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Impedance Spectroscopy as a Tool for the Diagnosis of the State of Vegetable Oils Used as Lubricants

E. Delgado[*], *W. Aperador, A. Hernández*

School of Engineering, Universidad Militar Nueva Granada, Bogotá-Colombia
[*]E-mail: energía.alternativa.ed@gmail.com

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In this research the performance of sesame seeds and sweet almond oils was analyzed used as lubricants in preventive wear testing (AW) in a four-ball tribometer. The impedance spectroscopy technique was used in the frequency range of 0.2 to 2000 kHz as a tool for diagnosis of the state of the oils. Impedance measurements were performed on the oils before and after wear testing. The results obtained were compared with the behavior of two mineral oils with different viscosity, oils 255 and 360, used as lubricants under the same conditions. From the test results of wear testing it was determined that the sweet almond oil has greater lubricity compared with sesame oil and therefore the impedance spectra of fresh and used oil haven't presented any significant differences. From the comparison of the impedance spectra of sesame and mineral base oils, it was established that the higher the degree of wear, the greater the difference between the impedance spectra of fresh oils and used ones. Finally, based on the results it was showed that the impedance spectroscopy technique can be used to differentiate between vegetable and mineral oils.

Keywords: sesame oil, sweet almond oil, preventive wear, impedance spectroscopy, tribology.

1. INTRODUCTION

The progressive depletion of world reserves of fossil fuels and concerns about the environmental impact caused by their use are some of the reasons that has driven the development of new technologies to develop products from renewable sources that are environmentally friendly [1-2]. Today, lubricants based on vegetable oils are classified as potential substitutes for mineral oils derived from petroleum, not only because they are renewable raw materials, but also because they are biodegradable and non-toxic. The polar nature of their constituent molecules (triglycerides) gives them most of the properties required for lubrication: high viscosity index, low volatility and good lubricity [2-3]. However, they have disadvantages as low thermal, oxidative and hydrolytic stability, and poor fluidity at low temperatures [4- 5], requiring the addition of additives in the formulation of lubricants based on vegetable oils to improve these properties and ensure optimum performance in the application required.

Recently, the interest has been increased in research on the use of vegetable oils (soybean, palm, sunflower, castor beans, corn oils, etc.) as possible lubricants, where additive and implementation techniques for evaluating their performance have been emphasized in their characterization [6]. The constant search for alterative vegetable oils has revealed the benefits of other commodities such as sesame seeds and sweet almonds. In previous studies, it was found that sesame oil (Sesamum indicum L.) and sweet almonds (Prunus amygdalus var. Dulcis) are raw materials of great interest for the development of green lubricant materials because, compared to other vegetable oils, they have better fluidity at low temperatures due to their high content of unsaturated fatty acids: oleic acid (sesame seeds 41.4%, almonds 62.0 to 86.0%) and linoleic acid (sesame seeds 39.4%, almonds 20.0 to 30.0%). In addition, test results of preventive wear (AW) and extreme pressure (EP), revealed that these vegetable oils have higher lubricity compared to mineral oils [7-9].

Furthermore, regular evaluations of the state of an oil used as a lubricant in a given application are important to determine when it loses its lubricating and thermal properties and should be replaced. So the wear, which limits the lifetime of the lubricated parts and can lead to a catastrophic failure, is avoided. For quality control of vegetable oils there have been developed sophisticated analytical methods such as gas chromatography, liquid chromatography, infrared Fourier transform spectroscopy, Raman spectroscopy and nuclear magnetic resonance techniques. But, unfortunately, these methods are expensive and not readily applicable for routine analysis or continuous industry monitoring. Therefore, it is necessary to develop alternative testing methods that are economical, quick, accurate and easy to apply. In this context, in recent years there has been an increase in the number of research projects that study and suggest the use of the dielectric spectroscopy to characterize vegetable oils [10-12].

The dielectric or impedance spectroscopy (IS) is an effective, economical and non-destructive method which can determine the electrical properties of various materials (concrete, paper, liquids, bio-fuels, etc.). This technique involves the analysis of how a material responds to the application of an electromagnetic field; the response analysis is done in the frequency domain to determine the impedance [13]. The information obtained describes the dielectric behavior of a material and can be correlated with several of its properties. For vegetable oils and bio-fuels, the dielectric properties may correlate with properties such as density, viscosity, distribution of molecular size and the amount of polar components [10][12].

