New Insights on the Impact of Automatic Transmission Fluid (ATF) Additives on Corrosion of Copper

- The Application of a Wire Electrical Resistance Method -

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ABSTRACT: A new method for monitoring the corrosion of copper by automatic transmission fluid additives through the measurement of the electrical resistance of copper wires is presented. The effect of driveline lubricant additive components upon the corrosion rate of copper is discussed. The information on corrosion generated by this method provides details of the corrosion processes that are not obtained from traditional corrosion tests and insight as to how to formulate oils to better protect copper and copper alloys.

KEY WORDS: power transmission, copper, corrosion, transmission, lubricant, electrical resistance, wire [A2]

1. INTRODUCTION

Modern automotive transmissions contain copper in the form of washers and bushings, brazed joints and electrical components. The latter is in part due to legislative requirements in the automotive industry driving new technologies with a growing number of vehicles having an increased number of electrical components in the driveline. One example of such is the hybrid electric vehicle. Elements of electrical circuits are subject to the same corrosion and material compatibility concerns as other transmission components that incorporate copper alloys or polymeric parts. Corrosion of electrical contacts could potentially interfere with the function of these circuits leading to a malfunction of the vehicle control systems and loss of vehicle drivability. Current lubricant tests for copper corrosion provide single measurements, such as a strip rating such as in the ASTM D130 test (1) or an end of test concentration of copper in solution, but 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 (2) on metals used in electrical circuits as well as traditional copper alloy hardware. A wire resistance measurement method is used that allows real time monitoring of the corrosion process in copper. The electrical resistance of copper wires is used to monitor the corrosion that occurs and no resistive or ohmic heating induced corrosion is generated.

2. EXPERIMENTAL SECTION

2.1. Background

In this work we are monitoring the electrical resistance of copper wires to monitor the corrosion of copper by automatic transmission fluid additives. A similar method has been used previously to investigate the interactions of extreme pressure additives with iron and was referred to as the “hot wires” method (1-5). 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. 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.

The test design is shown in Figure 1, and consists of a 1-meter long, 64-micrometer diameter copper wire suspended in the test fluid with a direct current of 1 mA applied. The wire resistance measured in the test is governed by Ohm’s law.

\[ R = \frac{V}{I} \]

Where \( R \) = resistance (\( \Omega \)), \( V \) = voltage (V), \( I \) = current (A)

Fig. 1. Schematic of electrical wire resistance test.

The resistance of the copper wire is inversely dependent upon the cross sectional area \( \pi r^2 \), where \( r \) = radius of the wire. The resistivity (\( \rho \)) and wire length (\( L \)) are constants when isothermal conditions are maintained.
\[ R = \frac{\rho L}{\pi r^2} \]

Using these relationships it is possible to detect corrosion taking place at the surface of the copper wire as these reactions are detected as a change in resistance measured by the circuit due to decreases in the conducting cross sectional area.

2.2. Experimental conditions

The test fluid is held at 130 ± 0.25 °C by means of a thermostatically controlled heating oil bath. The duration of a typical test is 10 days. Pure (99.9%) bare copper wire is supported in a beaker containing 400 ±1 ml of test oil per test. Because the wires are not exactly the same length, a process of normalizing the data can be undertaken. This involves measuring the resistance at the start of the test and then using that measurement to calculate the actual length of wire. This difference in length can then be compared to a normalized length of 1 m.

A 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 seconds. The low current applied does not result in ohmic heating of the wires. The repeatability of this is ±0.05 Ω at end of test.

Surface analysis of the wire is conducted using a Scanning Electron Microscope (Hitachi TM-1000), with an energy dispersive spectroscopy module sensitive to atoms of atomic number greater than 11. Atomic distributions for Cu and S are given as percentages and are approximate and relative to each other. The images are captured for example at magnification x1500 with a 50 micron scale included at the bottom of each image. An approximate diameter measurement is taken during the SEM imaging. An example of a new wire is shown in Figure 2.

Supplemental checks on the fluids are performed with measurements taken by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES using ASTM D4951) in order to detect any metal dissolved in the oil at end of test.

