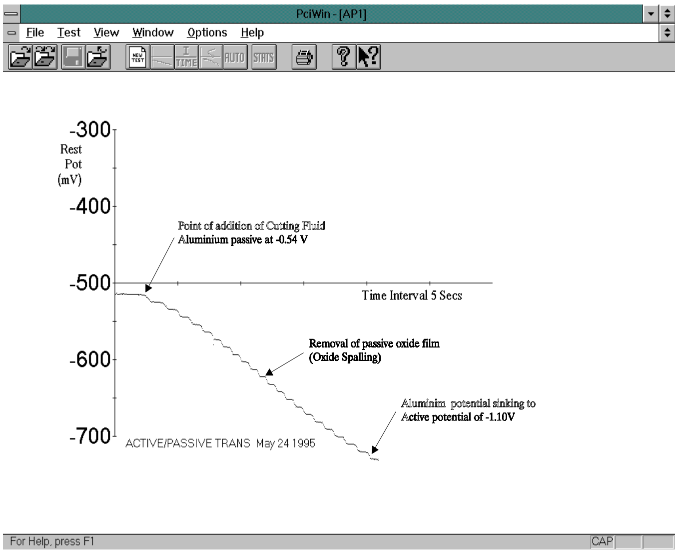
8.0 INTERPRETATION OF SWEEP CURVES

8.1 *Active Passive Transitions*

As illustrated in section 5.1 of the "User Guide" , ***Rest Potential*** test measurements can be used to visualise the changes which occur at metal surface/solution interfaces. When a metal specimen is placed into a solution after a short period of time an equilibrium potential is reached, this can be due to a mono oxide passive layer formation , inhibitors adsorbing on the surface or active corrosion or redox reactions.



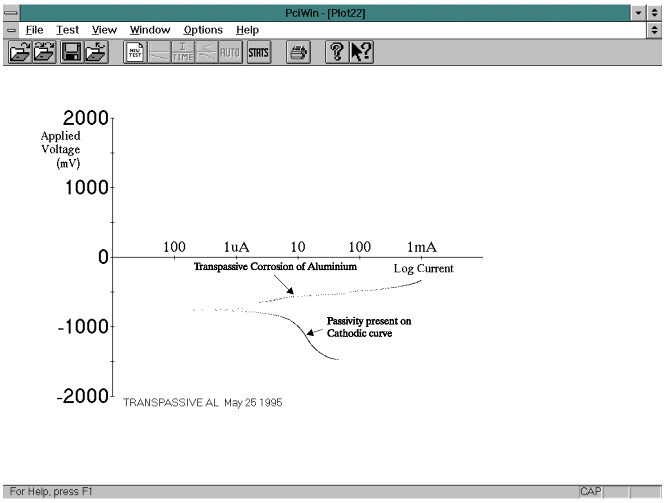
Point of addition of Cutting Fluid
Aluminium passive at -0.54 V

Removal of passive oxide film
(Oxide Spalling)

