

# **ORGANIC CORROSION INHIBITORS**

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**This thesis is presented for the degree of  
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**I declare that this thesis is my own account of  
my research and contains as its main content work  
which has not previously been submitted for a degree  
at any tertiary education institution.**

*Tan Sweetkin*

**To my parents for so many reasons**

**but particularly for:**

**warning me to be aware of the bad in the best of us;**

**teaching me to look for the good in the worst of us.**

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## ABSTRACT

The overall aims of this thesis were to conduct a broad survey of possible organic corrosion inhibitors in near-neutral chloride solutions and to elucidate the mechanisms of such action.

Altogether, 130 organic compounds were studied as possible corrosion inhibitors for pure iron, mild steel, copper and aluminium in aerated near-neutral (pH = 8.4) solutions containing 500 ppm NaCl and 100 ppm NaHCO<sub>3</sub>, conditions often encountered in water-based automotive engine coolants. Inhibitor behaviour was investigated using steady-state electrochemical techniques including polarisation curves, Stern-Geary and corrosion potential ( $E_{\text{corr}}$ ) measurements.

The organic compounds examined were found to be highly specific in their inhibitive action toward the metals studied. Typical examples of highly effective corrosion inhibitors were: sebacate and octanoate for pure iron; oleate and sebacate for mild steel; benzotriazole and 2-mercaptobenzothiazole for copper; and laurate and oleate for aluminium.

$E_{\text{corr}}$  was found to provide a rapid and convenient screening test for evaluating the inhibitor performance of organic compounds toward pure iron, mild steel and aluminium but was less useful for copper.

Good organic inhibitors were found to act as anodic inhibitors toward pure iron and mild steel but as anodic or mixed-type inhibitors toward copper. For aluminium, the majority of the compounds studied were found to act as anodic inhibitors.

However, it was also found that only pit initiation was inhibited, i.e. existing pits were not prevented from developing. Optical microscopy of pitted aluminium surfaces indicated their nature varied considerably with inhibition efficiency.

The role of complex formation in organic corrosion inhibitors was found to vary with the metal. Complexation of either iron(II) or iron(III) ions was found to have an insignificant effect on mild steel. The corrosion rate of copper was found to increase with the copper(II) complex stability, thus indicating complex formation to be the rate-determining step. For aluminium, the observed effects were found to depend on complex stability. For weak to moderate complexants, inhibitor efficiency (measured as  $E_{\text{pit}}$ ) increased with increasing complexation. However, very strong complexing agents were sufficiently stable to dissolve the aluminium oxide surface, leading to poor inhibition. Aluminium pit morphology was found, using scanning electron microscopy, to change from hemispherical in the uninhibited solution to irregular in the presence of complexing inhibitors.

No simple relationships between inhibitor efficiency and molecular structure were found. However, carbon chain length, the nature of functional group(s) and their location in the molecule were found to be important but varied according to the metal.

The inhibiting ability of sebacate (a straight chain  $C_8$  dicarboxylate) was found not to be compromised by water movement (stirring) or pre-existing corrosion product layers. Immersion tests showed that passive film formation on mild steel in sebacate solution involved two stages and was complete only after ~100 h immersion.

The ion selective properties of several iron(III) carboxylates and hydrated iron(III) oxide films were studied by membrane potential measurements in neutral sodium chloride solutions. Some specimens were also studied by Mössbauer spectroscopy.

These results show that dicarboxylates are good inhibitors toward mild steel because they form impermeable films. Poor inhibitor performance is associated with the anion selectivity of the film which in turn appears to be related to the film purity. A model is suggested for the inhibition mechanism of mild steel corrosion by dicarboxylates in aerated near-neutral chloride solutions.



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