii)

where \( \theta_a \) and \( \theta_b \) are the fractions of the metal surface covered by the inhibitor ((\( W_a \) - \( W_b \))/\( W_a \)) at temperatures \( T_1 \) and \( T_0 \) (K), respectively, and \( Q \) is the heat of adsorption. From Table 1 it is evident
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Table 1—Effect of Temperature on Inhibitive Efficiency, Energy of Activation (E), Heat of Adsorption (Q) and Free Energy of Adsorption (ΔGₐ) for B26S Aluminium in 0.5 M H₂SO₄ Containing TPM Dyes

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>E (kJ mol⁻¹)</th>
<th>Q (kJ mol⁻¹) for the range</th>
<th>ΔGₐ (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°−60°</td>
<td>40°−60°</td>
<td>50°−60°</td>
</tr>
<tr>
<td>Nil</td>
<td>62.1</td>
<td>42.7</td>
<td>39.1</td>
</tr>
<tr>
<td>Victoria blue</td>
<td>61.1</td>
<td>13.7</td>
<td>2.1</td>
</tr>
<tr>
<td>Fast green</td>
<td>61.1</td>
<td>5.4</td>
<td>2.2</td>
</tr>
<tr>
<td>Light green</td>
<td>60.8</td>
<td>6.4</td>
<td>2.4</td>
</tr>
<tr>
<td>Malachite green</td>
<td>64.6</td>
<td>4.9</td>
<td>2.3</td>
</tr>
<tr>
<td>Fuchsinine base</td>
<td>63.5</td>
<td>4.3</td>
<td>2.1</td>
</tr>
<tr>
<td>Fuchsinine acid</td>
<td>63.5</td>
<td>2.1</td>
<td>0.9</td>
</tr>
<tr>
<td>Crystal violet</td>
<td>63.5</td>
<td>1.3</td>
<td>0.9</td>
</tr>
<tr>
<td>Methyl violet 6B</td>
<td>64.4</td>
<td>3.0</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The values in parentheses indicate weight-loss (mg) in plain 0.5 M H₂SO₄.

Table 2—Tafel Parameters and Inhibitor Efficiencies of Triphenylmethane Dyes for B26S Aluminium in 0.5 M H₂SO₄

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Open circuit potential mV vs SCE</th>
<th>Tafel slope mV decade⁻¹</th>
<th>Cathodic Current (A cm⁻², x10⁻⁹, from extrapolation of</th>
<th>Inhibitor efficiency (%) calculated from</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cathodic</td>
<td>Anodic</td>
<td>Cathodic</td>
<td>Anodic</td>
</tr>
<tr>
<td></td>
<td>Tafel line</td>
<td>Tafel line</td>
<td>Tafel line</td>
<td>Tafel line</td>
</tr>
<tr>
<td>Nil</td>
<td>-755</td>
<td>138</td>
<td>450</td>
<td>9.0</td>
</tr>
<tr>
<td>Victoria blue</td>
<td>-755</td>
<td>108</td>
<td>220</td>
<td>3.4</td>
</tr>
<tr>
<td>Fast green</td>
<td>-755</td>
<td>97</td>
<td>140</td>
<td>1.66</td>
</tr>
<tr>
<td>Light green</td>
<td>-755</td>
<td>117</td>
<td>220</td>
<td>2.34</td>
</tr>
<tr>
<td>Malachite green</td>
<td>-755</td>
<td>108</td>
<td>220</td>
<td>1.63</td>
</tr>
<tr>
<td>Fuchsinine base</td>
<td>-755</td>
<td>103</td>
<td>190</td>
<td>2.63</td>
</tr>
<tr>
<td>Fuchsinine acid</td>
<td>-755</td>
<td>97</td>
<td>320</td>
<td>2.7</td>
</tr>
<tr>
<td>Crystal violet</td>
<td>-755</td>
<td>26</td>
<td>110</td>
<td>2.51</td>
</tr>
<tr>
<td>Methyl violet 6B</td>
<td>-750</td>
<td>57</td>
<td>203</td>
<td>2.48</td>
</tr>
</tbody>
</table>

That in almost all the cases the Q values decrease for higher ranges of temperatures.

