

Edible Natural Ester Oils as Potential Insulating Fluids

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ABSTRACT

Three types of edible natural ester oils (soya, rice and sunflower) were aged with and without antioxidant additives. The properties of these aged oils were analyzed in comparison with a commercial natural ester insulating product (Biovolt A). Dissolved gases in these aged oils under thermal and electrical stress were also investigated.

Indexing Terms — Vegetable insulating oil, natural ester insulating oil, oxidation stability, aging, dissolved gases.

1 INTRODUCTION

LIQUID-IMMERSED transformers have generally been filled with mineral oil for more than 100 years. The use of this petroleum-based product has been justified until now by its wide availability, low cost and good chemical and electrical properties. However, because of increasing environmental concerns, efforts have been made to find natural products with high biodegradability and similar cost to petroleum-based products. Among the possible replacements for mineral oil to insulate transformers are natural ester fluids based on “renewably sourced” [1-5].

The wide biodiversity of Brazilian sources of natural ester oils is an important factor for efforts to find new classes of suitable natural ester oils for insulation applications. The present paper analyzes the main characteristics of three different natural ester oils (soya, rice and sunflower) as potential insulating fluids and their aging behavior before and after blending with antioxidant additives. We used the induction period to evaluate the effect of adding oxidation inhibitors to the natural ester oils. An oxidation stability test is not specified for unused natural ester insulating oils in ASTM D6871 standard or IEEE service guide [6]. With respect to the methods available to determine oxidation stability, we adopted the EN 14112 method (or Rancimat), the standard method for determining oxidation stability for biodiesel in Europe [7] and in Brazil, according to Resolution 7 (DOU 20.3.2008) from the National Petroleum, Natural Gas and Biofuels Agency (ANP). This method is considered the most appropriate for biodiesel analyses because the induction time, which is derived from conductivity measurement, displays the best correlation

with the stages involved in the onset or preliminary events of oxidative degradation, when compared to other methods from the American Oil Chemistry Society (AOCS). Examples of these include the peroxide index (method Cd 8-53), the acid number (method Cd 3d-63) and the o-anisidine value (method Cd 18-90), as well as the pressurized differential scanning calorimetry method (P-DSC) [7, 8]. The Rancimat method was used by Wilhelm et al. to compare the performance of different antioxidant additives in reclaimed in-service natural ester-based insulating fluid by induction period measurement [9].

Domingos et al [10] concluded that among synthetic antioxidants evaluated for the increased stability of soybean oil ethyl esters, butyl hydroxytoluene (BHT) was most effective. On the other hand, tert-butyl hydroxyquinone (TBHQ) displayed greater stabilizing potential for esters with lower stability.

In this study, we also monitored the formation of dissolved gases by the different edible oils to evaluate the effect of chemical composition on the amount of gases formed. The technique of analysis of dissolved gases (DGA) is used to diagnose transformer failures. A number of diagnostic methods are available to identify the types of failures and their intensities. These include the IEC, IEEE standard and Duval triangle diagnosis methods [11]. Two broad categories of transformer faults can be detected by DGA: thermal and electrical failures. The various DGA standards then subdivide these basic types in different ways. In IEC 60599, thermal faults are represented as being in three temperature bands, 300 °C, >300 °C and >700 °C [11]. Electrical faults can be further classified as partial discharges of the cold plasma (corona) type (PD), low energy discharges (D1), and high energy discharges (D2). The triangular graphical representation of Duval, which is

used to visualize a DGA fault diagnosis, uses the same subdivisions as the IEC standard. However, instead of using the concentration of five gases and three ratios to define the type of fault, the relative percentage of three gases is used for the analysis in the Duval diagnosis technique [11].

Several articles have been published recently on the formation of gases dissolved in natural ester-based insulating oils [12-16]. In a recent study, Liu, Li and Zhang evaluated the formation of dissolved gases of two insulating oils, camellia oil and Envirotemp FR3 [15]. The content of carbon-carbon double bonds of the high oleic insulating camellia oil used was higher than that in FR3. The authors concluded that the content of these double bonds was responsible for the observed differences in the formation of dissolved gases under thermal faults for the two oils [15].

2 EXPERIMENTAL

2.1 MATERIALS

Mineral insulating oil (MIO), AV-62 IN, acquired from Petrobras, was used in this study.

Three types of refined natural ester oils (VO-1, VO-2 and VO-3) with different unsaturated fatty acid quantities (Table 1) acquired from Brazilian suppliers were tested. The performance of these refined natural ester oils was compared with a commercial natural ester insulating oil, Biovolt A, used as received, acquired from the Brazilian firm Mineraltec.

Different antioxidant additives (Table 1), all with purity grades above 99%, were provided by different suppliers and were used as received.

The basic chemical composition of the studied oil was obtained from the manufacturer and is described in Table 2.

Table 1. Details of oils and antioxidant additives.