According to the ideas above, the main purpose of this research was to test a method of analysis based on the technique of impedance spectroscopy to assess the state of sesame seeds and sweet almonds oil used as possible lubricants in preventive wear testing (AW) in a four-ball tribometer. The data obtained were compared to the behavior of two oil samples of different viscosity - mineral base oils 255 and 360, in order to establish whether there is a correlation between the degree of wear determined in the tribological tests and the electrical properties observed in the impedance spectra of fresh and used oils.

2. MATERIALS AND METHODS

2.1. Materials

Sesame seeds and sweet almonds unrefined oil were purchased in the local market and had the following characteristics: sesame oil: density of 0.98 g/cm^3, kinematic viscosity at 40°C: 34.64 cSt; sweet almond oil: density of 0.916 g/cm^3, kinematic viscosity at 40°C: 86.48 cSt. The mineral base oils 255 and 360 were used as received without further purification and without additives, their characteristics are the following: mineral oil 255: density of 0.82 g/cm^3, kinematic viscosity at 40°C: 24.21 cSt; mineral oil 360: density of 0.86 g/cm^3, kinematic viscosity at 40°C: 67.45 cSt.

2.2. Tribological preventative wear tests (AW)

The lubricity of mineral and vegetable oils was determined by preventive wear testing (AW) in a four-ball tribometer. The tests were conducted according to ASTM D4172-94, under the following conditions: 75°C, 1200 rpm, load of 15 kgf (147 N), testing time of 60 min. Chromium alloy steel balls AISI 52100 were used. The samples used as lubricating oil in the AW assays were analyzed by impedance spectroscopy. The parameter for evaluating the lubricity of oils was the average size of the wear scar diameters (WSD).

2.3. Impedance spectroscopy (IS)

In order to obtain the impedance of the oil samples, it was necessary to measure the magnitude and phase relationships between the current and voltage, taking into account equations (1) to (3).

Rewriting Ohm's law to replace resistance with impedance (1):

$$V = I * Z \qquad (1)$$

It can be seen that the impedance *Z*, acts as a linear transformation of the current, changing its magnitude and phase to obtain the voltage.

Z is a complex number that can be described in polar (2) or Cartesian (3) coordinates, where θ is the phase difference between voltage and current.

Polar coordinates:

$$Z = |Z|e^{j\theta} \qquad (2)$$

Cartesian coordinates:

$$Z = |Z|\cos\theta + j|Z|\sin\theta \qquad (3)$$

Moreover, considering that the impedance is frequency dependent, waveform signals of current and voltage were captured at different frequencies by a oscilloscope method of direct measurements [13].

Determining experimental impedances of vegetable and mineral oils used in preventive wear tests is conducted in an experimental set of parallel discs (Fig. 1). 340 stainless steel electrodes were used, which were secured with a spring system, which evenly distributes the pressure of the electrodes on the sample.

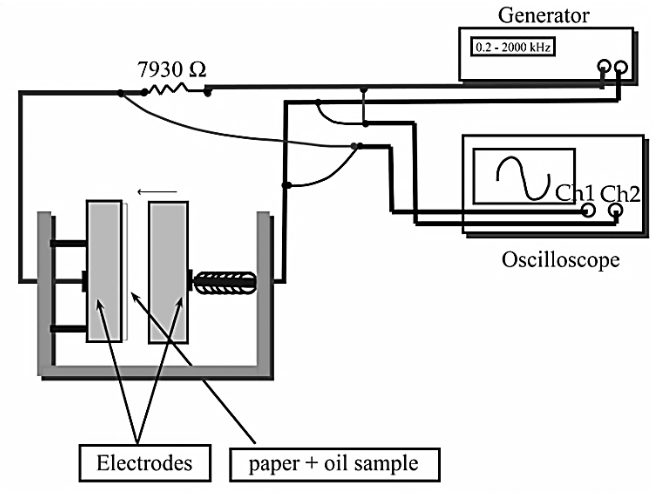

Figure 1. Experimental setup

Between electrodes, paper impregnated with 3 drops (approx. 0.1 g) of the oil sample to be analyzed (Table 1) was placed. The sample was evenly distributed throughout the paper. The diameter of the paper was the same as the electrodes (5.40 ± 0.05 cm) and its thickness was 0.07 mm. The tests were performed at room temperature (18°C) with alternating current (AC) in the frequency range of 0.2 to 2000 kHz. For each sample frequency measurements were taken in triplicate.