The values of free energy of adsorption from aqueous solution (ΔGₐ) were calculated with the help of the equation²⁰:

\[ \log C = \log \frac{\theta}{(1-\theta)} - \log B \quad (iii) \]

where, \( \log B = -1.74 - (\Delta G_a/2.303 RT) \)

The values of ΔGₐ (Table 1) show that malachite green and fast green which are the most efficient inhibitors of all the dyes used exhibit more negative free energies of adsorption. This suggests that they are strongly adsorbed on the metal surface. Crystal violet which is the least efficient inhibitor shows a less negative free energy of adsorption.

**Polarisation behaviour:** B26S aluminium when immersed in 0.25 M H₂SO₄ developed a steady state potential of -755 mV vs SCE. In the presence of various dyes also the corrosion potentials were found to be almost the same (within ±10 mV, Table 2). This suggests that the inhibitors have no preferential action on local anodes or cathodes.

Anodic and cathodic galvanostatic polarisation curves for B26S aluminium in 0.25 M H₂SO₄ alone and containing 0.002 M concentration of the various inhibitors are shown in Fig. 7. The curves show polarisation of both, the anodes as well as the cathodes.

**Mechanism of inhibition:** The TPM dyes are considered to be cationic compounds²¹ having the general structure²¹:

\[ \text{R} = \text{H}, \text{NH}_3, \text{NHCH}_3, \text{N(CH}_3)_2, \text{N(CH}_3)_2 \text{Cl, and, R} = \text{H, CH}_3, \text{C}_2 \text{H}_5, \text{C}_6 \text{H}_5. \]

In addition, fuchsinine acid and fuchsinine base contain some other substituent groups while victoria blue contains a naphthalein ring instead of a benzene one. In strong acid media, the ionisation of the molecules will be suppressed and the cationic
form will not be more predominant. This will result in the inhibitor molecule functioning as a single entity and getting adsorbed through the polar units like nitrogen, chlorine etc. Such adsorption may lead to diminution of attack, and the efficiency will depend on the orientation of the molecule.

The corrosion potentials of B25S aluminium in inhibited acid are almost the same (within ±10 mV) as that in plain 0.25 $M$ $H_2SO_4$ and thus indicate general adsorption of the inhibitors. The anodic and cathodic galvanostatic polarisation curves for aluminium in inhibited acid also show the polarisation of both, the local anodes as well as the cathodes. Further, when log $\theta/(1-\theta)$ is plotted against log $C$ straight lines are obtained in the case of fast green, light green, victoria blue, fuchsia acid and methyl violet 6B (Fig. 8). In case of malachite green, crystal violet and fuchsine base, straight lines are obtained at higher range of concentrations (0.05—0.5%). Thus the data suggest that the inhibitors cover both the anodic and cathodic regions through general adsorption following Langmuir isotherm.

Acknowledgement

The authors thank the Uttar-Purva Gujarat Uchcha Kelvanl Mandal, Pilvai, for facilities.

References

3. Ibid., 3, p. 66.
17. Ref. 8, p. 21.
18. Ref. 8, p. 23.
DYES AS CORROSION INHIBITORS FOR ALUMINIUM ALLOYS IN ACID MEDIA - I TRIPHENYL METHANE DYES AS INHIBITORS FOR ALUMINIUM-MAGNESIUM ALLOY IN HYDROCHLORIC ACID

J. D. Talati and J. M. Daraji

Chemistry Department,
Shri U. P. Arts, Smt. M. G. Panchal Science and Shri V. L. Shah Commerce College, Pilvai (N. G.) (382850), India

Abstract: The inhibitive efficiency of triphenylmethane dyes in HCl of various concentration up to 5M have been studied. The efficiency of almost all the compounds increases with a rise in temperature, the values of the energy of activation being generally lower in inhibited than that in uninhibited acid. Galvanostatic polarisation data for M57S alloy show negligible anodic but significant cathodic polarisation.

Pure (2S) aluminium suffers less corrosion than aluminium alloys, the order of corrodiibility being 2S < B26S < M57S < 3S at lower and 2S < M57S < 3S < B26S at higher acid concentrations. However, the dyes studied accelerate the corrosion of 2S aluminium and confer varied degrees of protection (15 to 92%) to the three alloys. The inhibitors appear to function through general adsorption following Langmuir isotherm.