	Acronym	Description
Commercial insulating fluids	Biovolt A	Natural ester-based insulating fluid. Formulated with a mixture of oils, corn oil is the major component*
	MIO	Mineral insulating oil
Edible natural ester oils	VO-1	Refined soya oil
	VO-2	Refined rice oil
	VO-3	Sunflower refined oil
Antioxidant additives	AD-1	α -tocopherol
	AD-2	BHA, butylated hydroxyanisole
	AD-3	BHT, butylated hydroxytoluene
	AD-4	TBHQ, tertiary butylhydroquinone
	AD-5	Baynox Plus

* According to the manufacturer's information.

Table 2. Saturated and unsaturated fatty acid composition of natural ester oils*.

Oil type	Saturated fatty acid (%)	Monounsaturated fatty acids (%)	Polyunsaturated fatty acids (%)
VO-1	15.3	24.5	60.2
VO-2	12.4	15.9	71.7
VO-3	20.7	41.4	37.9
Biovolt A	15.0	27.6	57.3

* According to the manufacturer's information.

2.2 PHYSICAL AND CHEMICAL CHARACTERIZATION OF THE OILS

First the edible natural ester oils were dried with silica gel pellets (with diameter of 1 – 3 mm), at a ratio of 1g of silica to 100 mL of oil under constant stirring of 500 rpm for 6 h. The moisture content of the oils was determined by the Karl Fischer titration method, according to ASTM D6304.

The edible natural ester oils (VO-1, VO-2 and VO-3) and the commercial insulating oil (Biovolt A) were characterized in the laboratory through physical and chemical tests according to the ASTM D6871 standard.

2.3 ADDITION OF ANTIOXIDANT ADDITIVES TO EDIBLE NATURAL ESTER OILS

The antioxidant additives (Table 1) were mixed with the edible natural ester oils (VO-1, VO-2 and VO-3). 0.3 g of each of these antioxidants was directly dissolved in 100 g portions of the dried edible natural ester oil samples by means of vigorous mechanical agitation. The induction times (IT) of these mixtures were determined in a model 743 Rancimat system (Metrohm AG, Herisau, Switzerland), according to official BS EN 14112 method. The IT determinations were carried out at an air flow rate of 10 L.h⁻¹. The temperature of the heating blocks was adjusted to 130 °C and the temperature correction factor (DT) was adjusted to 1.5 °C, as recommended by the manufacturer.

2.4 ACCELERATED AGING TESTS

The commercial insulating oil and all edible natural ester oil samples without antioxidant and with 3000 ppm of antioxidant additive AD-4 (Table 1) were subjected to aging tests. These tests were performed with 800 mL oil samples in a thermo-stabilized bath at 95 °C for 102 h, at an oxygen flow rate of 1 L.h⁻¹. Samples of aged oils were tested for acid number (ASTM D974), kinematic viscosity at 40 °C (ASTM D445) and dissipation factor at 90 °C (ASTM D924).

2.5 FORMATION OF GASES DISSOLVED UNDER THERMAL AND ELECTRICAL OVERSTRESS

To evaluate the gases formed due to thermal and electrical overstress, all the oils (VO-1, VO-2, VO-3, Biovolt A and MIO) were investigated.

First, the Ostwald coefficient values of nitrogen, oxygen, hydrogen, ethane (C₂H₆), ethylene (C₂H₄), acetylene (C₂H₂), carbon dioxide (CO₂), carbon monoxide (CO) and methane (CH₄) gases in the edible natural ester oils (VO-1, VO-2, VO-3) were determined according to ASTM D2780 method. This method is based on saturating a sample of oil with a fixed gas (in this case: C₂H₆, C₂H₄, C₂H₂, CO₂, CO or CH₄), extracting this gas quantitatively in a vacuum extractor, transferring it to a gas buret where its volume is determined, and calculating its solubility coefficient from the results.

To generate electrical arc discharge to evaluate electrical overstress, discharges of around 40 kV were applied in all

oils, using a dielectric breakdown voltage test device (Baur DPA model) with flat electrodes spaced at 2.5 mm. In each tested oil (400 mL) 15, 45, 75 and 105 discharges were applied. After each group of discharges (15, 45, 75 and 105 discharges), a 40 mL aliquot of oil was removed for analysis of the gases dissolved in the oil by gas chromatography using the ASTM D3612 method.

To evaluate the thermal overstress, 200 mL of each of the oils was placed in a sealed bottle and heated in an oven at 150 °C for 288 h. After regular aging time intervals, 40 mL of each tested oil was removed for analysis of dissolved gases by gas chromatography using the ASTM D3612 method.

3 RESULTS AND DISCUSSION

3.1 OILS CHARACTERIZATION

The characterization results of commercial natural ester-based insulating fluid shown in Table 3 are in compliance with the ASTM D6871 specifications. VO-2 edible oils met all the limit values specified by ASTM D6871 (Table 4). VO-1 did not meet the acid number requirement and VO-3 did not reach the dissipation factor limit values, probably due to different refining process applied at this oil (Table 4). The pour point limit also was not reached due to higher saturated fatty acids content in comparison with the other natural ester oils (Table 2).