Aluminim potential sinking to
Active potential of -1.10V

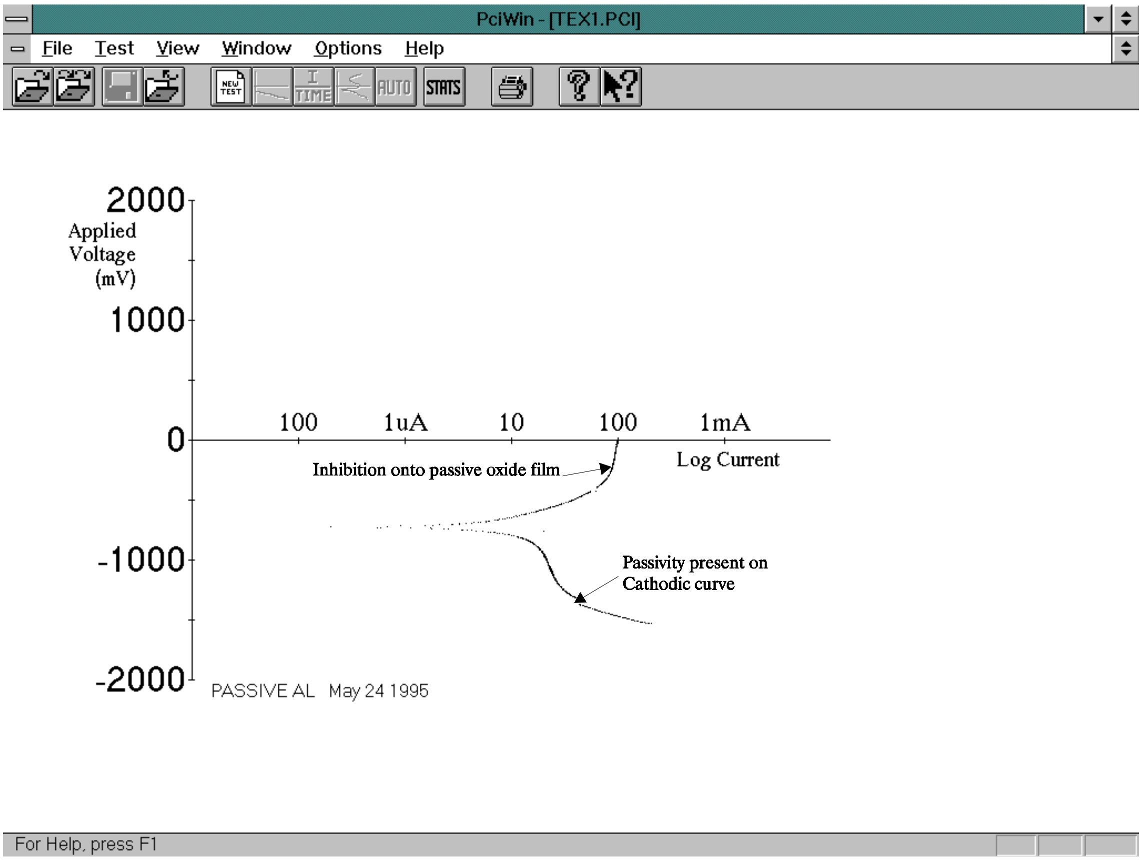
Metals such as Aluminium alloys and Stainless Steels which exhibit both active and passive potentials can be studied with respect to additions of industrial fluids. Fluids can be screened for aggressiveness towards Aluminium alloys by adding the fluid concentrate to an already passive aluminium specimen in neutral water. The test screen shows an example of an addition of a cutting fluid which contains chlorine in it's E.P agent which is known to be aggressive to Aluminium. The effect of the agressive component in the soluble oil can be clearly visualised.

The **Sweep** curve of a metal in it's passive state is characterised by a very steep cathodic portion of the curve below the X axes, indicating resistance to charge transfer across a passive surface, and a rapid flow of anodic current above the X axes usually referred to as Trans-Passive metal dissolution (corrosion). An example of Trans-Passive behaviour of Aluminium in aerated neutral water is shown opposite.
If the PCI Mini-Cell is immersed into a cutting fluid that is known not to be aggressive towards Aluminium then the sweep curve produced in this fluid should exhibit a similar cathodic curve but will show inhibition instead of corrosion above the X axes as below.