INTRODUCTION

Solutions of hydrochloric acid are frequently used for pickling of aluminium or for chemical or electrochemical etching of aluminium foils [1] and lithographic plates used as substitute for Zinc [2]. The acid being highly aggressive for the metal, it is desirable to inhibit these solutions by adding various additives which may either retard the unnecessary dissolution of the base metal or improve the etching qualities of the etchant. The inhibition of corrosion of various aluminium alloys using aldehyde, ketones, amino acids, hydrazines, phenols, esters, amines, alkaloids, colloids, heterocyclic compounds and organosulfur compounds has been studied by various workers [3-22]. Data regarding the use of dyes as inhibitors for aluminium in acid media are not so plentiful [23-24]. In earlier communications [25-26] the inhibition of corrosion of B26S aluminium (Al-4% Cu) in hydrochloric acid by triphenylmethane, xanthene and azo dyes has been reported. Such studies are extended to the role of some triphenylmethane dyes as corrosion inhibitors for aluminium-magnesium alloy (Al-2% Mg).
Rectangular specimens of various aluminium alloys (supplied by Indian Aluminium Co. Ltd., Bombay), of size $50 \times 40 \times 0.9$ mm with a small hole of $\sim 2$ mm dia. near the upper edge of the specimen, were used for the determination of the corrosion rates. The amounts of copper, magnesium, manganese, iron and silicon in the alloys were determined according to the method of Vogel [27].

The specimen was polished to a mirrorlike finish, using jeweller's rough followed by tripoli composition and were degreased with carbon tetrachloride. The test specimens were exposed to hydrochloric acid solutions in the range $0.1 - 10.0$ M, containing controlled additions of the following in the range 0 to 1.0%.

- Fuschine acid (FA)
- Fuschine base (FB)
- Crystal violet (CV)
- Methyl violet 6B (MV)
- Malachite green (MG)

For polarisation studies metal specimens of circular design, with handle and the auxiliary platinum electrode were coated with a mixture of perspex and wax from chloroform solution, leaving only the circular portion of the specimen exposed. An H-type cell, with the Luggin capillary was used. The potential was measured with a D. C. microvolt meter, using a saturated calomel reference electrode.

Observations:

In general, the specimens immersed in plain as well as in inhibited hydrochloric acid, develop a film of grey to blackish grey loose product which could easily be removed with a jet of water or by rubbing it with a rubber bung. On cleaning, the corroded specimens revealed a dull metallic and uniformly etched surface, whereas the uncorroded or very slightly corroded specimens were almost as bright as before. In concentrated acid ($> 1.0$ M) there was even grooving and channeling on the metal surface due to hydrogen evolution. In concentrated acid (3.0 to 10.0 M) the attack was so vigorous that the solution temperature at first increased appreciably.

RESULTS AND DISCUSSION

Effect of acid concentration and alloy composition on corrosion in plain acid:

In the case of all the four alloys, the corrosion increases with acid concentration. However, the increase is much greater in higher concentrations of the acid. Thus with an increase in concentration from 0.05 M to 1.0 M, the weight loss increases by $\sim 17\%$ (M57S alloy) to $36\%$ (3S alloy), whereas with
Dyes as corrosion inhibitors for aluminium alloys

An increase in concentration from 0.5M to 1.0 M, there is an eightfold increase in the corrosion of M57S alloy and thirty twofold increase in the corrosion of B26S alloy. From the results it may be generalised that of all the four alloys studied, pure (2S) aluminium suffers minimum corrosion at all the concentrations of the acid. In dilute acid 3S alloy suffers maximum corrosion whereas at higher concentrations of acid, B26S alloy suffers more corrosion. The increased corrosion of B26S alloy in concentrated acid may be traced to the fact that, because of the aggressiveness of the acid more alloy will go in solution but copper being cathodic to aluminium will get redeposited on the metal surface will then act as an efficient cathode for the evolution of hydrogen. When corrosion potentials were measured for M57S aluminium in 0.01 - 2.5 M HCl, it was observed that with increase in acid concentration, the weight loss due to corrosion increased whereas the corrosion potential decreased to more negative values, it being -675 and -900 mV in 0.01 and 2.5M acid respectively.

Effect of inhibitor concentration:

Studies on the effect of inhibitor concentration on the inhibitive efficiency of various dyes in 0.5M HCl, have indicated that the efficiency of CV remains almost constant (≈ 89%) throughout the ranges of inhibitor concentrations studied. The efficiency of FB first increases from 87.3% to 92.3% with 0.01% to 0.1% of inhibitor and then decreases to 86.4% at 1.0% of inhibitor. Here the average efficiency turns out to be ≈ 89%. In the case of MV, the efficiency increases from 62.8% to 81.9% with 0.01 to 0.2% of inhibitor and then remains almost constant up to 1.0% of the inhibitor. MG and FA confer about 82%—83% protection at 0.01% concentration but with an increase in inhibitor concentration, the efficiency decreases, it being 48.6% and 55.4% with 1.0% of MG and FA respectively. A comparison of inhibitive efficiencies of different dyes in 0.5 M HCl, has shown the following order. For 0.01% inhibitor: MV < FA < MG < FB < CV. For 1.0% inhibitor: MG < FA < MV < FB < CV.

