Statistical Analysis of Impedance Data for Jet Turbine Oil Additives

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Abstract

A gold, parallel-plate capacitor test cell was used to make electrochemical impedance spectroscopy (EIS) measurements on high resistivity gas turbine engine oil as a function of the oil additive type. The additive effects on the EIS response were determined by analyzing ester-based basestock oil mixed with a single additive. This work was performed for four different additives: antioxidant, metal deactivator, anti-wear, and extreme pressure. Multiple measurements were made for each basestock-single additive mixture. To determine whether the EIS response of each additive showed a significant difference, statistical analysis was performed on the data using a student's t-test. Low-frequency data showed the largest difference in additive responses. Statistical analysis showed that the extreme pressure additive has the greatest effect on oil impedance. Mixtures of antioxidant and metal deactivator additives did not show interaction.

Keywords: electrochemical impedance spectroscopy, sensor, turbine engine, oil, additive

1. Introduction

Recently, there has been a great interest in using electrochemical techniques as non-destructive methods for monitoring oil quality.[1-3] Oil quality can be a function of contamination, oil degradation, and additive depletion. This paper focuses on using electrochemical impedance spectroscopy (EIS) to study individual additive effects.

Based on earlier work that analyzed oil conditions using EIS, a gold, parallel-plate sensor was used to make measurements for various oil additives, figure 1.[4] The inert electrode materials allow for the direct measurement of an oil binary mixture (oil + single additive) by negating interfacial reactions that would occur using a bearing steel substrate. Several additives are used in oils and lubricants to protect the engine from heat and wear. Monitoring additive levels can provide insight into their role in preventing engine wear as well as signal timely oil replenishment. Making distinctions in impedance data requires analyzing statistical variations.

Oil additives in the synthetic ester basestock include: metal deactivator, extreme pressure, antioxidant and anti-wear. The extreme pressure additive forms a tribological film on the substrate under high pressures to reduce wear. The metal deactivator additive protects soft metals in the lubricant system such as Cu and Mg and chelates wear particles formed from these metals. A chelating agent is a molecule that bonds to specific ions in a solution and, in this case, prevents them from reacting/interfering with the lubricating properties of the oil. The anti-wear molecule creates a tribological film on the ferrous bearing and gear surface to reduce wear. The antioxidant molecule reacts with free oxygen in hot engine environments to prevent degradation of the oil basestock molecules. A more detailed summary of the additives is found shown in table 1. It should be noted that each additive concentration in the binary mixtures (oil + additive mixtures) closely corresponds to additive concentrations present in the full formulation for each respective additive.

EIS analysis was performed on the basestock oil plus single additive mixtures to understand the additive effects. In addition to the single additive mixtures, two additives were mixed to determine the effects of additive interaction. Since the metal deactivator additive tends to be acidic while the antioxidant additive tends to be basic, these two additives were mixed and tested for interaction.

To ensure that the variations in the EIS data were significant, statistical analysis was used to compare data sets. Accounting for the statistical variation in data sets is necessary for making predictions based on the impedance measurements (i.e. if the results are within the range of statistical error, no prediction can be made).

Oil Component	Code	Purpose	Compound and General Structure
Basestock	none	A 5 cSt oil. The 5 cSt oil gives the best thermal stability maintaining a deposit free engine (40K hrs between maintenance).	Fully Synthetic esters (Pentaerythritol + organic acid (C5 to C10 acids))
Antioxidant	AO	Phenyl-a-naphthylamine is used to react with free oxygen in hot environments so that the oxygen does not oxidize the basestock and cause deposits or make the oil acidic.	Aromatic Amine (phenyl-a-naphthylamine) N-(1-Naphthyl)aniline
Metal Deactivator	MD	Benzotriazole is used to chelate any wear products that can get into oil and deliver these particles to the filter.	Benzotriazole
Anti-Wear	AW	Tricresyl Phosphate associates with ferrous surfaces making a low shear stable film that acts as a sacrificial tribological or boundary layer to prevent wear.	Mix of para/meta isomers of Tricresyl Phosphate
Extreme Pressure	EP	Performs the same function as an anti-wear additive but at high pressures.	Generally compounds containing chlorine or sulfur.