Table 3. Physical-chemistry characterization of commercial natural ester-based insulating oil.

Property	Limit*	Biovolt A
Acid number, (mg KOH.g ⁻¹)	0.06, max	0.05
Water in Insulating Liquids, (mg.kg ⁻¹)	200, max	64
Density at 20 °C, (g.ml ⁻¹)	0.96, max	0.92
Dissipation Factor at 25 °C, (%)	0.20, max	0.15
Dissipation Factor at 90 °C, (%)	3.6, max	3.32
Dissipation Factor at 100 °C, (%)	4.0, max	4.00
Flash point, (°C)	275, min	312
Fire point, (°C)	300, min	346
Dielectric Breakdown Voltage, (kV)	30, min	55
Kinematic Viscosity at 40 °C, (x 10 ⁻⁶ m ² /s)	50, max	36.1
Kinematic Viscosity at 100 °C, (x 10 ⁻⁶ m ² /s)	15, max	8.45
Pour point (°C)	- 10, max	-21

Table 4. Physical-chemical characterization of edible natural ester oils.

Property	VO-1	VO-2	VO-3
Acid number, (mg KOH.g ⁻¹)	0.08	0.04	0.06
Water in Insulating Liquids, (mg.kg ⁻¹)	100	99	103
Density at 20 °C, (g.ml ⁻¹)	0.92	0.92	0.92
Dissipation Factor at 25 °C, (%)	0.16	0.15	0.36
Dissipation Factor at 90 °C, (%)	2.81	1.95	5.97
Dissipation Factor at 100 °C, (%)	3.17	2.10	6.96
Flash point, (°C)	318	318	312
Fire point, (°C)	352	357	350
Dielectric Breakdown Voltage, (kV)	42	37	37
Kinematic Viscosity at 40 °C, (x 10 ⁻⁶ m ² /s)	33.1	32.4	37.5
Kinematic Viscosity at 100 °C, (x 10 ⁻⁶ m ² /s)	7.8	7.7	8.4
Pour point, (°C)	-12	-15	-6

3.2 ANTIOXIDANT ADDITIVE TEST

Figure 1 shows the induction times for the edible natural ester and commercial natural ester-based insulating oil with and without antioxidant additive addition (Table 1). All edible oils without additives presented IT values below Biovolt A, and VO-2 present the lowest value due to its

high polyunsaturated fatty acids content (Table 2). Only the AD-4 additive increased the IT of edible oils to values near Biovolt A, with VO-3>VO-1>VO-2 according to the saturated fatty acids content (Table 2). The Rancimat method proved to be efficient in comparative evaluation of the induction time of the different natural ester oils under inquiry.

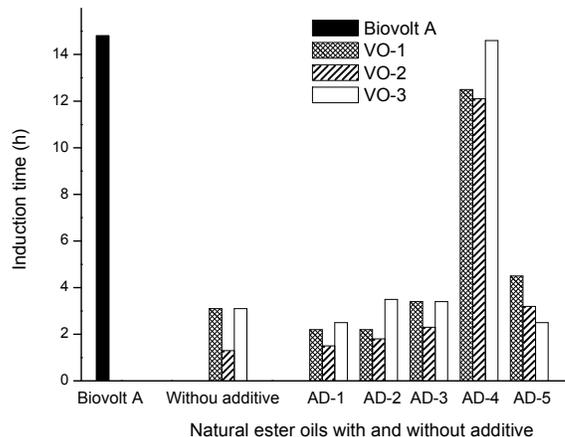


Figure 1. Induction times of natural ester oils: Biovolt A and edible oils with and without antioxidant additives (Table 1).

3.3 ACCELERATED AGING

According to the literature, the acidity, viscosity and dissipation factor of natural ester-based fluids are markers that should be monitored closely in transformers in service [16]. We therefore analyzed all these parameters for the aged oils. The results are shown in Figures 2-4.

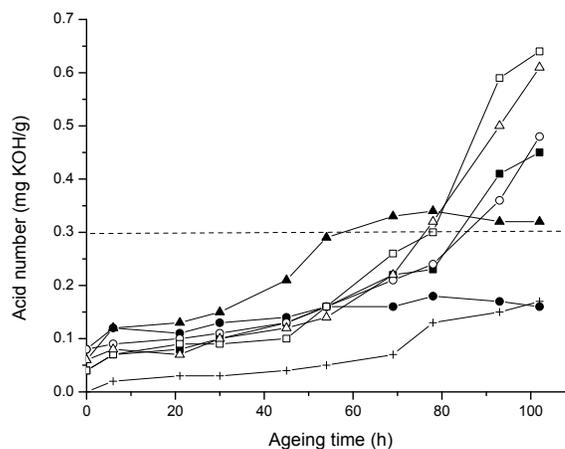


Figure 2. Aging effect on acid number for Biovolt A (+) and for edible oils without additives: (●) VO-1, (◻) VO-2, (Δ) VO-3; and with AD-4 additive: (○) VO-1, (◻) VO-2, (Δ) VO-3. The dotted line represents the threshold value for the acid number for natural ester-based insulating fluid in use, suggested in the IEEE guide [6].