The comparison of the averages of the impedances of oil, expressed as 20 $\log_{10}$ (magZ), was performed using an analysis of variance with a significance level of 5%, using the STATGRAPHICS® PLUS 5.0 software. A model of two factors (oil type and frequency) with various levels was used.

Table 1. Samples of fresh and used oils in tribological wear tests.

Test	Material
0	Paper
1	Paper + sesame oil
2	Paper + used sesame oil
3	Paper + almond oil
4	Paper + used almond oil
5	Paper + mineral oil 255
6	Paper + used mineral oil 255
7	Paper + mineral oil 360
8	Paper + used mineral oil 360

3. RESULTS AND DISCUSSION

Although for the selection of the assembly it was taken into account that this type of configuration has yielded the impedance spectra of various materials, it was necessary to adapt the assembly positioning between the electrodes paper, uniformly impregnated with oil of interest, for impedance measurements of each sample. According to the results, it was determined that the impedance spectrum of the paper without oil differs considerably from all spectra of paper impregnated with various oils. This indicates that the differences between the spectra of the samples studied are due solely to the nature of the oil or the degree of wear seen in tribological tests. The paper only acts as a support and has a constant effect on all measures, so it does not affect the differences observed between the impedance spectra of various oils studied.

Comparing the impedance spectra of sesame oil, before and after the tribological wear tests, it is observed that the impedance is frequency dependent in the range of 0.2 to 8.0 kHz and that in the region of 0 2 to 5.0 kHz there are significant differences ($\alpha < 0.05$) between the two oil samples (Fig. 2). After 8.0 kHz to 2000.0 kHz no dependence of impedance was observed on the frequency or the differences between fresh and used sesame oil. According to these results, the range of 0.2 to 5.0 kHz is useful for differentiating between samples of fresh and used sesame oil in wear preventive tests; in this frequency range, used sesame oil presents lower impedance values when compared to the fresh oil. The impedance of the used oil decreases because the metal particles in suspension, generated by the wear process of steel balls AISI 52100, increase the conductive nature of the oil samples.

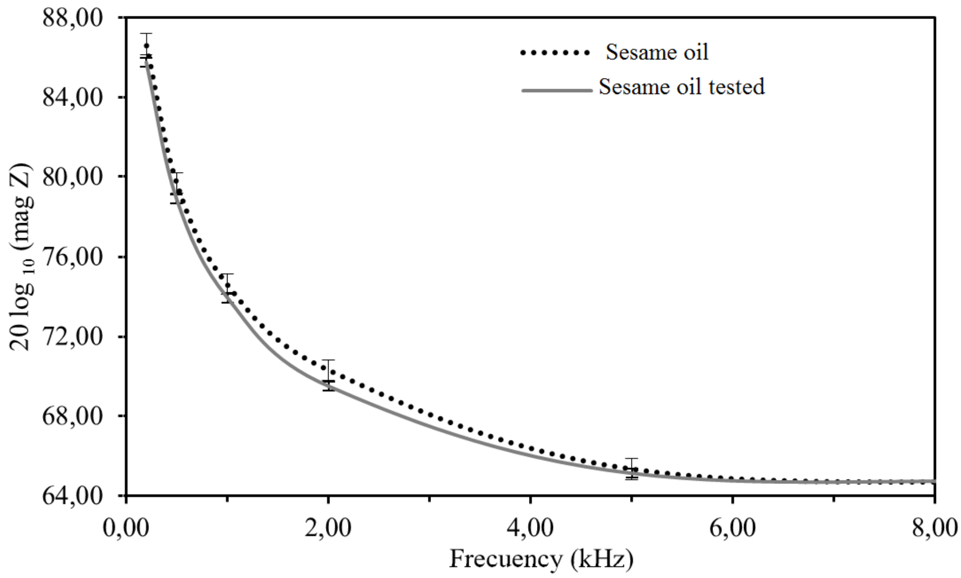

Figure 2. Comparison of the impedances of fresh and used sesame oil in the AW tests. Frequency range from 0.2 to 8.0 kHz.