Table 1. Summary of oil additives found in a commercial grade engine oil

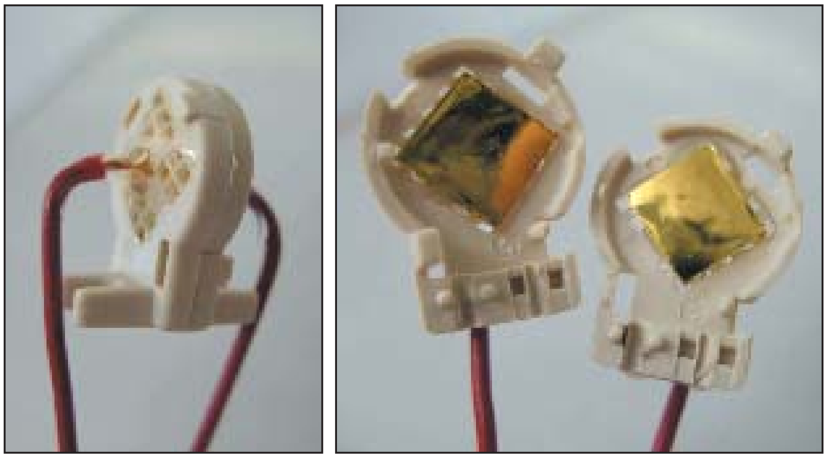

Figure 1. Capacitive Impedance Sensor constructed for use in additive testing. The plastic case keeps the electrode faces at a constant spacing.

2. Procedure

All EIS measurements were made using a Gamry Reference 600 Potentiostat/Galvanostat/ZRA inside of a copper Faraday cage. A two-electrode EIS set-up was used to make the measurements (to prevent impedance artifacts due to charging of a reference electrode). Both electrodes were made of high purity gold foil and all tests were performed at measured room temperature (23 ± 2° C).

Construction of a sensor from an existing casing allowed for a constant electrode spacing. The plastic superstructure of an HS1101LF-ND humidity sensor (obtained from Digi-key Inc.) was used for the sensor casing, figure 1.

Pure gold foil, attached to copper wire leads, was attached with epoxy to the inside of the case. Only the electrode faces were exposed to the oils. This sensor was immersed in each of the additive/oil mixtures and the open circuit potential was monitored for 10 minutes to ensure stability. All tests were performed in open air and as such, absorption of a small amount of ambient moisture by the oil was assumed. Absorption was considered to be consistent between tests and to have a minor effect on impedance. The first test used fresh oil and a clean sensor. For the second test, the oil was stirred but the sensor was not cleaned. For the third and fourth tests fresh oil was again used and the sensor was cleaned between tests. The AC amplitude was 1V. This amplitude was selected to reduce the noise in the data. (AC amplitudes as low as 100 mV were studied and the trends in the impedance response remained the same, however, the noise increased.) The measured frequency range for the test was 1,000,000 Hz to 0.001 Hz.

It should be noted that the gold electrode surfaces were slightly non-planar and this could lead to the appearance of a second double-layer capacitance, which appears as a second "hump" in a Nyquist plot of the data. Charge that builds up at the surface gives rise to a double-layer capacitance term. However, if the surfaces are not flat, this double-layer can vary over the surface of the electrode and can give rise to a second, or psuedo-double-layer capacitance.

For the tests involving the metal-deactivator and antioxidant mixtures the same setup and procedure was followed, except the frequency range was shortened. The frequency range tested was 1,000,000Hz to 0.01Hz. Three different ratios of antioxidant to metal deactivator were tested: 1:1, 1:2 and 2:1.

EIS data is typically displayed on Bode and Nyquist plots. When dealing with AC, Ohm's Law becomes V = IZ where Z is impedance with real and imaginary components. A Bode plot shows the magnitude of the impedance (|Z|, also called the modulus or Zmod) versus frequency on a logarithmic scale. Nyquist plots show the imaginary versus real components of impedance.

3. Results and Discussion

The data for the additive tests are shown in Figures 2 and 3.

