SUMMARY

In the present work the corrosion of M57S and B26S alloys and their inhibition in aqueous solutions of HCl, H₂SO₄ and H₃PO₄ has been studied. Moreover, data regarding 2S and 3S alloys have also been collected to determine the effect of alloying elements on the corrosion behaviour of aluminium in hydrochloric acid. The dyes studied as inhibitors in different acid media include:

(a) Triphenylmethane dyes:
   Fuchsine acid, fuchsine base, crystal violet, methyl violet 6B, malachite green, victoria blue, fast green, light green.

(b) Azo dyes:
   Resorcine yellow, fast garnet, alizarin yellow, naphthol blue black, metanil yellow, eriochrome black T, fast sulphone black F, methyl red.

The corrosion data have been collected with respect to the following:

(i) Concentration of inhibitor,
(ii) Concentration of corrodant,
(iii) Period of exposure,
(iv) Temperature.

Attempts have also been made to collect the potential and polarisation data under galvanostatic polarisation conditions to get an insight into the mechanism of corrosion.
INHIBITION OF CORROSION OF M57S ALUMINIUM IN HYDROCHLORIC ACID BY TRIPHENYL METHANE DYES:

The corrosion of all the four aluminium alloys increases with acid concentration, the increase being greater, the higher the acid concentration of the four alloys studied. BS (99.8%) suffers minimum corrosion whereas 3S alloy suffers maximum corrosion in dilute (0.01 - 0.1 M) acid. However, at higher acid concentrations B26S (Al - 4% Cu) alloy suffers more corrosion.

The inhibitive efficiency of crystal violet remains almost constant (≈ 89%) throughout the ranges of inhibitor concentrations studied in 0.5 M hydrochloric acid. The efficiency of fuchsine base first increases from 87.3% with 0.01% inhibitor to 92.3% with 0.1% and then decreases to 86.4% at 1% inhibitor concentration. In the case of methyl violet 6B, the efficiency increases from 62.8 to 81.9% with increase in inhibitor concentration from 0.01 to 0.2% of inhibitor and then remains almost constant up to 1% of inhibitor. Malachite green and fuchsine acid 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% of malachite green and fuchsine acid respectively.

The inhibitive efficiencies of different dyes at 1.0% concentration in 0.5 M hydrochloric acid are found to increase in the order:
malachite green < fuchsine acid < methyl violet 6B < fuchsine base < crystal violet.

At constant inhibitor concentration the efficiency of fuchsine base and crystal violet decreases continuously with increase in acid concentration. Fuchsine acid confers 83.5% protection in 1 M acid and then the efficiency decreases rapidly, there being hardly any inhibition in 10 M acid. With malachite green and methyl violet 6B, the efficiency increases with acid concentration up to 3M and 5M respectively and then decreases. This may be traced to the vigorous liberation of hydrogen which may not allow any chemisorption of inhibitors. The order of increase in efficiency is:

In 1 M acid: malachite green < methyl violet 6B < fuchsine acid < crystal violet < fuchsine base.

In 5 M acid: fuchsine acid < crystal violet < fuchsine base < malachite green < methyl violet 6B.

Thus methyl violet 6B and fuchsine base appear to be good inhibitors for pickling in higher concentrations of acid.

The inhibitive efficiency of all the dyes increases with a rise in temperature, the increase in inhibitive efficiency at 60°C in 0.5 M hydrochloric acid being in the order:

crystal violet (65.6%) < methyl violet 6B (68.0%) < malachite green (69.0%) < fuchsine base (81.1%) < fuchsine acid (83.5%).

For the corrosion of M57S aluminium in 0.5 M hydrochloric
acid, the energy of activation, \( E \), has a value of 77.3 kJ/mol. In inhibited acid the \( E \) values are lower and range from 37.8 (fuchsin acid) to 66.8 kJ/mol (crystal violet).

The heats of adsorption for fuchsin acid, fuchsin base, malachite green, methyl violet 6B and crystal violet are found to be 101.2, 77.3, 52.7, 48.5 and 49.4 kJ/mol respectively, whereas, the values of free energy of adsorption are -18.6, -18.0, -17.3, -17.4 and -17.2 kJ/mol respectively.

A specimen of M57S aluminium when immersed in 0.5 M plain hydrochloric acid develops a corrosion potential of -805 mV. In inhibited acid also the potentials are found to range from -800 mV (fuchsin acid) to -820 mV (fuchsin base and malachite green). The galvanostatic polarisation curves for M57S aluminium in 0.5 M hydrochloric acid containing 0.002 M inhibitor show negligible anodic but significant cathodic polarisation in plain as well as in inhibited acid.