Effect of acid concentration:

To determine the effect of acid concentration on inhibitive efficiency, weight losses were measured at constant inhibitor concentration of 0.1% in different concentrations (0.5 M - 10.0 M) of acid at 30°C. From the results it may be generalised that, the efficiency of FB and CV decreases continuously with increase in acid concentration. FA conferred 83.5% protection in 1.0M acid and then the efficiency decreased rapidly, there being hardly any inhibition in 10.0 M HCl with MG and MV, the efficiency was found to increase with acid concentration 3M and 5M respectively but, the efficiency decreased with further increase in acid concentration. This may be traced to the increased tendency of the metal to react with acid and liberate hydrogen vigorously [28]. This may not allow the establishment of the chemisorption process sufficiently rapidly resulting in decrease of inhibition. The
efficiency of the various inhibitors is found to increase in the order: in 1.0 M acid: MG < MV < FA < CV < FB. In 5.0 M acid: FA < CV < FB < MG < MV. From the results, methyl violet 6B and fuchsin base appear to be good inhibitors for pickling in higher concentrations of acid.

Effect of temperature on inhibitive efficiency:

To study the effect of temperature on inhibitive efficiency weight losses were determined in 0.5 M HCl containing 0.1% inhibitor at solution temperatures of 20°, 30°, 40°, 50° and 60°C. The results given in Table I show that although the weight loss due to corrosion, increases considerably (by a factor of about 2 to 3) for every 10°C rise in temperatures the inhibitive efficiency of almost all the compounds increases with rise in temperature from 20° to 60°C. Such inhibitors are of practical interest where retardation of attack on the metal is desired at elevated temperatures. The efficiency of different compounds at 60°C was found to increase in the order: CV < MV < MG < FB < FA.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Extent of Inhibition (P. I.) at temperature of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°C</td>
</tr>
<tr>
<td>Nil</td>
<td>(10.0)*</td>
</tr>
<tr>
<td>Fuchsin acid</td>
<td>-20.0</td>
</tr>
<tr>
<td>Fuchsin base</td>
<td>25.0</td>
</tr>
<tr>
<td>Crystal violet</td>
<td>40.0</td>
</tr>
<tr>
<td>Methyl violet 6B</td>
<td>40.0</td>
</tr>
<tr>
<td>Malachite green</td>
<td>35.0</td>
</tr>
</tbody>
</table>

* The values in parenthesis indicate the weight loss, mg, in uninhibited acid.

The values of energy of activations, $E$, were calculated from slopes of the Arrhenius plots of log$\rho$ vs 1/T where $\rho$ is the corrosion rate and T, the absolute temperature (Fig.1). The $E$ values given in Table II indicate that for the corrosion of M57S aluminium in 0.5 M HCl, the energy of activation
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has a value of ca. 78.1 kJ/mol (18.7 kcal/mol). In inhibited acid, the E values are lower and range from 37.9 (FA) to 66.8 kJ/mol (CV). It may be noted that FA and FB which function as more efficient inhibitors have comparatively lower activation energies. Generally, the lower values of E, in inhibited acid suggest that such inhibitors, like the catalysts which do not change the temperature coefficient of the reaction, are firmly held on the metal surface [29]. According to Machu [30], the kinetics of such corrosion process acquires the character of a diffusion process, in which at higher temperatures the amount of inhibitor present at the metal surface is greater than that at lower temperatures. This increases the surface area of the metal covered by the inhibitor molecules. The reaction between the metal and the acid can then only proceed by diffusion of acid anions through the pores of the protective layer formed. Hoar and Holliday [31] suggest that the enhancement of inhibitive efficiency at higher temperature may be due to higher activation energy available for adsorption, and the higher rate of diffusion of inhibitor molecules. Singh et al. [32], consider that with increase in temperature some chemical changes occur in the inhibitor molecules leading to an increment in the electron densities at adsorption centres of the molecule causing an improvement in inhibitive efficiency.

Fig. 1. Arrhenious plots for corrosion of M57S aluminium in plain acid as well as in inhibited 0.5 M HCl.