Compiling the data from the four trials, an average impedance value, with its standard deviation, was calculated at two different frequencies (at a high and low frequency). The stated variance

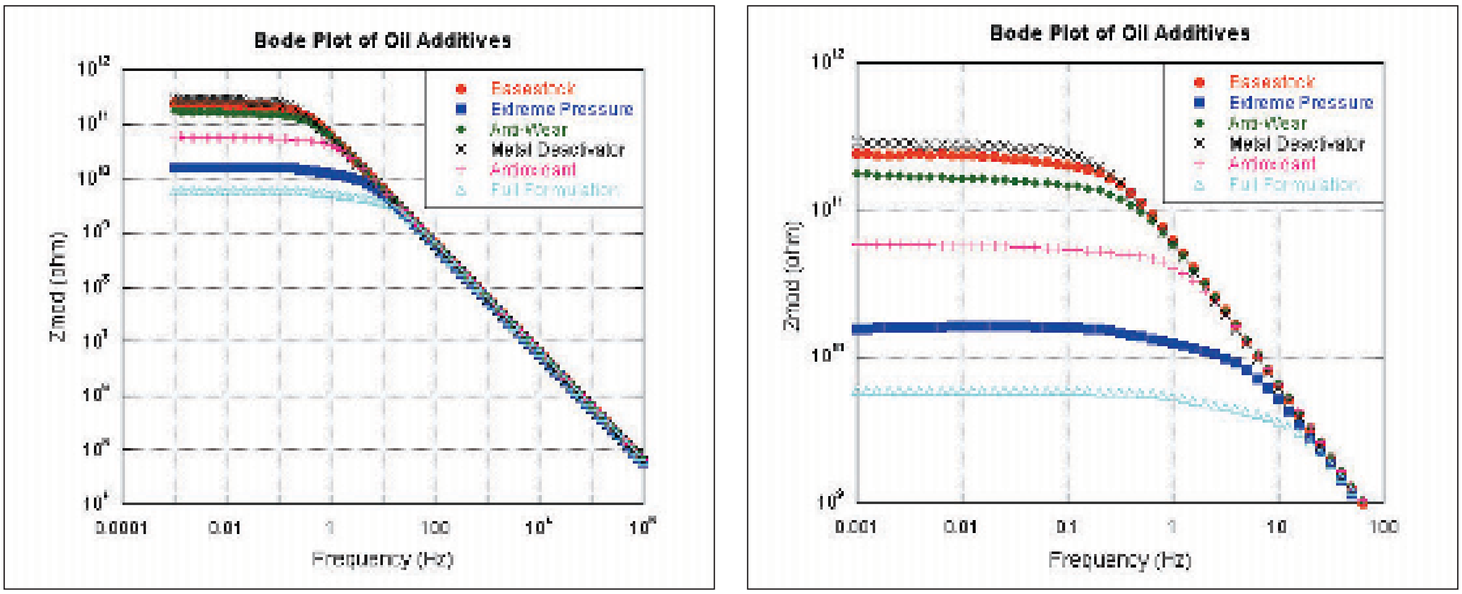

Figure 2. Bode magnitude plot of each BP oil tested. The left shows the full frequency range tested. The high frequency data shows no difference between the oils. The graph on the right is an enlarged view of the low frequency range. The curve selected for each oil was the one closest to the mean.

