

New Perspectives on the Temperature Dependence of Lubricant Additives on Copper Corrosion

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ABSTRACT

Modern automotive transmissions contain copper and copper alloys in the form of washers, bushings, brazes and electrical components. Corrosion that occurs with any of these components especially with electrical contacts can result in a malfunction of the vehicle control systems and loss of vehicle drivability. The compatibility of transmission lubricants with copper and copper alloys is an increasingly important consideration in the design of new additive technology. Traditional methods for monitoring corrosion processes and mechanisms in real time can be both time consuming and challenging to interpret, especially when evaluations at multiple temperatures are required. This work challenges some of the industry-held beliefs around lubricant additive corrosion processes, especially at elevated temperature ($>130\text{ }^{\circ}\text{C}$). These new insights on the kinetics and mechanisms of copper corrosion in the presence of lubricant additives over a range of operating temperatures using a new wire resistance test that enables real-time corrosion monitoring will be discussed. The corrosion processes observed here are highly dependent upon temperature and accelerating tests based on increasing temperature presumes the dominant kinetic mechanism remains constant between real world and accelerated conditions. In the past, with end point tests, there was no easy way to assess whether this was the case. The new test does allow an assessment of corrosion mechanism, and demonstrates that certain lubricants do not maintain the same mechanism between real world and typical test temperatures.

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INTRODUCTION

Traditional lubricant tests for determining the extent of copper corrosion provide single end point measurements such as the ASTM D130 strip rating [1]. These tests can be expanded to include additional information such as an end of test concentration of copper in solution or mass loss/gain information, however these types of test in isolation provide no detail about the chemical kinetics or time dependence of the corrosion process. Such information is useful in evaluating the impact of oil formulary on metal corrosion. Furthermore the purpose of performing these strip end point tests is to provide assurance about lubricant compatibility and corrosion performance of in-service lubricants. Correlation of in-service conditions are therefore a function of the temperature and duration test conditions mandated by the specification requirements placed on the lubricant. The desire to differentiate lubricant performance and reduce the testing time often result in increased temperature conditions to accelerate the corrosion process. This approach is appropriate only if the same corrosion process occurs at the elevated temperature and is not affected by new or competing reactions that are only viable at the elevated temperature.

Evaluating chemical reactions at temperatures unobtainable for in-service lubricants may not provide the assurance required for chemical compatibility and corrosion performance. In the past, with end point tests, there was no easy way to assess whether this was the case.

A wire resistance measurement method is used that allows real time assessment of the corrosion mechanism, and demonstrates that certain lubricants do not maintain the same mechanism between real world and typical test temperatures [2-3]. A similar principle to this has been used to investigate the interactions of extreme pressure additives with iron and was referred to as the "hot wires" method. However, in those experiments the wires were resistively heated to temperatures representative of those in gear contacts through the application of increasing current. The increase of resistance of the wire was then used to quantify the extent of the antiwear film formation [4, 5, 6]. In the work presented here the electrical resistance of copper wires is used only to monitor the corrosion that occurs and no resistive or ohmic heating induced corrosion is generated.

Several inter-related reaction pathways contribute to copper corrosion in oil based systems over time [7, 8, 9]. Diffusion controlled, activation controlled and mixed kinetics play a role and can with the correct choice of experiment be distinguished between each other. However these dynamic kinetic approaches are rapid and simple, and are not quantitatively applicable to autocatalyzed systems. Autocatalyzed systems are characterized by the formation of an intermediate species which markedly accelerates the reaction. In diffusion controlled processes the corrosive substance that penetrates to the metal surface is immediately converted into the corrosion product which migrates back into the oil phase. Once the diffusion

controlled process has been established the corrosive substance is consumed at a constant rate. The concentration of corrosion byproduct will increase linearly with time and this can be mistakenly considered as a sign of an activation controlled process. A more detailed evaluation would require modification to the measurement setup by introducing agitation to confirm the dominant kinetics in this case. With activation controlled kinetics the reaction rate at which the corrosive substance is converted into the corrosion product depends on the local concentration of the reagents and reaction products in the conversion zone [10]. For example if the corrosion product does not form a passive surface film, the conversion rate may follow the simple first order kinetic equation. If the reaction on the metal surface is the rate determining step then the number of copper atoms and concentration of additives should remain constant since the diffusion of copper and additives is fast. In the case of mixed kinetics both diffusional and activation limitations play a role. The corrosive substance diffusing to the metal surface or away from it should be considered along with the boundary conditions describing the surface reaction kinetics [11]. The measurement method reported here is able to provide insights upon the kinetic behavior of the test lubricants though comparisons of the rate of reaction as a function of temperature and time.