Table II gives the various thermodynamic parameters viz heat of adsorption $\Delta G^o$ and activation energy E.

The results show that MV, MG and CV which exhibit almost the same efficiencies have approximately the same free energy of adsorption. FA and FB being slightly more efficient inhibitors, give slightly more negative free energy of adsorption.
ENERGY OF ACTIVATION (E) HEAT OF ADSORPTION (Q) AND FREE ENERGY OF ADSORPTION (ΔG°A) OF TRIPHENYL METHANE DYES DURING CORROSION OF 575S ALUMINIUM IN 0.5M HCL

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Molecular formula</th>
<th>P. l. at 60°C</th>
<th>Energy of activation, E (kJ/mol)</th>
<th>Heat of adsorption, Q (kJ/mol)</th>
<th>Average free energy of adsorption ΔG°A, (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystal violet</td>
<td>C₁₄H₂₆N₈Cl</td>
<td>65.5</td>
<td>66.8</td>
<td>49.4</td>
<td>-17.2</td>
</tr>
<tr>
<td>Malachite green</td>
<td>C₂₅H₃₈CIN₂</td>
<td>69.0</td>
<td>63.2</td>
<td>62.7</td>
<td>-17.3</td>
</tr>
<tr>
<td>Methyl violet 6B</td>
<td>C₂₁H₂₆N₇Cl</td>
<td>68.0</td>
<td>65.3</td>
<td>48.5</td>
<td>-17.4</td>
</tr>
<tr>
<td>Fuchsine base</td>
<td>C₂₅H₂₆N₈Cl</td>
<td>81.1</td>
<td>49.8</td>
<td>77.8</td>
<td>-18.6</td>
</tr>
<tr>
<td>Fuchsine acid</td>
<td>C₂₅H₁₄N₈S₅N₉Na₈</td>
<td>83.5</td>
<td>37.8</td>
<td>101.2</td>
<td>-18.6</td>
</tr>
</tbody>
</table>

Polarisation behaviour:

A specimen of M57S aluminium, when immersed in 0.5M uninhibited hydrochloric acid, develops a corrosion potential of ——— 805 mV (Table IV). In inhibited acid, the potentials are found to range from ——— 800 (FA) to ——— 820 mV (FB and MG), i.e. the inhibitors do not have any appreciable effect on the corrosion potential of M57S aluminium in hydrochloric acid.

The anodic and cathodic galvanostatic polarisation curves for M57S aluminium in 0.5M HCl alone and containing 0.002M of the various inhibitors are shown in Fig. 2. The curves show negligible anodic but significant cathodic polarisation in plain as well as in inhibited acid. The preferential polarisation of local cathodes under the influence of an external current in the present case, suggests that the inhibitors may prove to be of value when cathodic protection of aluminium in acid media is desired.

Inhibitive efficiencies calculated from corrosion current obtained by extrapolation of the cathodic Tafel lines are given in Table III. In all the cases, the Tafel plot efficiencies are lower than the values calculated from weight loss data.
<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Open circuit potential (mV)</th>
<th>Cathodic Tafel slope (mV/decade)</th>
<th>Energy transfer coefficient (cathodic)</th>
<th>Corrosion current $\times 10^{-4}$ (A/cm²)</th>
<th>Inhibitor efficiency ($%$) calculated from extrapolation weight of cathodic loss</th>
<th>Total line</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nil</td>
<td>-805</td>
<td>0.3</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fuchsine acid</td>
<td>-800</td>
<td>1.5</td>
<td>1.288</td>
<td>3.162</td>
<td>81.9</td>
<td>-</td>
</tr>
<tr>
<td>Fuchsine base</td>
<td>-820</td>
<td>0.6</td>
<td>0.6</td>
<td>2.089</td>
<td>34.0</td>
<td>89.1</td>
</tr>
<tr>
<td>Crystal violet</td>
<td>-815</td>
<td>1.6</td>
<td>1.660</td>
<td>2.042</td>
<td>35.5</td>
<td>88.0</td>
</tr>
<tr>
<td>Methyl violet 6B</td>
<td>-810</td>
<td>1.6</td>
<td>1.660</td>
<td>1.660</td>
<td>47.6</td>
<td>82.3</td>
</tr>
<tr>
<td>Malachite green</td>
<td>-820</td>
<td>1.2</td>
<td>1.2</td>
<td>1.862</td>
<td>41.2</td>
<td>76.9</td>
</tr>
</tbody>
</table>