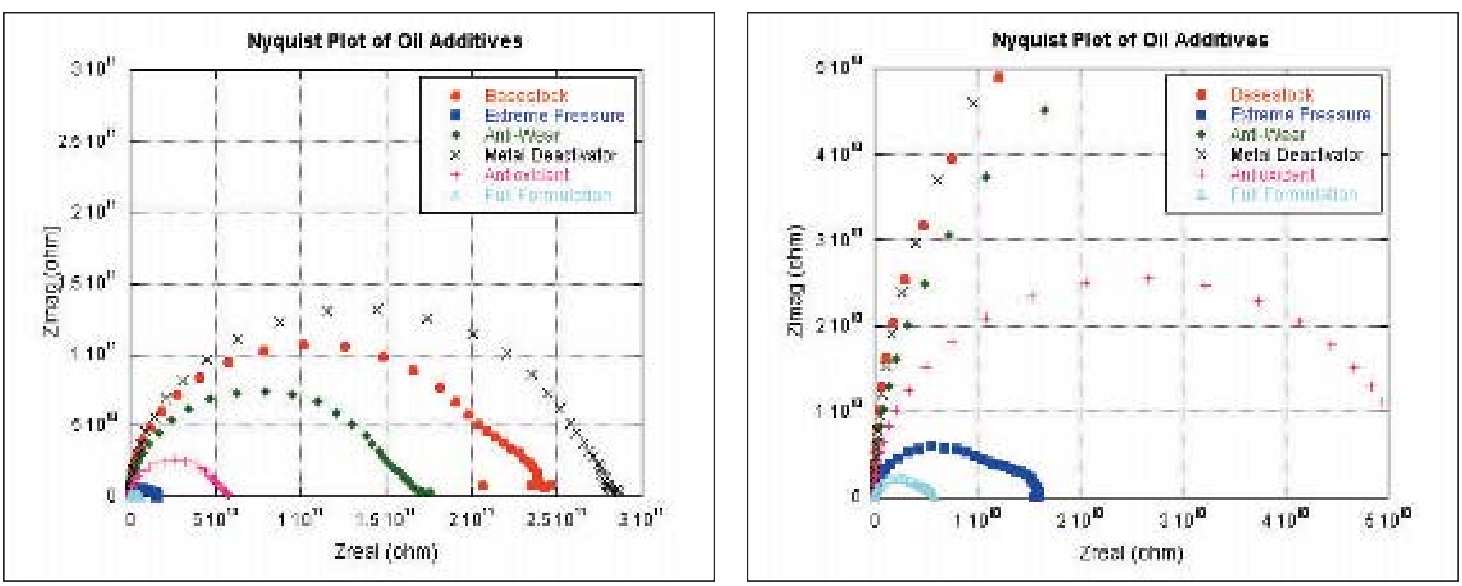

Figure 3. Nyquist plots of the oil additives. The figure to the right shows a zoomed in view of the lower impedance oils (extreme basestock and full-formulation).

in the tables represents one standard deviation. For the high frequency range value, 100 kHz was selected because it lies in the linear range of the Bode plots. For a low-frequency point on the Bode plots 10 mHz was chosen. At this point the slope has changed and the impedance value appears stable.

Statistical analysis was performed for each sample using a paired t-test.[5] Each sample was first compared to the basestock oil then to the full formulation. The t-test values on the table indicate a statistical significance at a 95% confidence level. The probability of the null hypothesis (that there is no difference in the samples, H_0) is also included to show the how far from the confidence level each sample is. The data is summarized in table 2. Variance from the mean is one standard deviation. T-test values indicate statistical significance at 95% confidence; = indicates no statistical significance, +/- indicate significantly higher or lower values. H_0 values indicate the t-probability associated with the paired t-test values showing confidence levels for all tests. The top group shows a comparison of each oil to the basestock oil while the second group shows a comparison to the full formulation. The 10 mHz impedance data is summarized on the following graph, figure 4, where the mean value for each oil is plotted with error bars representing one standard deviation.

10mHz						
Oil/Additive	Zmod (GΩ)		N	t-test	H_0	% change
Basestock	189.85	± 91.1	4			
EP	14.60	± 2.0	4	-	0.032	-92.3
AW	177.10	± 10.3	4	=	0.792	-6.8
MD	264.35	± 60.9	4	=	0.279	39.2
AO	59.59	± 4.2	4	=	0.060	-68.6
Full	6.18	± 0.2	4	-	0.027	-96.8
Full	6.16	± 0.2	4			
EP	14.60	± 2.0	4	+	0.004	137.0
AW	177.10	± 10.3	4	+	< 0.001	2775.0
MD	264.35	± 60.9	4	+	0.003	4191.4
AO	59.59	± 4.2	4	+	< 0.001	867.4
100kHz						
Oil/Additive	Zmod (kΩ)		N	t-test	H_0	% change
Basestock	627.55	± 30.0	4			
EP	591.86	± 34.4	4	=	0.342	-5.7
AW	653.75	± 22.1	4	=	0.338	4.2
MD	624.45	± 28.1	4	=	0.844	-0.5
AO	628.08	± 56.9	4	=	0.978	0.1
Full	658.13	± 15.0	4	=	0.063	4.9
Full	658.13	± 0.2	4			
EP	591.86	± 2.0	4	=	0.060	-10.1
AW	653.75	± 10.3	4	=	0.827	-0.7
MD	624.45	± 80.9	4	=	0.057	-5.1
AO	628.08	± 4.2	4	=	0.249	-4.6

Table 2. Summary of impedance data at two frequencies, 10mHz and 100kHz.