As regards the effect of alloy composition on inhibitive efficiency, it may be generalised that in plain 0.5 M acid the order of decreasing corrosibility of the alloys is:

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M57S > 3S > B26S > 2S
\]

i.e., pure aluminium suffers minimum corrosion. In inhibited acid, there is an acceleration of corrosion of 2S aluminium while the other three alloys get some degree of protection by the inhibitors. Thus the order of decreasing corroodibility in 0.5 M hydrochloric acid containing 0.1 % inhibitor is:

\[
2S > 3S > B26S > M57S
\]
The rectilinear nature of the plots of \( \log \theta/(1 - \theta) \) vs \( \log C \) show that the inhibitors function by covering the anodic as well cathodic region through general adsorption following Langmuir isotherm. The point of first attachment appears to be \( N \) of the quinonoid structure.

(ii) INHIBITION OF CORROSION OF B26S ALUMINIUM IN PHOSPHORIC ACID BY TRIPHENYL METHANE DYES:

The corrosion potential and the solution pH decrease with increase in concentration of phosphoric acid. However, the extent of corrosion of B26S aluminium increases with acid concentration as well as exposure period.

The inhibitive efficiency of all the eight triphenylmethane dyes increases with inhibitor concentration in 0.33 M phosphoric acid at 30°C. At 0.5% inhibitor concentration the efficiency is found to increase 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%).

The efficiency of almost all the inhibitors decreases with increase in acid concentration. In 1.33 M acid the dyes confer only 9.4% (fuchsine acid) to 24.9% (fast green) protection. Thus the behaviour of the inhibitor in phosphoric acid is quite different from that in hydrochloric acid. Experiments with
addition of chloride ions to inhibited phosphoric acid show that the chloride ions augment the inhibitive behaviour of the dyes perhaps by the in situ formation of compounds like (inhibitor) $\text{Al}_{x}\text{Cl}_y\text{H}_2\text{O}$ on the metal surface.

The efficiency of the inhibitors decreases with a rise in temperature. At 60°C the inhibitive efficiencies for B26S aluminium in 0.167 M phosphoric acid increase in the order:

- fuchsine acid < fuchsine base < victoria blue <
- light green < crystal violet < methyl violet 6B <
- malachite green < fast green.

The energy of activation for the corrosion of B26S aluminium in 0.167 M plain phosphoric acid is 52.4 kJ/mol. In inhibited acid also the values are almost the same (within $\pm$ 10 kJ/mol).

A comparison of the values of inhibitive efficiencies and the free energies of adsorption show that those compounds which show better efficiency have more negative free energy of adsorption.

A specimen of B26S aluminium when immersed in 0.033 M phosphoric acid develops a corrosion potential of -755 mV vs SCE. In inhibited acid the potentials are found to range from -740 (fuchsine acid) to -805 mV (crystal violet). The galvanostatic polarisation curves for B26S aluminium in 0.033 M phosphoric acid alone and containing 0.002 M of the inhibitor show polarisation of both, the cathodes as well as the anodes, the anode being polarised to a greater extent.
The linearity of the plots \( \log \frac{\theta}{(1 - \theta)} \) vs \( \log C \) suggest that the inhibitor covers both, the anodic as well as the cathodic regions following Langmuir isotherm. The quinonoid group of the inhibitor appears to be the main anchoring group for the adsorption of the inhibitor. The introduction of methyl (\(-\text{CH}_3\)) or ethyl (\(-\text{CH}_2\text{-CH}_3\)) group on the quinonoid nitrogen increases the efficiency, it being greater, the higher the chain length of the alkyl group.

(iii) Inhibition of corrosion of B268 aluminium in sulphuric acid by triphenylmethane dyes:

The pH value of the solution decreases while the specific conductivity and the rate of corrosion (mg dm\(^{-2}\) day\(^{-1}\)) increase with an increase in acid concentration. Further, the extent of corrosion and relative corrosivity also increase with time. The extent of corrosion \(Q\) varies with acid concentration \(C\) following the parabolic equation of the type, \(C = kQ^n\), where \(n\) is a positive number and \(k\) is a constant.

The inhibitive efficiencies of various triphenylmethane dyes in 0.25 M sulphuric acid are found to increase with inhibitor concentration, the general order of increase in efficiency being:

- methyl violet
- fuchsin base
- fuchsin acid
- crystal violet
- victoria blue
- light green
- malachite green
- fast green
At 0.5% concentration, fast green and malachite green are the most efficient inhibitors exhibiting an efficiency of ~ 83%.