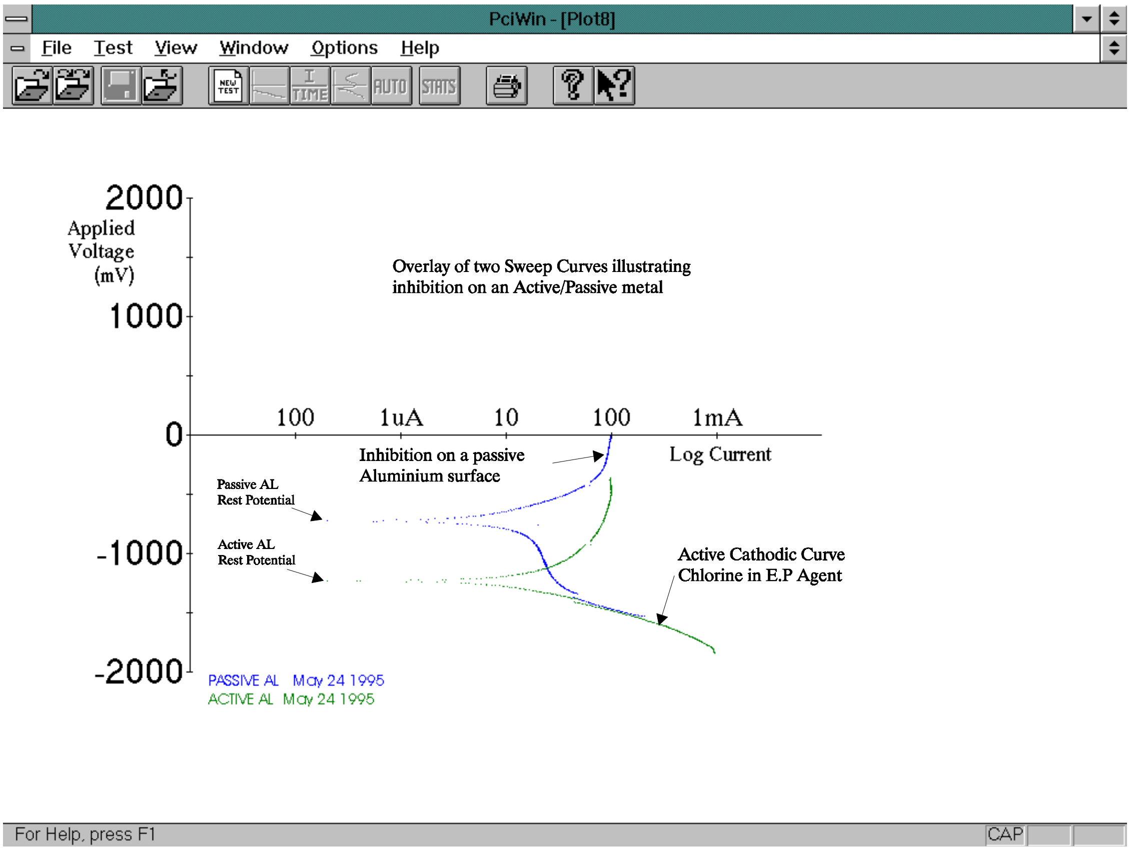


Transpassive Corrosion of Aluminium

Passivity present on
Cathodic curve

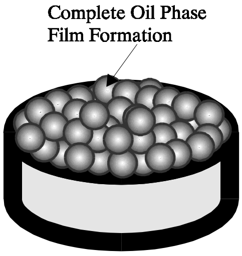


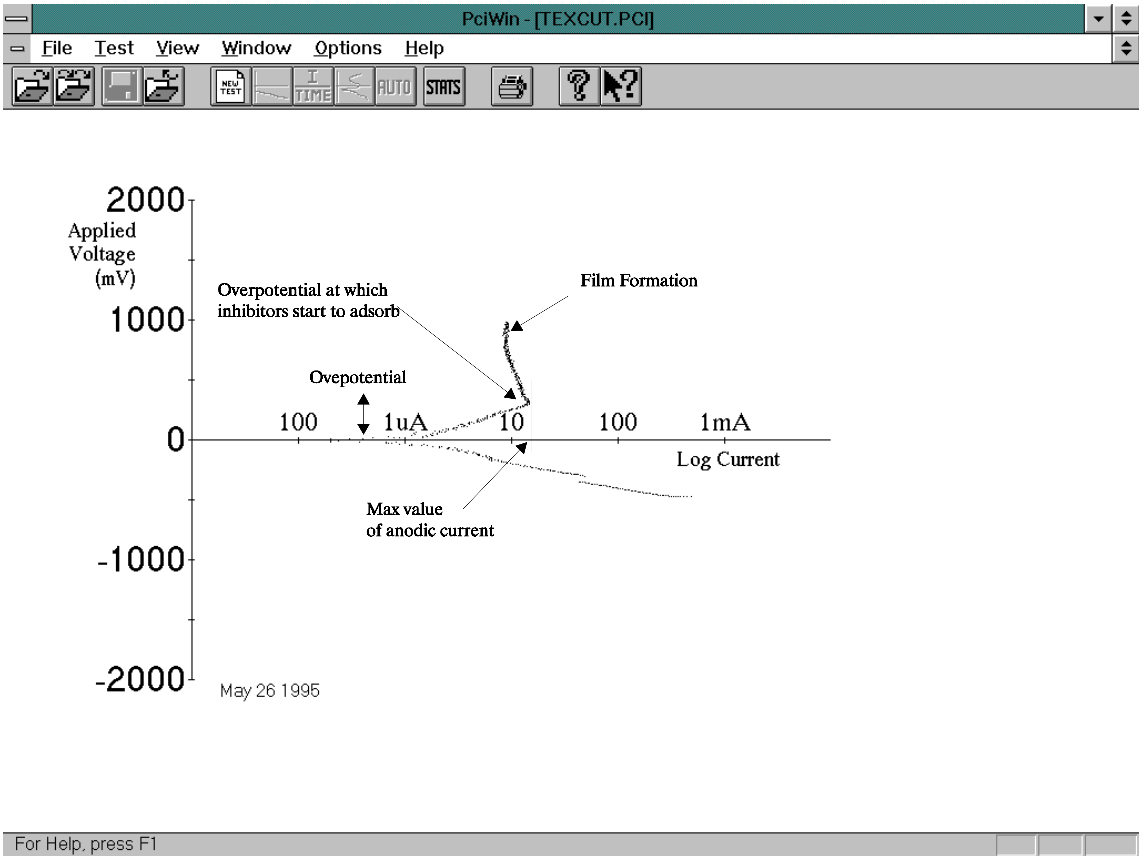
The points to note about this curve are that the cutting fluid has not removed the natural passivity on the Aluminium metal surface as illustrated by the "Rest Potential" recorded (500-600 mV) and the shape of the cathodic curve, and that the adsorption of inhibitors above the X axes is onto a mono-oxide layer as opposed to an active metal surface. Compare this with a curve for produced in a fluid known to have an aggressive agent present.



8.2 *Surface Films*

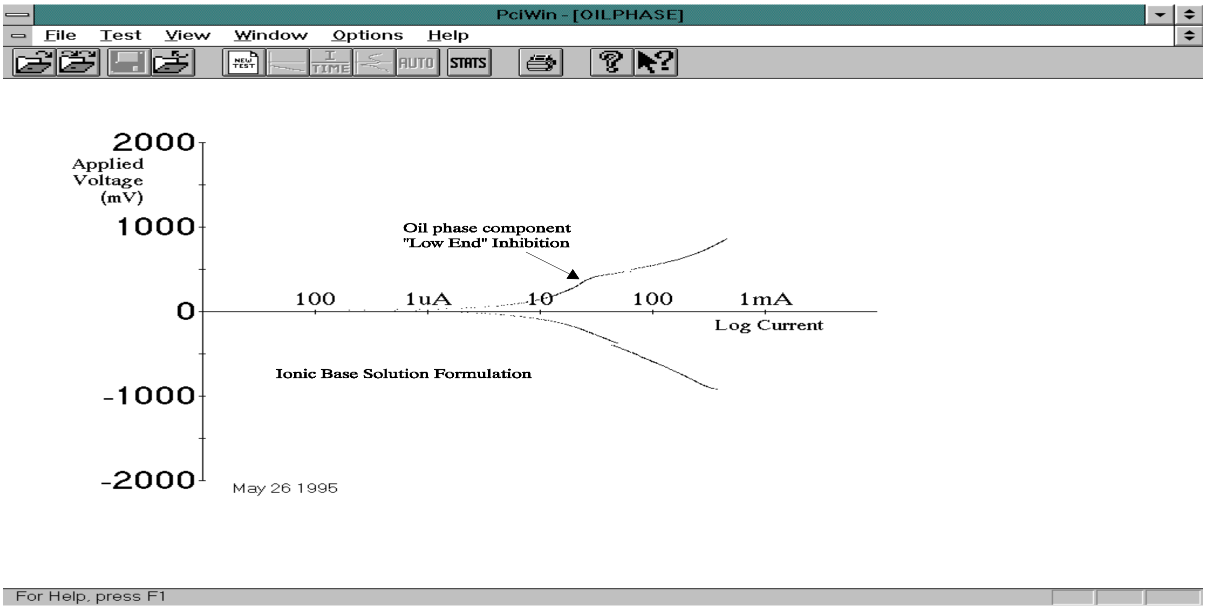
The interpretation of **Sweep** curves can be explained in terms of the surface films produced on the PCI metal specimen. A Sweep test on a good fluid should produce a curve as illustrated, where the metal surface is completely filmed by the inhibitors present in the fluid. Industrial fluids, cutting fluids and soluble oil formulations usually contain several active corrosion inhibitors. Some of these compounds are present in the oil phase such as petroleum sulphonates and others added such as additional fatty acid amides can be present in either phase. Complete film formation is characterised by a low overpotential value of inhibitor adsorption, and a definite barrier line to anodic current flow usually not exceeding 10uA/cm2.