In previous studies, the techniques of FT-IR spectroscopy and differential scanning calorimetry (DSC) were used for analyzing the properties of used sesame oil as a lubricant in preventive wear and extreme pressure tests. It was found that under conditions in which the tribological tests were developed, the oil does not rust, but the presence of metallic particles in suspension catalyzes the oxidation reaction starting at 156,99°C [9]. In this work the electrical measurements were performed at room temperature (18°C), thus the decrease in the impedance of used oil is correlated with the degree of wear presented in the metal pieces and not with the degradation of the vegetable oil.

In the impedance spectra of sweet almond oil, before and after the tribological wear tests (**Fig. 3**), it is observed that the impedance is frequency dependent in the region of 0.2 to 8.0 kHz. However, among the samples of fresh and used almond oil no significant differences were found in the value of the impedance in the frequency range studied (0.2 – 2000 kHz).

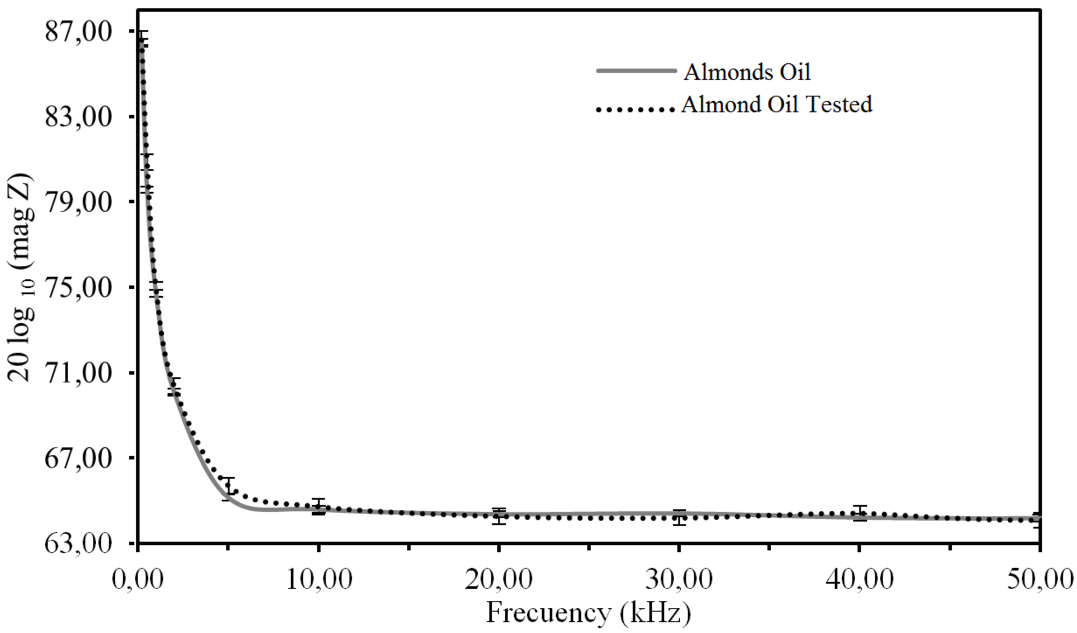

Figure 3. Comparison of the impedances of fresh and used sweet almond oil in the AW tests. Frequency range from 0.2 to 50.0 kHz.

From preventive wear tests, it was established that the balls lubricated with sweet almond oil have less wear (WSD = 1.63 mm) compared to balls lubricated with sesame oil (WSD = 1.81 mm) (**Table 2**). Between these two vegetable oils, almond oil exhibits better lubricity and consequently the amount of metal particles which emerge from the balls during the preventive wear tests is not sufficient for the impedance spectrum of the used oil to present any differences from the specter of fresh oil. Probably, the best lubricity shown by this oil is directly related to its higher content of unsaturated fatty acids compared to sesame oil [7] [14].

Table 2. The average size of the wear scar diameters obtained in preventive wear tests.