3. RESULTS

Evaluation of lubricating oil compatibility is required due to base oil and additive chemistry influence on corrosion. The new test discussed here provides information on corrosion rate and events occurring that are not captured by current industry standard test methods.

3.1. Evaluation of automotive driveline fluids

A range of automotive transmission fluids were selected. See Table 1. These were automatic transmission fluids as well as fluids based on traditional extreme pressure (EP) gear oil technology. The fluid F1 is an API GL-4 EP type and is intended for axles with spiral bevel gears operating under moderate to severe conditions of speed and load. The fluid F2 is API GL-5 and is a lubricant intended for gears, particularly hypoid gears under various conditions of high-speed/shock load and low-speed/high torque applications. Fluids F3-F6 are automatic transmission fluids.

| Fluid number | Description | Base Oil Type | Kinematic Viscosity at 100°C, cSt (ASTM D445) |
|--------------|-------------|---------------|---------------------------------------------|
| F1           | EP gear oil API GL-4 | Mineral       | 9                                           |
| F2           | EP gear oil thermally stable API GL-5 | Synthetic | 15                                          |
| F3           | Automatic Transmission fluid (1) | API Group III | 7                                           |
| F4           | Automatic Transmission fluid (2) | API Group III | 7                                           |
| F5           | Automatic Transmission fluid (3) | Synthetic | 7                                           |
| F6           | Automatic Transmission fluid (4) | Synthetic | 6                                           |

Figure 3 shows the change in resistance over time for wires exposed to these fluids. The two EP containing oils, F1 and F2, cause rapid corrosion of the wire resulting in complete disintegration of the wires after 30 and 60 hours and leaving only trace amounts of wire fragments. Fluids F3-F6 remained intact and exhibited little signs of corrosion.

![Fig. 2. SEM image of a new copper wire.](image1)

![Fig. 3. Electrical resistance for fluids F1 to F6 at 130 °C.](image2)
The SEM images for the test fluids F1 to F6 are shown in Figure 4. Only a few remnants of the wires from F1 and F2 were found.

![SEM images of wires at the end of test for fluids F1-F6](image)

The SEM image of F1 and F2 wire remnants shows the extent of corrosion that has occurred. The F3 wire shows a small degree of pitting whereas the F4 wire has a clean and uncorroded appearance similar to the new wire. The wires F5 and F6 though uncorroded show some surface variation from being exposed to the hot automatic transmission fluids.

### 3.2. Dispersant and inhibitor study: Part A

The test fluids consisted of performance packages blended along with pour point depressant into available American Petroleum Institute (API) Group III base oil. The fluid formulation type is described in Table 2. The kinematic viscosities were measured according to ASTM D445 and the Brookfield viscosities were measured to ASTM D2983.

| Test Fluid | % Dispersant 1 | % Dispersant 2 |
|------------|----------------|----------------|
| A1         | 100            | 0              |
| A2         | 80             | 20             |
| A3         | 70             | 30             |
| A4         | 60             | 40             |
| A5         | 40             | 60             |
| A6         | 20             | 80             |
| A7         | 0              | 100            |

Table 2 ATF Fluid formulation

| Base oil            | Weight, % |
|---------------------|-----------|
| Group III, 4 cSt    | 40.86     |
| Group III, 3 cSt    | 49.94     |
| Pour point depressant| 0.2      |
| Additive package    | 9         |
| Kinematic viscosity at 100°C, cSt | 4.3 |
| Brookfield viscosity at -40°C, cP | 5000 |

The detected changes in corrosion are highlighted in Figure 6. For all fluids there is an induction period of approximately 2-4 hours. For fluid A1 the corrosion rate is steady and appears to increase after 80 hours. All other fluids contain dispersant 2 and the impact of even a small amount of dispersant 2 reduces the corrosion rate significantly. Fluid A7 has the lowest overall corrosion rate of the samples tested in this study.

![Graph showing electrical resistance for Fluids A1-A7](image)
The SEM images for the test fluids A1 to A7 are shown in Figure 7, with the numbers in brackets representing relative dispersant amount of type 1 and type 2. Two different areas are highlighted for formulation A7. The SEM image of A1 shows the appearance of chemically induced pitting corrosion, whereas with A7 the copper wire has accumulated a film. Fluids A5 and A6 show evidence of a film, (refer to the left side of the wire) which is perhaps polymeric, with a slight flaking off of a material that had coated the wire indicating that it is rather loosely bound. However the underlying protection is still in place as evidenced by the low resistance change in figure 6. Fluids A3 and A4 have a clean and uncorroded appearance.