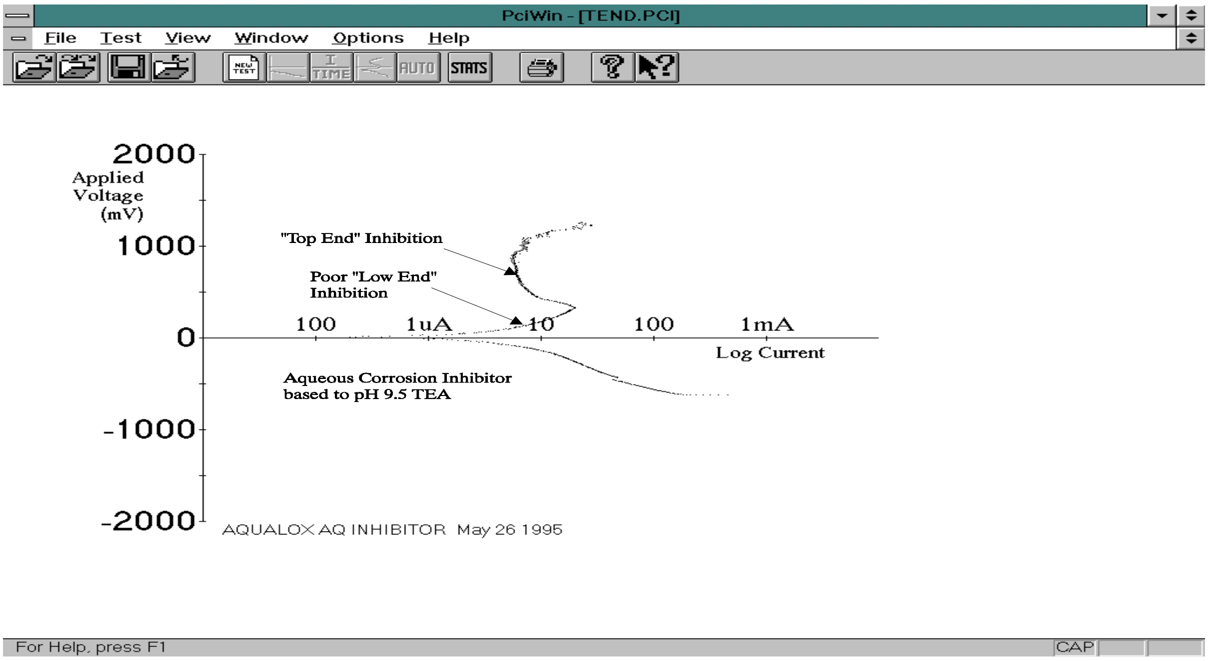


When a metal specimen is removed after such a test it's appearance is as smooth and as polished as before the test. However industrial fluids have to cope with a diversity of water types varying from locality to situation and availability ie Offshore , Mining etc. Corrosion inhibitors in fluids have to compete with other negatively charged ions such as sulphates , carbonates , chlorides etc in practice, all of which can act to prevent effective film formation. The effectiveness of an inhibitor is a function of it's solubility, molecular weight and the functionality and placement of it's polar group on the molecule. Effective film formation can be caused by a combination of factors, too low a molecular weight inhibitors for the water type, fluid depletion, bad formulation, all of which can be diagnosed electrochemically.