The aim of this paper is to introduce this corrosion measurement technique as a means for providing detailed understanding of a lubricants copper corrosion behavior with temperature and time and show that evaluating chemical reactions at temperatures unobtainable for a in-service lubricant do not provide the assurance required for chemical compatibility and corrosion performance as assessed by more simple end point tests such as ASTM D130.

METHOD

The test design consists of a 1 m long, 64 μm diameter copper wire suspended in the test lubricant with a direct current (DC) of 1 mA applied. The lubricant is held at the desired temperature $\pm 0.25^\circ\text{C}$ by means of a thermostatically controlled heating oil bath. Pure (99.99%) copper wire is supported in a beaker containing 400 ± 1 mL of lubricant per test. Because the wires are not exactly the same length, a process of normalizing the data is undertaken. This involves measuring the resistance at the start of the test and then using that measurement to calculate the length of wire. This difference in length can then be compared to a normalized length of 1.01 m and is outlined below in equations 1, 2, 3, 4, 5, 6. Resistivity changes with temperature and it is important to capture this change when comparing resistance measurements at different temperatures, equations 1, 2, 3 show how to incorporate the resistivity change and to allow for the results to be normalized due to small changes in wire length and thermal expansion. If this is process is done correctly then comparisons of corrosion reactions at different temperatures can be attributed directly to the corrosion process and are themselves not masked or enhanced due to measurement differences resulting from measurements at higher temperature. The wire resistance measured in the test is governed by Ohm's law.

$$R = \frac{\rho l}{\pi r^2} \quad (1)$$

Where R = resistance in Ω , ρ = resistivity of copper in Ωm , l = length of wire in meters (m), r = radius of the wire in meters (m).

To account for the temperature dependence of the resistivity of the copper, the resistivity at the temperature of interest must be determined, this is done through the use of equation 2.

$$\rho_{CuT} = \rho_{Cu20} + \alpha \Delta T \rho_{Cu20} \quad (2)$$

Where ρ_{CuT} = resistivity of copper wire at the measurement temperature, ρ_{Cu20} = resistivity of copper at 20°C , α = temperature coefficient per degree for the copper wire, ΔT = difference in temperature between the measurement temperature and 20°C .

Equation 1 can now be rearranged to account for the value of ρ_{CT}

$$l = \frac{R \pi r^2}{\rho_{CuT}} \quad (3)$$

Calculation of the resistance based upon a length of 1.01 m using equation 1 and 3 provides normalization of resistance to a value using equation 4.

$$R_{normalised} = \left[\left(\frac{1.01}{l} \right) * (R) \right] \quad (4)$$

Where R_n is the resistance which accounts for temperature and length of the wire at the measurement test temperature. Similarly the copper corroded can be calculated using equation 5 and 6.

$$r_{normalised} = \sqrt{\frac{(\rho_{CuT} 1.01)}{(\pi R_n)}} \quad (5)$$

$$\Delta r = \sqrt{(r_n - r_0)^2} \quad (6)$$

Equations 1, 2, 3, 4, 5, 6 describe how to normalize resistance measurements and convert them into an equivalent radius change whilst accounting for temperature effects upon the resistance measurements and initial length differences. Δr is measured in Angstroms ($\text{\AA}$).

The constant current of 1 mA DC is applied by means of a resistance temperature detector. Data is acquired by means of a compact data acquisition controller. This is networked to a local host computer for processing and logging. There is high-frequency data acquisition (10 kHz) and a variable deterministic resistance logging rate, which in this case is every 10 s. The low current applied does not result in ohmic heating of the wires, neither does this contribute to differences in corrosion processes when energized.

Surface analysis of the wire is conducted using a scanning electron microscope (SEM) with an energy dispersive spectroscopy module sensitive to atoms of atomic number greater than 11. An approximate diameter measurement is taken during the SEM imaging. Accurate diameter measurements were obtained using a MultiBeam SEM-focused ion beam (FIB) at the University of Warwick, UK to section the wire and measure the corrosion layer.