3.3. Dispersant and inhibitor study: Part B

In this set of experiments the additive package was based on the same general formulation as described in Part A but without a metal deactivator present (MDA). Additive packages B1 to B7 were prepared with the same varying amounts of dispersant type used in Part A while keeping the same total dispersant percent weight. Additionally B8 was prepared using 100% dispersant 2 and the MDA, providing an analogous formulation to B7. The formulations are summarized in Table 4.

| Test Fluid | % Dispersant 1 | % Dispersant 2 |
|------------|---------------|---------------|
| B1         | 100           | 0             |
| B2         | 80            | 20            |
| B3         | 70            | 30            |
| B4         | 60            | 40            |
| B5         | 40            | 60            |
| B6         | 20            | 80            |
| B7         | 0             | 100           |
| B8 (includes MDA) | 0   | 100           |

The lack of a metal deactivator has a pronounced effect on the corrosion rate as shown in Figure 8. An induction period of approximately two hours is observed. Without the presence of a metal deactivator the corrosion increases significantly for B1 and B2. The addition of increasing amounts of dispersant 2 has a pronounced effect on reducing the corrosion rate. Of note, B7 and B8, which both contain 100% dispersant 2, but differ in the presence of an MDA have almost identical corrosion behaviors but different wire surfaces at the end of the test. The SEM images for the test fluids B1 to B8 are shown in Figure 9. SEM images for B1 and B2 show the chemically induced wire thinning. The removal of the copper from the wire has left a smooth and rippled surface. The fact that there is no evidence for a thick film suggests that copper is dispersed away from the surface and into the oil, preventing appreciable material build-up.
As the series progresses the increasing concentration of dispersant 2 produces a surface on the wire that indicates material build up, with the surface of the B6 wire having a sporadic covering and dark gaps in the cover. The surface differences of B7 and B8 indicate that the presence of a metal deactivator is required to produce a protective film.

Fig. 9. SEM images of wires at the end of test for fluids B1-B8.

3.4. Dispersant and inhibitor study: Part C

In this set of experiments the dispersant type 1, dispersant type 2 and metal deactivator were added individually to base oil only. The dispersant results show little corrosion and only slight differences between dispersant types as shown in Figure 10.

Fig. 10. Electrical resistance for dispersant type 1 and 2 in base oil.

The metal deactivator shows a similar activity to dispersant type 1, again with little significant corrosion over the course of the test conditions, as shown in Figure 11.

Fig. 11. Electrical resistance for metal deactivator in base oil.

4. CONCLUSION

A new method for using the electrical resistance of copper wires to monitor the corrosion of copper by automatic transmission fluid additives has been presented. The results show there are significant differences in the corrosion rates of driveline fluids. The EP containing fluids are extremely corrosive to bare uncoated copper and the corresponding increase in corrosion rate identifies this behavior. The other automatic transmission fluids show little effect on the corrosion of uncoated copper.

The ability to monitor the rate of corrosion offers insights into the mechanistic factors that affect corrosion. The choice of dispersant with or without corrosion inhibitor show differences in the fundamental chemical processes that are involved regarding corrosion.
The formation of a surface film with increasing amounts of dispersant 2 and the presence of the metal deactivator coincides with a reduction in the corrosion rate. This suggests that this film offers protection to the copper surface through a barrier method or passivating film by reducing the diffusion rate of aggressive species to the copper surface. The surface structure of the film produced differs depending upon the presence of corrosion inhibitor. The increasing amount of dispersant 2 without corrosion inhibitor also shows a reduction in the rate of corrosion, however the surface is not covered with a protective film. Interestingly however is that similar levels of protection of the copper surface are achieved.

Neither dispersant 1, 2 nor the corrosion inhibitor have been observed to form this protective film independently, suggesting that film formation is a complex process that is dependant upon a number of conditions with additive chemistry choice being a major factor.

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