The first set of data in Table 2 compares the additive oil mixtures to the basestock. The basestock displays the most variance in data. Although the values are not statistically significant, the addition of an additive reduces the variance. It was found that only the extreme pressure additive and the full formulation are significantly different from the basestock (using a 95% confidence level) but that the antioxidant additive had a H_0 probability of 0.06 indicating it is close to the confidence level. It is possible that with larger sample sizes this additive also could be shown to be significantly different from the basestock.

The second set of data in Table 2 compares the additives to the full formulation. All additives are significantly higher when compared to the full formulation (as noted by the + sign in Table 2). The extreme pressure additive appears to have the

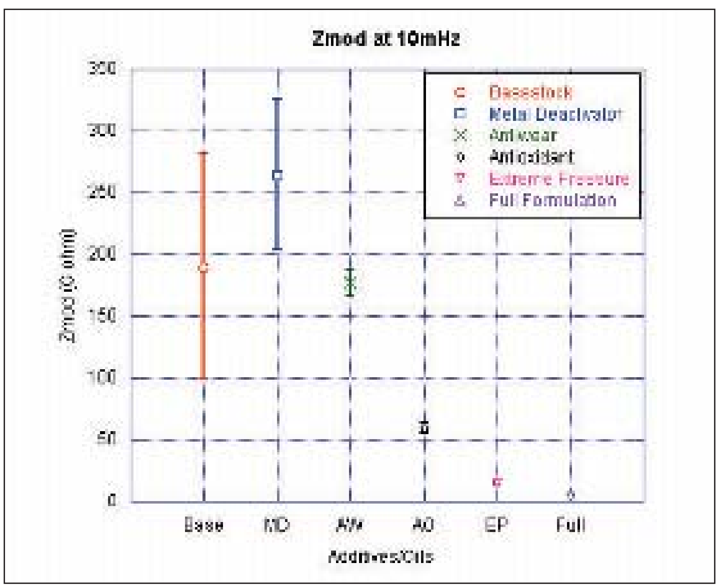

Figure 4. The mean value of each oil plotted with error bars representing one standard deviation. Only the extreme pressure additive and full formulation are statistically significant from the basestock (using a 95% confidence level).

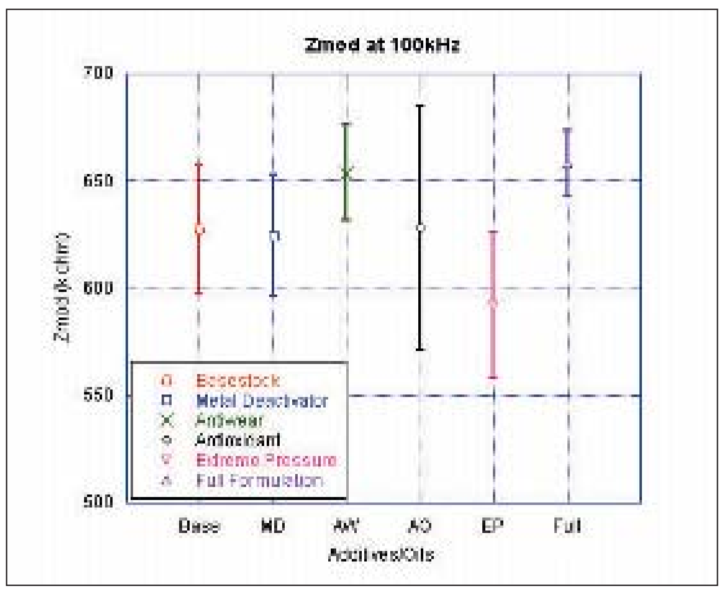

Figure 5. Mean value and standard deviation error bars of oil additives at 100 kHz. None of the tests were significantly different from one another.