Considering the provisional acid number guideline of service-aged natural ester fluids for triggering prompt additional investigation suggested by the IEEE guide [6] (0.3 mg KOH.g⁻¹), only Biovolt A and VO-1 without additive did not attain this value at the end of 102 h of

accelerated aging. The AD-4 additive had a negative effect on the acid number of the aged edible oils because values greater than $0.3 \text{ mg KOH.g}^{-1}$ were reached at the end of the accelerated aging test (102 h) in relation to the same oil without antioxidant addition. These data show that AD-4 is not a good additive for acid number maintenance of the studied edible oils.

The IEEE guide [6] suggests that prompt additional investigation should be performed when the service-aged natural ester fluids present a 10% viscosity increase from the value at the time of initial energization. Table 3 shows these viscosity limits for the studied oils.

Table 3. Acceptable viscosity limit for Biovolt A and edible oils according to the IEEE guide [6].

Viscosity at 40 °C for:		
	Non aged oil	Aged natural ester fluids (10% increase viscosity)
Biovolt A	$36.1 (x 10^{-6} \text{ m}^2\text{.s}^{-1})$	$39.7 (x 10^{-6} \text{ m}^2\text{/s})$
VO-1	$33.1 (x 10^{-6} \text{ m}^2\text{/s})$	$36.4 (x 10^{-6} \text{ m}^2\text{/s})$
VO-2	$32.4 (x 10^{-6} \text{ m}^2\text{/s})$	$35.6 (x 10^{-6} \text{ m}^2\text{/s})$
VO-3	$37.5 (x 10^{-6} \text{ m}^2\text{/s})$	$41.2 (x 10^{-6} \text{ m}^2\text{/s})$

For Biovolt A, the allowed guideline for viscosity of service-aged oils would be $39.7 x 10^{-6} \text{ m}^2\text{/s}$. The results of Figure 3 show that only Biovolt A did not reach the viscosity limit value after 102 h of accelerated aging ($39.7 x 10^{-6} \text{ m}^2\text{/s}$, according to Table 3). Natural ester oils VO-1 and VO-3, without antioxidant addition, reached the limit value defined at Table 3 (21 h), and VO-2 did so after 30 h of aging. After addition of AD-4, the time to reach the viscosity limit value (Table 3) increased to 69 h for VO-1 and VO-3 and 54 h for VO-2. These results show that the additive was efficient in maintaining the viscosity of the aged oils for a longer time than without the additive in the accelerated aging tests, but the obtained results were not so good in comparison with the commercial natural ester fluid (Biovolt A).

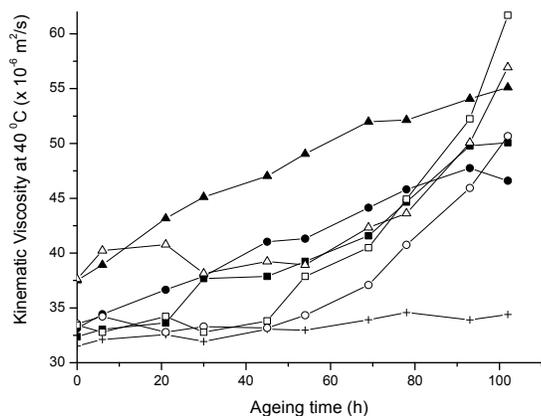


Figure 3. Aging effect on kinematic viscosity for Biovolt A (+) and for edible oils without additive: (●) VO-1, (■) VO-2, (▲) VO-3; and with AD-4 additive: (○) VO-1, (□) VO-2, (△) VO-3.

The IEEE guide suggests for service-aged natural ester fluids a maximum dissipation factor of 3% at 25 °C, and does not define a value for 100 and 90 °C. In this study, the

dissipation factor at 90 °C and at 25 °C of aged samples was measured. The correlation of these measurements can be observed in Figure 4A. Based on this correlation, it is possible to extrapolate the IEEE limit value for service-aged oil recommended at 25 °C (3%) to 90 °C as approximately 30% (Figure 4A).

The results in Figure 4B show that none of the oils reached this limit and that Biovolt A presented the lowest values. At the end of the accelerated aging test (102 h), Biovolt A presented a dissipation factor of 1.6% and the edible oils without antioxidant present 9.1, 7.1 and 3.4% in the following order: VO-3>VO-1>VO-2. After AD-4 addition, this order changed to VO-2>VO-3>VO-1 at the end of the accelerating aging test (102 h). Considering the value obtained of 102 h, it is possible to conclude that AD-4 was efficient in maintaining the dissipation factor of VO-1 and VO-3 but inefficient for VO-2, showing that each natural ester oil needs a specific additive to improve a particular property.