Validation of Resistance Measurement

The conversion of the resistance measurement into a radius measurement is outlined in [equations 1, 2, 3, 4, 5, 6](#). This technique is sensitive to corrosion layer formation when the copper is removed or reacted in such a way as to no longer participate in electrical conduction.



Figure 1. Optical microscope image of the end of test copper wire after 180 hours at 120 °C in commercial driveline lubricant L3.

Figure 1 shows the end of test wire after 180 hours at 120 °C in the presence of lubricant L3. The calculated and measured corrosion layers are presented in [table 1](#) below.

Table 1. Calculated and measured corrosion layer thickness

Technique	Corrosion layer thickness (μm)
FIB-SEM measurement	1.09
Calculated thickness from resistance measurement	1.10

There is good agreement between the calculated corrosion layer thickness from this technique and the measured thickness of the corrosion layer from the SEM. Focused Ion Beam (FIB) - Scanning Electron Microscope (SEM) technique was used to section and then measure the corrosion layer [12]. Figure 2 shows the trench formation and a protective carbon layer is deposited on the surface of the wire prior to exposure to the FIB. The measurement of the corrosion layer from commercial driveline lubricant L3 is shown in [figure 3](#).

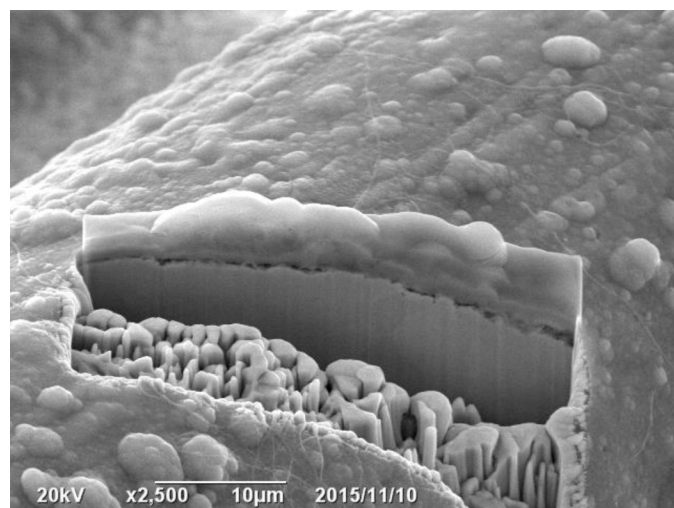


Figure 2. FIB-SEM image of a copper wire exposed to commercial driveline lubricant L3 at 120 °C for 180 hours. A protective carbon layer is deposited on the surface to allow for trench formation.

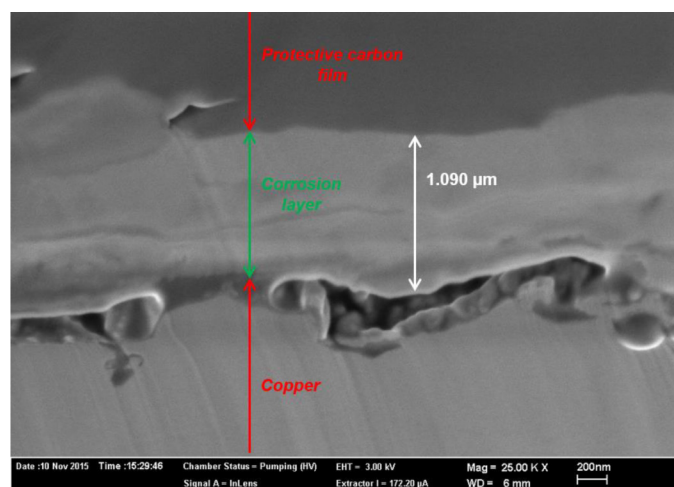


Figure 3. SEM image of a sectioned copper wire exposed to commercial driveline lubricant L3 at 120 °C for 180 hours. The protective carbon layer is deposited on the corrosion layer surface to enable the cross-section to be imaged.

The interface between the copper and the corrosion layer are indicative of a difference in grain boundaries between the copper and the subsurface of the copper which is consistent with a decrease in conduction. Measurements of the fresh copper wire were also performed, there is no evidence for the presence of grain boundaries in the virgin material, indicating this layer is formed from corrosion.

Repeatability of Measurements

The pooled standard deviation [13] was calculated for three samples each repeated three times at 130 °C for 180 hours. The pooled standard deviation method is used for estimating the variance of several different populations when the mean of each population may