Mixtures
10mHz

Oil/Additive	Zmod (kΩ)	N	t-test	H_0	% change
MD	264.35 ± 60.9	4			
1AO-2MD	132.3 ± 8.7	4	-	0.015	-50.0
1AO-1MD	140.7 ± 24.4	4	-	0.027	-46.8
2AO-1MD	91.63 ± 5.5	4	-	0.009	-65.3
AO	59.59 ± 4.2	4	-	0.006	-77.5
AO	59.59 ± 4.2	4			
1AO-2MD	132.3 ± 8.7	4	+	< 0.001	121.9
1AO-1MD	140.7 ± 24.4	4	+	0.005	136.0
2AO-1MD	91.63 ± 5.5	4	+	< 0.001	53.8
1AO-2MD	132.3 ± 8.7	4			
1AO-1MD	140.7 ± 24.4	4	=	0.578	6.4
2AO-1MD	91.63 ± 5.5	4	-	0.001	-30.7
1AO-1MD	140.7 ± 24.4	4			
2AO-1MD	91.63 ± 5.5	4	-	0.020	-34.9

Table 3. Summary of data from mixture tests

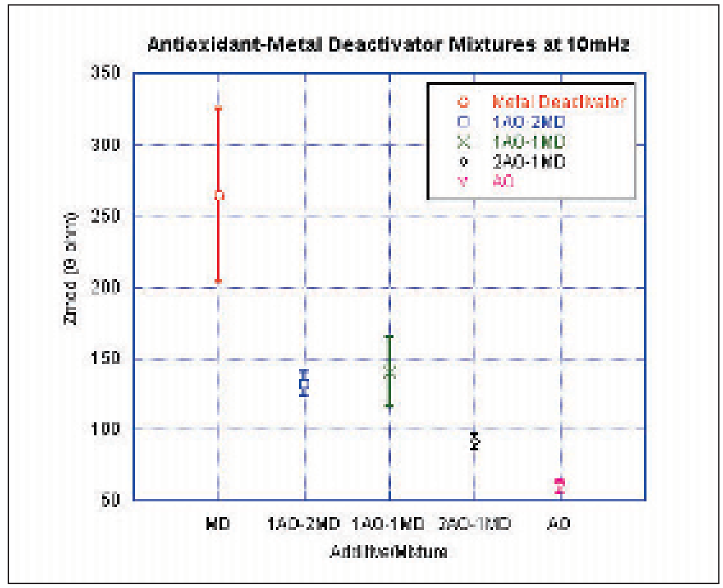

Figure 7. Mean values of the additives and mixtures with one standard deviation error bars. Each mixture was significantly different from each single additive, but only the 2AO-1MD mixture is significantly different from all other mixtures.