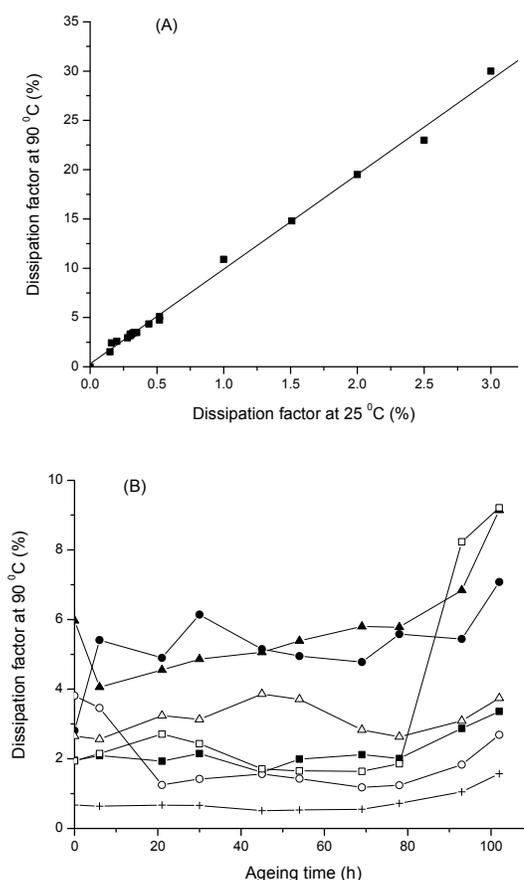


Figure 4. (A) Correlation between dissipation factor measurement at 25 and 90 °C for aged natural ester. (B) Aging effect on dissipation factor for Biovolt A (+) and for edible oils without additive: (●) VO-1, (■) VO-2, (▲) VO-3; and with AD-4 additive: (○) VO-1, (□) VO-2, (△) VO-3.

3.4 DISSOLVED GAS GENERATION

The solubility coefficients for different gases in oils are shown in Table 4. The solubility of gases in natural ester oils differs slightly from their solubility in mineral oil.

These results were used in calculating the concentration of dissolved gas-in-the oil samples.

Table 4. Gas solubility (Ostwald) coefficients.

Dissolved Gas	Ostwald solubility coefficient at 25 °C for:				
	VO-1*	VO-2*	VO-3*	Biovolt A**	MIO***
H ₂	0.050	0.047	0.046	0.054	0.056
O ₂	0.150	0.097	0.105	0.100	0.179
N ₂	0.070	0.059	0.074	0.071	0.098
CH ₄	0.300	0.230	0.270	0.305	0.438
CO	0.090	0.079	0.105	0.110	0.133
CO ₂	1.330	0.920	1.025	1.190	1.170
C ₂ H ₆	1.450	1.160	1.425	1.374	2.590
C ₂ H ₄	1.190	1.180	1.430	1.303	1.760
C ₂ H ₂	1.630	1.200	1.230	1.520	1.220

* Determined as described in section 2.5.

** Data supplied by the manufacturer.

*** Data from ASTM D 3487.

Figures 5-9 present the dissolved gases generated during electrical and thermal overstress. The same gases were produced in natural ester oils as in the MIO.

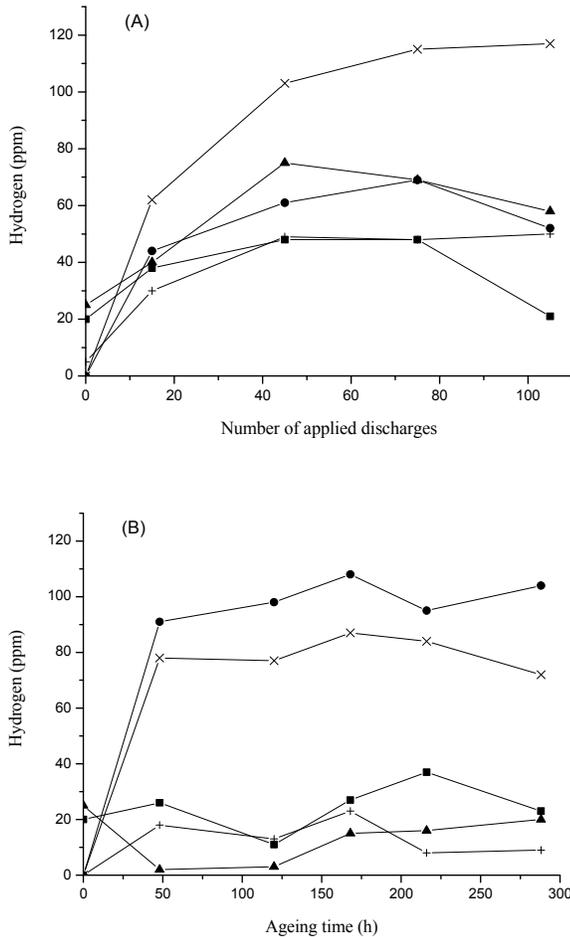


Figure 5. Hydrogen formation at (A) electric over-stress and (B) thermal overstress for: Biovolt A (+), MIO (x), (●) VO-1, (■) VO-2, (▲) VO-3.