At 0.1% inhibitor concentration in 0.25 M sulphuric acid, the efficiency of different dyes is found to increase in the order:

- methyl violet 6B (27.0%) < fuchsine base (29.0%) < fuchsine acid (34.5%) < crystal violet (38.0%) < victoria blue (38.5%) < light green (49.5%) < malachite green (58.5%) < fast green (66.0%).

However, in 8.0 M acid the order of increase in efficiency is:

- methyl violet 6B (35.5%) < fuchsine base (36.1%) < fuchsine acid (40.2%) < victoria blue (42.0%) < light green (43.9%) < crystal violet (44.2%) < malachite green (48.2%) < fast green (58.8%).

The inhibitive efficiency of all the inhibitors increases with a rise in temperature. The inhibitors thus belong to a class of compounds which can be considered for providing protection at elevated temperatures. In general, in the range 30 - 60°C, the efficiency of the inhibitors is found to increase in the order:

- crystal violet < fuchsine acid < methyl violet 6B < light green < victoria blue < fuchsine base < fast green < malachite green.

The energy of activation for the corrosion of B26S aluminium in 0.5 M plain as well as inhibited sulphuric acid is ~ 64.0
The values of heats of adsorption, $Q$, decrease for higher ranges of temperatures in almost all the cases, indicating a rise in inhibitive efficiency. The mean values of free energy of adsorption, $\Delta G_A^0$, are more negative in the case of those inhibitors which are more efficient.

A specimen of B26S aluminium when immersed in 0.25 M sulphuric acid develops a corrosion potential of $-755$ mV vs SCE. In inhibited acid also the potentials are found to be almost the same (within ± 10 mV). The galvanostatic polarisation curves for B26S aluminium in 0.25 M sulphuric acid alone and containing 0.002 M of the inhibitor show polarisation of both, the cathodes as well as the anodes, the anode being polarised to a greater extent. The rectilinear nature of the plots of $\log \theta/(1-\theta)$ vs $\log C$ show that the inhibitors function by covering the anodic as well as cathodic regions through general adsorption following Langmuir isotherm. The point of first attachment appears to be the quinonoid portion of the molecule.

(iv) INHIBITION OF CORROSION OF B26S ALUMINIUM IN HYDROCHLORIC ACID BY AZO DYES:

At constant hydrochloric acid concentration, the corrosion of B26S aluminium increases with exposure period whereas at constant exposure period, the extent of corrosion increases with acid concentration.

In 0.5 M hydrochloric acid at 30°C, the inhibitive efficien-
cides of metanil yellow, alizarin yellow and naphthol blue black decrease with increase in inhibitor concentration. The efficiency of fast green and resorcine yellow first increase with inhibitor concentration, becomes maximum at 0.1% concentration and then decreases with further increase in inhibitor concentration. At 0.5% inhibitor concentration, the efficiency is found to increase in the order:

alizarin yellow < naphthol blue black <
resorcine yellow < fast garnet < metanil yellow.

At constant inhibitor concentration of 0.1%, the inhibitive efficiencies of all the five inhibitors are found to increase with increase in acid concentration up to 1.0 M; the general order of increase in efficiency in 0.01 - 0.1 M hydrochloric acid being:

alizarin yellow < naphthol blue black <
resorcine yellow < fast garnet < metanil yellow.

In 5.0 M hydrochloric acid, the order of efficiency of different inhibitors is found to be:

alizarin yellow < metanil yellow (95.8%) <
naphthol blue black (97.8%) < fast garnet (98.7%) <
resorcine yellow (98.8%).

However, in 10.0 M acid, the efficiency drops considerably and is found to lie in the range 16.2% (Resorcine yellow) - 25.7% (metanil yellow).

The photomicrographs show that the specimens immersed in
plain 1 M acid, give a highly etched surface at x 100. At x 450 some pits are also evident. In inhibited acid the attack is much reduced and the photomicrographs reveal that the intensity of etching and the depth of pits are considerably reduced.

The inhibitive efficiency of all the inhibitors is found to increase with a rise in temperature in the temperature range studied. At 60°C, the order of increase in efficiency is found to be:

alizarin yellow (42.9 %) < naphthol blue black (49.9 %) < fast garnet (75.7 %) < resorcine yellow (82.3 %) < metanil yellow (83.9 %).

The inhibitors may thus prove to be of value when inhibition is required at higher temperatures.

The energy of activation for the corrosion of B26S aluminium in 0.5 M hydrochloric acid is found to be 93.7 kJ/mol. In inhibited acid the values are found to lie in the range 72.8 (resorcine yellow) - 87.4 kJ/mol (alizarin yellow).