Lubricant	WSD (mm)
Almond oil	1,63
Sesame oil	1,81
Mineral oil 255	4,23
Mineral oil 360	5,28

In Figs. 4 and 5 the impedance spectra of two different viscosity mineral oils (oils 255 and 360) are shown, before and after preventive wear testing. In the spectra it shows that the impedance is frequency dependent in the range of 0.2 to 8.0 kHz. From the statistical analysis, it was determined that in the entire frequency range studied (0.2 to 2000 kHz) there are significant differences between samples of fresh and used mineral oils. Across the spectrum, the used oils have higher impedance values compared to the fresh oils; these variations are likely to be associated with changes in oil viscosity, which is known to modulate mobility loads [15]. Furthermore, in the case of mineral oil 360 it was found that the difference between the impedance values of fresh and used oil is considerably larger than the difference between samples of mineral oil 255.

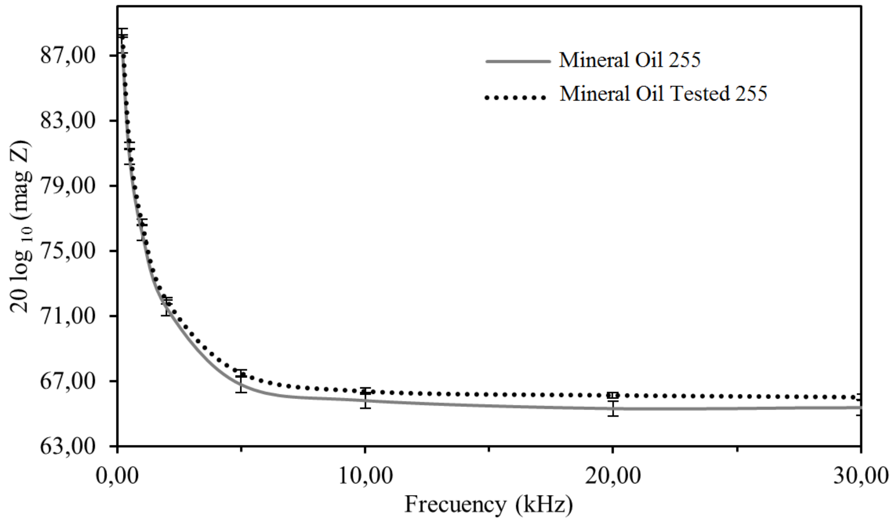

Figure 4. Comparison of the impedances of fresh and used mineral oil 255 in the AW tests. Frequency range from 0.2 to 30.0 kHz.

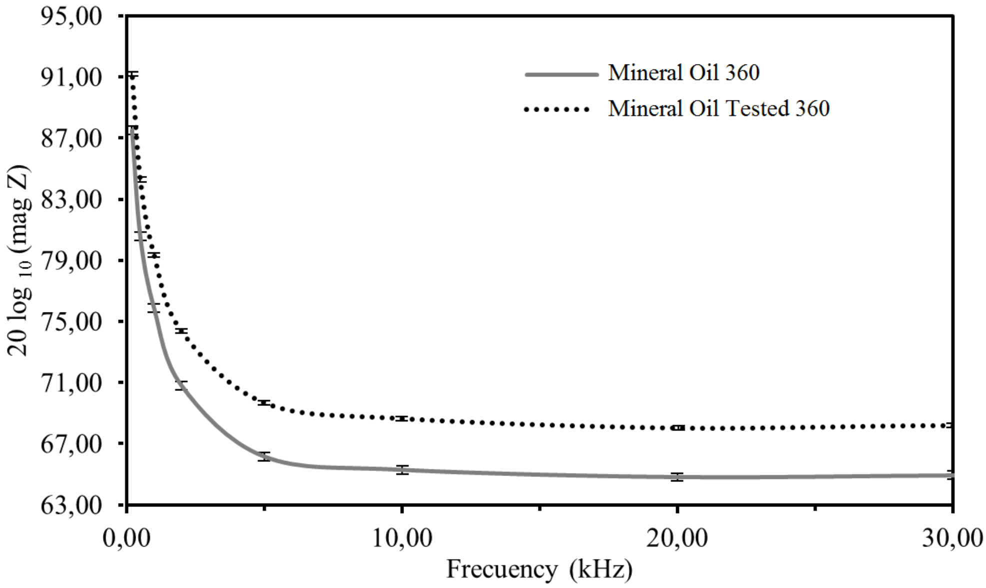

Figure 5. Comparison of the impedances of fresh and used mineral oil 360 in the AW tests. Frequency range from 0.2 to 30.0 kHz.