Under the same magnitude of electrical overstress, the natural ester oils typically produced somewhat smaller quantities of dissolved gases than did the mineral oil

(Figures 5A-8A). For all the oils, acetylene was generated in the highest quantities in the electrical overstress test, followed by hydrogen gas, ethylene and methane. As in MIO, acetylene can be used as a tool to aid in detecting and diagnosing failures and abnormal operating conditions in equipment insulated with natural ester oils. The lower gas content generated in natural ester oils in relation to MIO can be attributed to the different chemical properties. In relation to the MIO, the natural ester oils have chemical structures containing more oxygen atoms and unsaturated bonds. However, the interpretation of the different amounts of gases in the different natural ester oils and their significance for identifying failures should be studied further. Reference points for each dissolved gas concentration in equipment insulated with natural ester oils have not been established yet.

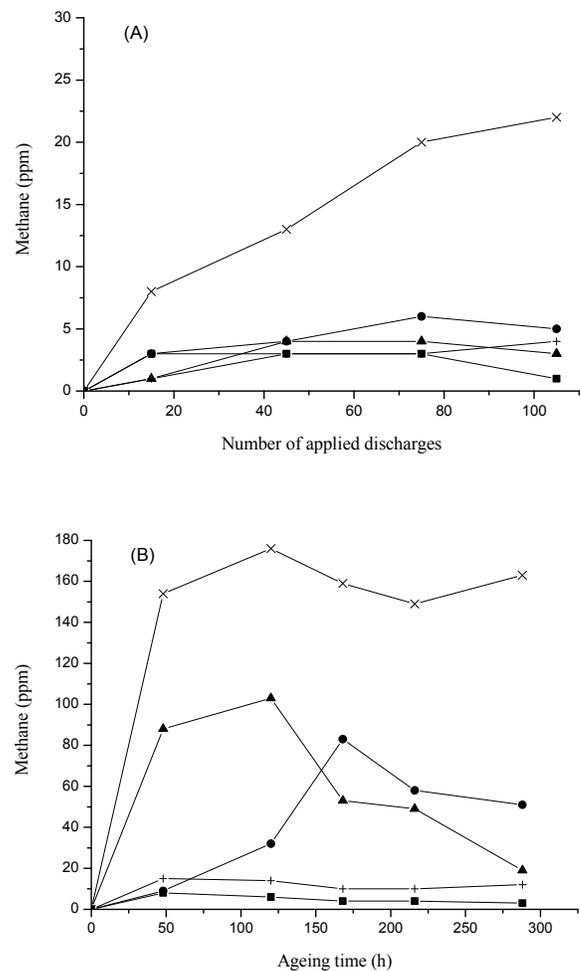


Figure 6. Methane formation at (A) electric overstress and (B) thermal overstress for: Biovolt A (+), MIO (x), (●) VO-1, (■) VO-2, (▲) VO-3.

In the thermal overstress tests, acetylene was not formed and the formation of dissolving gases did not follow a set pattern. With respect to hydrogen gas, only VO-1 showed higher values in relation to MIO (Figure 5B). The other oils showed lower values. For methane,

all the oils had lower gas formation in relation to MIO. For the other gases (ethylene, ethane and acetylene), only VO-2 presented lower values than MIO. The other oils showed higher values (Figure 6B).

It was not possible to correlate the formation of gas with the chemical composition of the different natural ester-based insulating oils. It seems that factors other than chemical composition of fatty acids as additives and contaminants interfere on the formation of fault gases.

We applied the IEC 60599 method to the DGA data obtained in this study to check whether the type of defect that could be diagnosed by this method was related to the type of stress applied to the oils (thermal and electrical). The IEC 60599 method was applied to the DGA data obtained at the end of the overstress period, which corresponds to the application of 105 electrical arc discharge in the electrical stress test and 288 h of accelerated aging in the thermal stress test (clause 2.5). The results are displayed in Table 5 and show that for the electrical stress, the natural ester oils had equal diagnoses, coherent with the type of stress applied the oils (electrical