By performing **Sweep** tests on components of an industrial fluid for example a base solution containing only emulsifiers, mineral oil, cosolvent and amine to base the pH an indication of the activeness of the base components can be evaluated. It is the experience of BKT that the ionic petroleum sulphonate based formulation show significantly more "Low End" inhibition than their non ionic ethoxylated alcohol counterparts.



From the experience of BKT it is our understanding that the higher MWT more polar molecules adsorb onto newly formed anodic sites followed by the aqueous corrosion inhibitor phase. A complete inhibitor film consists of both oil and water phase present at the metal surface. An aqueous inhibitor typically used in Semi-Synthetic cutting fluid formulations that illustrates good "Top End" inhibition is shown below.

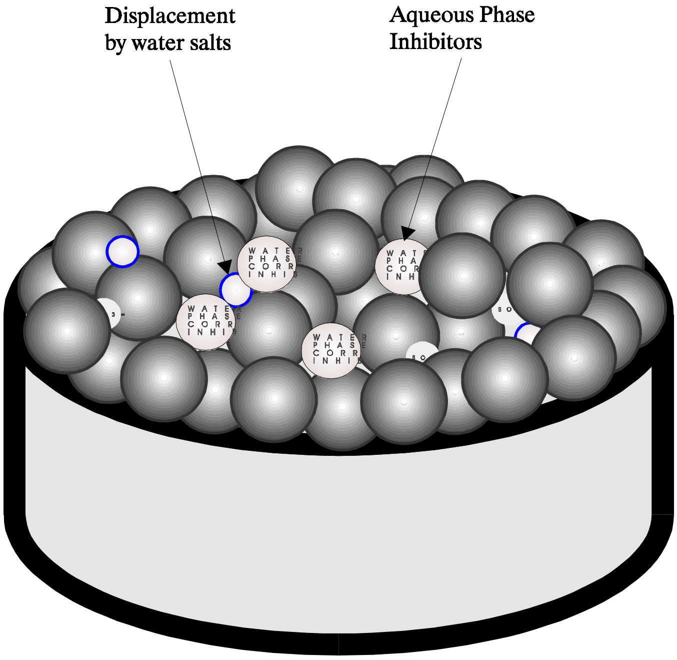


By electrochemically screening additives and base solutions the PCI user can predict synergic combinations of additives.

8.3 *Aggressive Ions*

The PCI instrument can be used as a technical service Q.A tool to screen formulations in varying regional hardness waters. For example a field service operative engineer can despatch a particular regional water for screening at base. Effective film formation can prove problematical in some severe test waters, below is an example of the performance of the same formulation in both 200ppm hardness water and DIN 51360 test waters.

The performance breakdown of a film in an aggressive test water can be explained by the displacement of the lower MWT aqueous phase inhibitors by water salts which initiate pit formation. This argument is based on the loss of "Top End" inhibition, and pitted nature of the resulting steel specimen. The model of this analogy is represented in the illustration.



8.4 *Dilution Sensitivity*

A good test of the completeness of a product formulation is the term "Dilution Sensitivity" . If the product has a good balance of components and is not dependent on the concentration of one particular additive to hold the stability of the system together, it will film form at varying dilution's. By performing Sweep tests at varying dilution's the "Dilution Sensitivity" of a product can be determined. Below are two examples of such tests with the top overlay of sweep curves depicting a product with questionable dilution sensitivity and the bottom a product whose synergy is not affected by dilution.