Moreover, in tribological wear tests it was found that the balls lubricated with mineral oil 255 present less wear (WSD = 4.23 mm) compared to the balls lubricated with mineral oil 360 (WSD = 5.29 mm). Given these results and the results obtained from vegetable oils of sesame and sweet almond, we can establish a correlation between the degree of wear, in terms of the average size of the wear scar diameters (Table 2), and the difference between the impedance spectra of fresh and used oils (Figs. 2-5). The higher degree of wear, the greater the difference is between the impedance values of fresh and used oil. The impedance spectra of the used oils have greater difference from the spectra of fresh oils compared to vegetable oils which exhibit better lubricity. This difference can be explained by the structure and chemical nature of the vegetable oils, which are mixtures of triglycerides consisting of fatty acids, while mineral oils are mixtures of saturated non-polar hydrocarbons [4]. High polar molecules of the vegetable oils allow them stronger interactions with the metal to lubricate and, therefore, greater adsorption capacity, inhibiting metal to metal contact [16]. While comparing the impedance spectra of fresh vegetable and mineral oils, it was found that sesame and sweet almond oils differ significantly from mineral oils 255 and 360 in the whole frequency range (Fig. 6). Between the spectra of sesame and fresh almonds oils, statistically, no significant differences were found ($\alpha > 0.05$), while among mineral oils 255 and 360 the differences in the impedance values of the samples were detected.

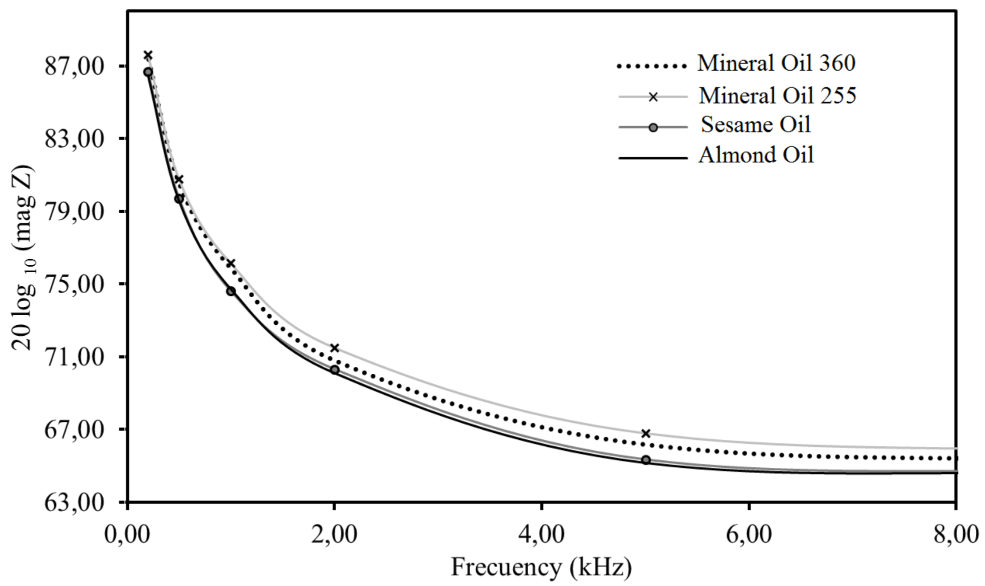

Figure 6. Comparison of the impedances of fresh vegetable and mineral oils.

Based on the results obtained, it is shown that the impedance spectroscopy technique can be used to differentiate vegetable oils from mineral oils because the electrical properties of these materials depend solely on their chemical nature and structure [17-18]. Vegetable oils contain molecules of polar nature (triglycerides) with permanent electric dipoles, therefore they have lower impedance values compared to mineral oils, which contain non-polar hydrocarbons (Fig. 6). Between sesame and almond oils no differences can be detected as both oils are mixtures of triglycerides and differ only in the composition of saturated and unsaturated fatty acids [19-20]. Furthermore, the differences found between the impedance values of mineral oils of different viscosity suggest that the chemical structure of saturated hydrocarbons varies considerably from one oil to another, possibly, due to a difference in the size of the hydrocarbon chains; mineral oil 360 has a higher viscosity than the oil 255, thus it is presumed that the oil 360 possesses longer hydrocarbons chains [14].