The values of the heats of adsorption of the inhibitors range from 29.7 (naphthol blue black - 74.5 kJ/mol (resorcine yellow) suggesting that the inhibitors with higher Q values are more efficient. The values of the free energy of adsorption, $\Delta G_A^0$, show that metanil yellow and resorcine yellow which are more efficient give more negative free energies of adsorption.

B26S aluminium immersed in 1 M hydrochloric acid, develops a corrosion potential - 820 mV SCE. In inhibited acid also the
values are almost the same. This suggests that the inhibitors do not have any preferential action on the local anodes or cathodes. Galvanostatic polarisation curves show that in plain as well as in inhibited acid, there is negligible anodic but appreciable cathodic polarisation. The inhibitors appear to function through general adsorption following Langmuir isotherm.

(v) **INHIBITION OF CORROSION OF B26S ALUMINIUM IN PHOSPHORIC ACID BY AZO DYES:**

At constant phosphoric acid concentration, the inhibitive efficiencies of different inhibitors are found to increase with inhibitor concentration. At 0.2% inhibitor concentration, the efficiency increases in the order:

- methyl red (19.0%) < fast garnet (24.0%) < metanil yellow (37.4%) < eriochrome black T (38.8%) < alizarin yellow (39.2%) < resorcine yellow (46.9%) < fast sulphone black F (50.4%) < naphthol blue black (54.9%).

At constant inhibitor concentration, the inhibitive efficiencies of the different inhibitors are found to decrease with increase in acid concentration. Thus in 0.667 M phosphoric acid the increase in efficiency is found to be:

- methyl red (0.8%) < metanil yellow (2.0%) < fast garnet (3.8%) < eriochrome black T (5.1%) < alizarin yellow (6.6%) < fast sulphone black F (6.8%) < naphthol blue black (11.5%) < resorcine yellow (18.3%).
A rise in temperature has an adverse effect on the inhibitive efficiency. In general, in the range 30 - 60°C, the order of increase in efficiency is found to be:

methyl red < metanil yellow < alizarin yellow < fast garnet < eriochrome black T < resorcin yellow < fast sulphone black F < naphthol blue black.

The energy of activation of B26S aluminium, in plain 0.167 M phosphoric acid is ~ 52 kJ/mol. In inhibited acid also, except resorcin yellow, the E values are almost the same as that in plain acid. Resorcin yellow shows a slightly higher value of 62.7 kJ/mol. The values of heat of adsorption, Q, are found to range from -17.6 kJ/mol (naphthol blue black) to -79.1 kJ/mol (metanil yellow) while the free energies of adsorption are found to vary from -10.9 kJ/mol (metanil yellow and methyl red) to -14.2 kJ/mol (naphthol blue black).

The corrosion potential of -755 mV (vs SCE) for B26S aluminium in 0.033 M phosphoric acid is not much affected by the addition of the inhibitor. Under galvanostatic polarisation conditions the anode is polarised to a greater extent than the cathode in plain as well as in inhibited phosphoric acid.

The extent of corrosion of B26S aluminium in 0.1 N solutions of different acids is found to increase in the order:

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\begin{align*}
\text{H}_2\text{SO}_4 \ (14.4 \text{ mg}) & < \text{HCl} \ (16.4 \text{ mg}) < \text{H}_2\text{C}_2\text{O}_4 \ (20.2 \text{ mg}) < \\
\text{HNO}_3 \ (21.5 \text{ mg}) & < \text{H}_3\text{PO}_4 \ (33.7 \text{ mg})
\end{align*}
\]
The order of increase in efficiency of metanil yellow in different acids is found to be:

\[
\begin{align*}
\text{HNO}_3 \ (7.9 \%) &< \text{H}_2\text{SO}_4 \ (11.8 \%) < \text{H}_2\text{C}_2\text{O}_4 \ (20.8 \%) < \\
\text{H}_3\text{PO}_4 \ (20.8 \%) &< \text{HCl} \ (40.2 \%).
\end{align*}
\]

The different combinations of acids and inhibitors show that metanil yellow, fast sulphone black F and fast garnet are comparatively better inhibitors in 0.1 N hydrochloric acid. In phosphoric and nitric acid as well as in sulphuric acid, naphthol blue black is a good inhibitor, whereas, in oxalic acid, eriochrome black T shows an inhibition of \( \sim 30 \% \). In mixed hydrochloric-phosphoric acids, naphthol blue black gives about 26 \% inhibition.

It may be generalized that of the various azo dyes, the dyes containing an \(-\text{OH}\) group in the ortho position to the azoic nitrogen show better efficiency.