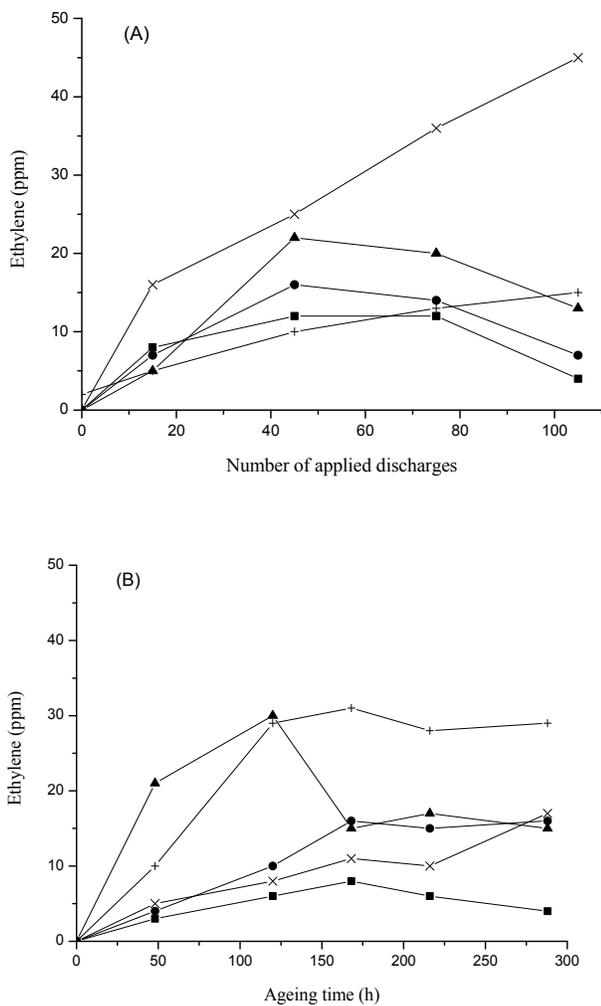


Figure 7. Ethylene formation at (A) electric overstress and (B) thermal overstress for: Biovolt A (+), MIO (x), (●) VO-1, (■) VO-2, (▲) VO-3.

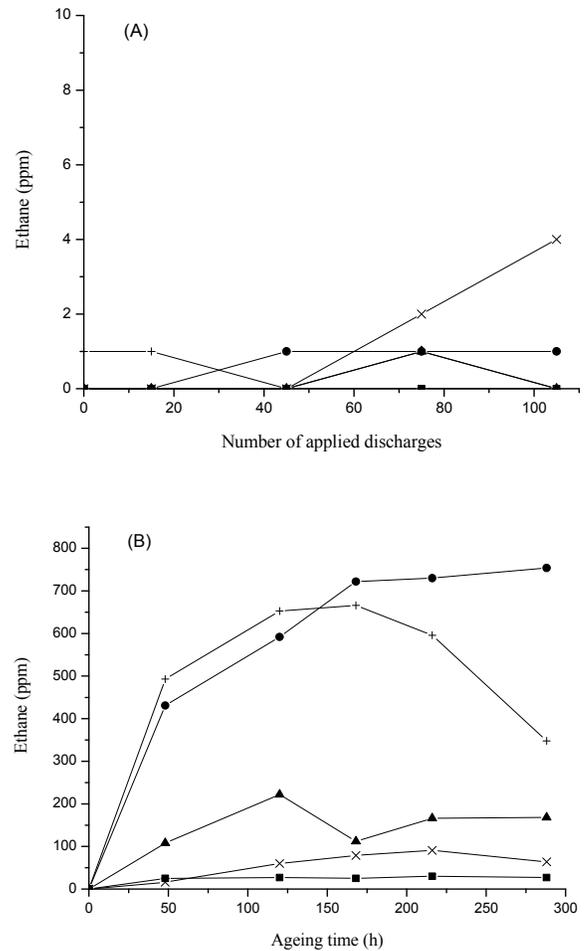


Figure 8. Ethane formation at (A) electric overstress and (B) thermal overstress for: Biovolt A (+), MIO (x), (●) VO-1, (■) VO-2, (▲) VO-3.

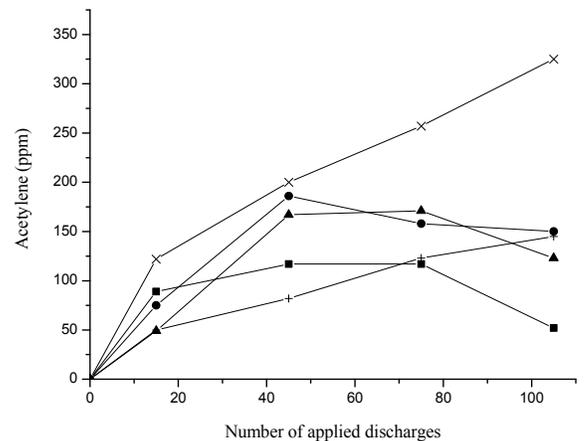


Figure 9. Acetylene formation at (A) electric overstress for: Biovolt A (+), MIO (x), (●) VO-1, (■) VO-2, (▲) VO-3.

arc discharge). For the thermal stress, the diagnosis obtained for the MIO and commercial natural ester-based insulating oil (Biovolt A) was equal and coherent with the type of treatment applied to the oil, while for the other

edible oils it was not possible to define the type by application of the IEC 60599 method.