4. CONCLUSIONS

The impedance spectroscopy technique allowed to analyze the performance of samples of vegetable and mineral oils used as lubricants in tribological preventive wear tests. In the impedance spectra of all the fresh and used oils it was found that the impedance is frequency dependent in the range of 0.2 to 8.0 kHz, but the impedance values of used oil vary with respect to fresh oil in certain frequency ranges, depending on the type of oil used. The range from 0.2 to 5.0 kHz is useful for differentiating between samples of fresh and used sesame oil. Between samples of fresh and used sweet almond oil no significant differences occur throughout the frequency range studied (0.2 to 2000 kHz), because this vegetable oil exhibits better lubricity and consequently the amount of metallic particles in suspension is not enough for the impedance spectrum of used oil to present differences from the specter of fresh oil. With respect to mineral oils 255 and 360, which have lower lubricity (WSD is higher) compared to vegetable oils, it was noted that used oils have higher impedance values compared to fresh oils, in the whole spectrum. Moreover, a correlation between the degree of wear, in terms of the average size of the wear scar diameter, and the difference between the impedance spectra of oil samples was found: the higher degree of wear, the greater is the difference between the impedance values of fresh and used oils.

The results of this study demonstrate that the impedance spectroscopy technique can be used to assess the state of a vegetable or mineral oil used as a lubricant in a given application. The proposed analysis method is effective, economical, easy to apply, non-destructive and requires small amounts of sample material; all these characteristics certify it as able to facilitate regular analysis of the state of a lubricating oil.

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References

1. J. C. J. Bart, E. Gucciardi, S. Cavallaro, *Biolubricants Science and technology*, Woodhead Publishing Limited (2013) 249

2. J. C. J. Bart, E. Gucciardi, y S. Cavallaro, *Biolubricants Science and technology*, Woodhead Publishing Limited (2013) 121
3. K. R. Sathwik, N. H. Jayadas, S. Kailas, *Green Tribology*, (Nosonovsky, M.; Bhushan, B., Eds.), Springer, (2012) 287
4. N. H. Jayadas, K. P. Nair, *Tribol. Int. 39* (2006) 873
5. N. J. Fox, G. W. Stachowiak, *Tribol. Int.* 40 (2007) 1035
6. J. C. J. Bart, E. Gucciardi, S. Cavallaro, Renewable lubricants. Biolubricants, Woodhead Publishing (2013)
7. A. Hernández, C. M. Zacconi, *Quim. Nova*, *32* (2009) 1342
8. J. K. Mannekote, S. V. Kailas, *J. Mater. Res. Tecnol.*, *1* (2012) 91
9. A. E. Delgado, W. A. Aperador, *Información tecnológica*, 25 (2014) 79
10. A. Cataldo, E. Piuzzi, G. Cannazza, E. De Benedetto, L. Tarricone, *Measurement*,43 (2010) 1031
11. A. T. Pérez, M. Hadfield, *Sensors*, *11* (2011) 10675
12. J. Corach, P. A. Sorichetti, S. D. Romano, *Int. J. Hydrogen Energy*, *37* (2012) 14735
13. J. R Macdonald, Impedance Spectroscopy. Theory, Experiment, and Applications. Number 2. John Wiley & Sons (2005).
14. L. A. T. Honary, E. Richter Chemistry of Lubricants. In *Biobased Lubricants and Greases*, John Wiley & Sons, (2011)
15. J.-C. M'Peko, D. L. S. Reis, J. E. De Souza, A. R. L. Caires, *Int. J. Hydrogen Energy*, *38* (2013) 9355
16. A. Kabuya, J. L. Bozet, In *Tribology Series*, Elsevier, (1995)
17. G. Knothe, *Fuel Process. Technol.*, 86 (2005) 1059
18. A. A. Refaat, *Int. J. Environ. Sci. Tech.*, 6 (2009) 677
19. J. Halambek, A. Zutinic, K. Berkovic, *Int. J. Electrochem. Sc.*, 8(2013) 11201
20. J. Bautista-Ruiz, W. Aperador, A. Delgado, M. Díaz – Lagos, *Int. J. Electrochem. Sc.*, 9(2014)4144