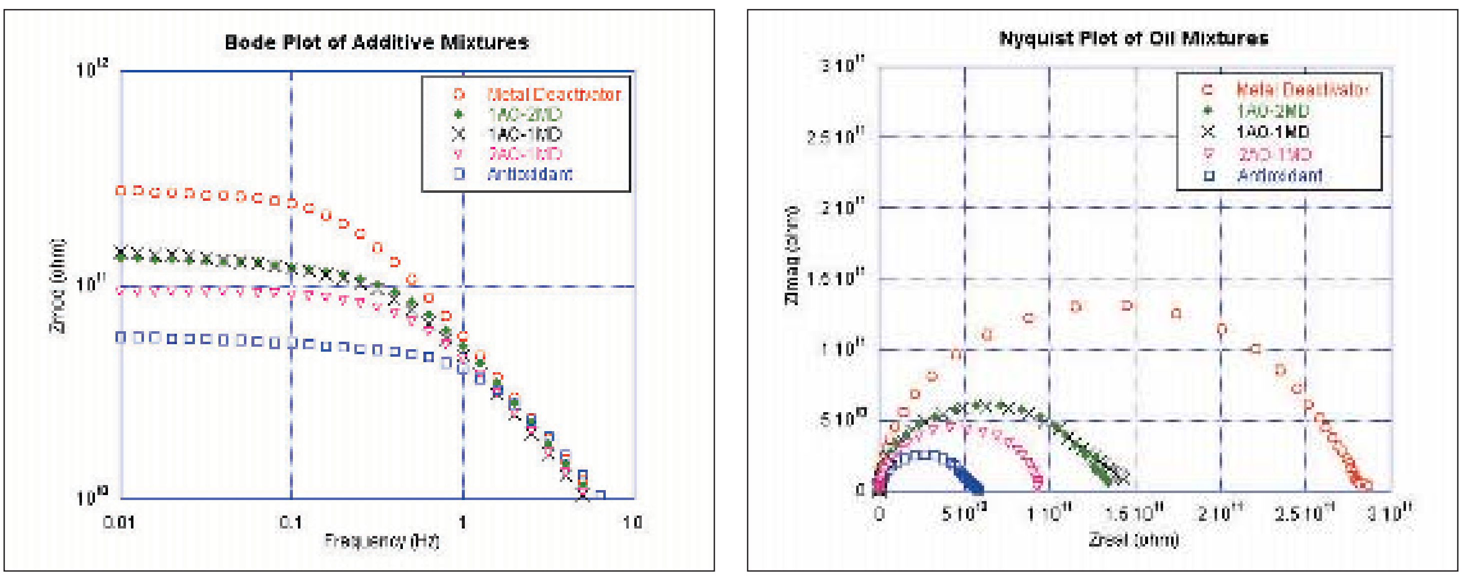

Figure 6. Bode and Nyquist plots of metal deactivator and antioxidant mixture data. The data from the straight metal deactivator and antioxidant additives is included. Only the low frequency data is shown on the Bode plot.

largest effect on impedance of all the additives. A comparison to the full formulation also indicates that the extreme pressure is not the only additive to have a significant effect but that there may be interaction between the additives in the full-formulation oil. Because each additive displays a higher mean magnitude, it is assumed that some interaction is occurring to cause the lower mean magnitude value displayed by a full-formulation.

For the 100 kHz data it can be seen that no difference is observed between the additives and both the basestock and the full formulation. This frequency is insufficient for impedance testing. Figure 5 shows the mean impedance values for each additive, with error bars representing one standard deviation.

The mixture studies with metal deactivator and antioxidant were performed to understand additive interaction and the effect it has on impedance. The data for each of these is shown in Figures 6 and 7 and Table 3. Variance from the mean is one standard deviation. T-test values indicate statistical significance at 95% confidence; = indicates no statistical significance, +/-

indicate significantly higher or lower values. H_0 values indicate the t-probability associated with the paired t-test values showing confidence levels for all tests. The first group compares the tests to the metal deactivator, the second to antioxidant and the last two groups compare the mixtures to each other. The data presented here is for the test that was closest to the mean. Because the 100 kHz frequency point was shown (see Fig. 5) to be ineffective in detecting differences in impedance, this data was ignored for the mixture tests.

The data shows there is a difference between the two additives, that the mixtures are different from both additives, but that each mixture is not significantly different from one another. If there was no interaction occurring, it would be assumed that the impedance magnitude would vary with the mixing ratio (i.e. the magnitude in Figure 7 would be linear). This trend appears to be the case, except for the 1AO:2MD ratio. For this ratio, it is evident that the antioxidant additive has a stronger contribution to the impedance. If the additives were interacting, the impedance magnitude for the mixtures would be expected to be very different from the single additives (i.e. not have a value between the single additives). This was not observed for any of the mixtures in this study.

4. Conclusions

The amount of variance in data is different for each additive. High frequency tests do not show any significant difference between oils/oil-additive mixtures and are unsuitable for impedance response tests. Compared to the basestock oil only the extreme pressure additive and full formulation are significantly lower using a 95% confidence level. All additives are significantly different from the full-formulation. The mixtures of metal-deactivator and antioxidant do not indicate interaction; however, the antioxidant additive appears to have a stronger contribution to the impedance. The impedance values for these mixtures are proportional to the mixing ratio.

To aid in the development of a suitable equivalent circuit, a model derived from the physical mechanisms related to electronic conduction in oils will need to be addressed. The goal is to "simulate" the response of a fully formulated oil (and incorporate the effects of water content and Cl^- contamination). In addition, future work will be focused on identifying the contributions of the interfacial reactions on the impedance.

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