Table 5. IEC 60599 interpretations for applied overstress to the oils.

Oil type	Electrical overstress*	Thermal overstress**
MIO	Discharge (low energy)	Thermal fault $T < 300^{\circ}\text{C}$
Biovolt A	Partial discharge	Thermal fault $T < 300^{\circ}\text{C}$
VO-1	Partial discharge	Not defined
VO-2	Partial discharge	Not defined
VO-3	Partial discharge	Not defined

* After 105 electrical arc discharge.

** After 288 h thermal aging.

4 CONCLUSION

The tests carried out in this study suggest that the performance of an antioxidant additive depends on the chemical composition of the natural ester oil.

The nature of the natural ester oils tested did not affect the type of dissolved gases formed, but did affect the concentration of each gas and hence the type of defect encountered by applying the IEC 60599 method. Further studies are needed to define criteria for use of this method to diagnose incipient defects in transformers insulated with different natural ester based fluids.

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REFERENCES

- [1] T.V. Oommen, "Vegetable oils for liquid-filled transformers," IEEE Electr. Insul. Mag., Vol. 18, No. 1, pp. 6-11, 2002.
- [2] K. J. Raap, C. P. McShane, J. L. Corkran, G. A. Gauger and J. Luksich, "Aging of paper insulation in natural ester dielectric fluid", IEEE Int'l. Conf. Dielectric Liquids, pp. 173-177, 2002.
- [3] K. J. Raap, C. P. McShane and J. Luksich, "Interaction mechanisms of natural ester dielectric fluid and Kraft paper", IEEE Int'l. Conf. Dielectric Liquids, pp. 393-396, 2005.
- [4] S. Tenbohlen and M. Koch, "Aging performance and moisture solubility of vegetable oils for power transformers," IEEE Trans. Power Del., Vol. 25, No. 2, pp.825-830, 2010.
- [5] M.A.G. Martins, "Vegetable oils, an alternative to mineral oil for power transformers – Experimental study of paper aging in vegetable oil versus mineral oil," IEEE Electr. Insul. Mag., Vol. 26, No. 6, pp. 7-13, 2010.
- [6] IEEE C57.147, "IEEE Guide for Acceptance and Maintenance of Natural Ester Fluids in Transformers", New York, USA, 2008.
- [7] G. Knothe, J. Van Gerpen and J. Krahl (eds.), *The Biodiesel Handbook*, AOCS Press, Champaign, Illinois, USA, pp. 302, 2005.
- [8] H. Zhao, Y. Cao, W. Orndorff, Y. H. Cheng and W. Pan, "Thermal behaviors of soy biodiesel", J. Therm. Anal. Calorim., Vol. 109, No.3, pp. 1145-1150, 2012.
- [9] H. M. Wilhelm, G. B. Stocco and S. G. Batista Jr., "In-service natural ester-based insulating fluids reclaiming: preliminary study", I IEEE Trans. Dielectr. Electr. Insul. Vol. 20, No. 1, pp.128-134, 2013.
- [10] A. K. Domingos, W. D. Vechiatto, E. B. Saad, H. M. Wilhelm and L. P. Ramos, "The Influence of BHA, BHT and TBHQ on the Oxidation Stability of Soybean Oil Ethyl Esters (Biodiesel)", J. Braz. Chem. Soc., Vol. 18, No. 2, pp. 416-423, 2007.

- [11] I. U. Khan, Z. Wang, I. Cotton, S. Northcote, "Dissolved gas analysis of alternative fluids for power transformers," IEEE Electr. Insul. Mag., Vol. 23, No. 5, pp.5-14, 2007.
- [12] N. A. Muhamad, B. T. Phung and T. R. Blackburn, "Dissolved gas analysis for common transformer faults in soy seed-based oil". IET Electric Power Applications, Vol. 5, No. 1, pp. 133-142, 2011.
- [13] M. Duval, "The Duval triangle for load tap changers, non-mineral oils and low temperature faults in transformers", IEEE Electr. Insul. Mag., Vol. 24, No. 6, pp. 22-29, 2008.
- [14] M. Jovalekic, D. Vukovic and S. Tenbohlen, "Dissolved gas analysis of alternative dielectric fluids under thermal and electrical stress," IEEE Int'l. Conf. Dielectr. Liquids (ICDL), pp.1-4, 2011.
- [15] Y. Liu, J. Li and Z. Zhang, "Gases dissolved in natural Ester fluids under thermal faults in transformers", IEEE Int'l. Conf. Dielectric Liquids, pp. 223-226, 2012.
- [16] H. M. Wilhelm, T. Tulio, R. Jasinski and G. Almeida, "Aging markers for in-service natural ester-based insulating fluids," IEEE Trans. Dielectr. Electr. Insul, Vol. 18, No. 3, pp.714-719, 2011.



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