TAFEL PARAMETERS AND INHIBITOR EFFICIENCIES OF TRIPHENYLMETHANE DYES FOR M57S ALUMINIUM IN 0.5 M HCl
(Surface area of the specimen: 40cm². Temperature: 30° ± 0.5°; Inhibitor concentration: 0.002 M)
Effect of alloy composition:

To determine the effect of alloying elements on the corrosion resistance behaviour of aluminium, weight losses of four different alloys, viz., 2S (99.76% Al), 3S (Al-1.3% Mn), B26S (Al-3.9% Cu), M57S (Al-2.2% Mg), were determined in 3.5 M hydrochloric acid containing 0.1% inhibitor. The results are given in Table IV. The results show that although pure (2S) aluminium suffers ten times less corrosion than M57S alloy in 0.5 M HCl, it fails to get any protection by any of the inhibitors used. Actually the five triphenylmethane compounds studied accelerate the corrosion of 2S aluminium by 43.5% (FA) to 648% (MV). With the other three alloys, the compounds show inhibitive effect ranging from 15.0% (Fuchsinic acid, 3S alloy) to 92.3% (fuchsinic base, M57S alloy). In general, the inhibitors confer more protection on the magnesium bearing alloy. The order of decreasing corrodedibility in uninhibited 0.5 M HCl is:

M57S > 3S > B26S > 2S,
that in inhibited acid is:
2S > 3S > B26S > M57S.

i.e., M57S alloy, which suffers maximum corrosion in uninhibited acid gets maximum protection (78% to 92%) in inhibited acid.
Dyes as corrosion inhibitors for aluminium alloys

**Table IV**

**EFFECT OF ALLOY COMPOSITION ON INHIBITOR EFFICIENCY OF TRIPHENYL METHANE DYES IN 0.5 M HCl.**

(Surface area of specimen, 40 cm²; Temperature, 30°C ± 0.5°C; Inhibitor concentration, 0.1%; Immersion period 1 day)

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>2S</th>
<th>3S</th>
<th>M57S</th>
<th>B26S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nil</td>
<td>(23.0)*</td>
<td>(153.0)*</td>
<td>(221.0)*</td>
<td>(86.1)*</td>
</tr>
<tr>
<td>Fuchsine acid</td>
<td>-43.5</td>
<td>15.0</td>
<td>78.7</td>
<td>31.7</td>
</tr>
<tr>
<td>Fuchsine base</td>
<td>-134.7</td>
<td>54.9</td>
<td>92.3</td>
<td>39.5</td>
</tr>
<tr>
<td>Crystal violet</td>
<td>-508.6</td>
<td>69.3</td>
<td>89.1</td>
<td>69.8</td>
</tr>
<tr>
<td>Methyl violet 6B</td>
<td>-647.8</td>
<td>38.5</td>
<td>79.8</td>
<td>49.9</td>
</tr>
<tr>
<td>Malachite green</td>
<td>-234.8</td>
<td>46.7</td>
<td>78.3</td>
<td>64.3</td>
</tr>
</tbody>
</table>

* The values in parenthesis indicate the weight loss, mg, in uninhibited acid.

If dyes are considered to be effective as inhibitors through adsorption on the metal surface, then it may be generalised that adsorption is more on the magnesium bearing alloy or that the adsorption bonds between the metal and the inhibitor are stronger with magnesium followed by copper followed by manganese. It appears that the dyes fail to get adsorbed on pure aluminium. It is also possible that the dyes may function as depolarisors in the case of pure aluminium and hence accelerate corrosion.

**Mechanism of inhibition:**

The corrosion potentials of M57S aluminium in 0.5 M hydrochloric acid containing various inhibitors are almost the same (within ± 15mV) as that in uninhibited acid and thus indicate general adsorption of the inhibitors. When log ([I]/[I-]) is plotted against log C (C = inhibitor concentration), straight lines are obtained for certain ranges of concentrations. (Fig. 3.) This suggests that the inhibitor covers both the anodic and cathodic regions through general adsorption following Langmuir isotherm. It appears that the point of first attachment is the N⁺ of the quinonoid structure in all the cases. The lower efficiency of fuchsine acid than fuchsine base in higher concentrations of hydrochloric acid may be due to the steric hindrance produced by the presence of different substituent groups in different positions. It is also possible that in strongly acid solution, the sodium atom may get replaced by the hydrogen and this may have a slightly adverse effect on the ionization behaviour and the adsorptivity of the inhibitor.
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