MINERAL OILS AND METHYL ESTERS OF NATURAL OILS IN ELECTRICAL ENGINEERING

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Abstract: This article describes the utilization of natural oils in electrical engineering, allocation by to the types of chemical structures and its variance for the different types of fatty acids. For the selection are described below the most important parameters determining the proper choice for insulating oils with satisfactory environmental requirements and sufficient oxidative stability which is a significant advantage to mineral oils. This work deals with experimental measurements of rheological and dielectric properties in the frequency range 100 Hz - 1 MHz. The conclusion is to evaluate the difference between the experimental samples using their activation energy.

Keywords: Activation energy, conductivity, dielectric constant, loss number, FAME, fatty acids, methyl oleate, methyl stearate, Midel, natural ester, plant oils, rapeseed oil, renewable.

1. INTRODUCTION

1.1. MINERAL AND NON-MINERAL OILS

Worldwide are in distribution systems electrical transformers filled with an insulating liquid. E.g., in 1998 there were used in the U.S. 30 million. This fluid must be electrically insulated well, functioning as a heat transfer medium and to be stable against oxidation for many years. Mineral oils are transformer oil refined from petroleum. Mineral oils are mixtures of various alkanes and as such they are unique from each supplier and may vary by electrical, chemical and physical properties. To determine the tolerance allowed values was created to ASTM, DIN, IEC, etc. so that the oil producers comply with the uniform tolerance parameter oils [1].

Mineral oil is used as a dielectric in transformers but also in cables and capacitors. The advantage of mineral oils in comparison with types of oils is their high resistance to aging. Transformer oil required low viscosity oils. For the correct selection oil must we chosen appropriate profile of the transformer and transformer oil with stable properties and experimentally verified rheological properties which may affect heat transfer, leakage or lack of oil in the transformer. For all types of mineral and non-mineral transformer oils, one needs to know in particular the following parameters: kinematic viscosity, density, flash point, pour point, breakdown voltage, relative permittivity, loss number and oxidative stability. The most important parameters of transformer oils include long-term stability of parameters that affects the reliability of equipment and especially the costs of operating transformers in distribution systems.

At this time, the persistently increasing ecological requirement for the use of natural oils (esters of higher fatty acids). Not all countries have haven't their own mineral oil deposits. These countries include, among else, Brazil, Argentina, Paraguay, India and Pakistan. These countries are engaged in growing crops, which can be used for the production of natural oils. Applicable crops are: canola, sunflower, flax, soybean, olive, poppy and other. Natural oils are natural esters with different fatty acid composition. Fig. 1 shows fatty acids in the most of oils.

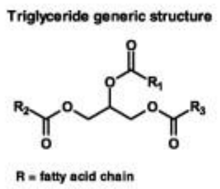
1.2. NATURAL AND SYNTHETIC ESTERS AS A COMPONENT OF OIL

Synthetic esters are usually liquid polyol esters (POES) with the required dielectric properties. Their biodegradability is better than that of mineral oils. The railways and other special applications began since 1984 to use these esters in transformers. The advantage of synthetic esters is their excellent thermal stability and low temperature setting. The seven main types of these esters include: diester, phthalate, trimellitate, pyromellitate, dimer acid ester, polyols, and polyoleates. The fundamental disadvantage of synthetic esters is their high price. A significant factor is the requirement to use alternative and regrown plants in large quantities in farming grown [1].

Natural esters and primarily rapeseed oil were previously considered unsuitable, especially due to low oxidative stability. Regrown and satisfactory materials for the production of natural esters are the seeds of oilseed crops grown commercially in farming. Liquids made from these seeds are composed of triglycerides. Triglyceride is a molecule of glycerol with three molecules bound him to fatty acids. Unsaturated fatty acids in the liquid exhibit lower oxidative stability and lower values of dynamic viscosity [1].

The experiment used a shorter name for methyl esters of acids such for example as lauric acid to methyl ester is methyl laurate used name.

A



	14:0	14:1	16:0	16:1	17:0	17:1	18:0	18:1	18:2	18:3	20:0	20:1
Canola	0.1	0.0	4.1	0.3	0.1	0.0	1.8	60.9	21.0	8.8	0.7	1.0
Corn	0.1	0.0	10.9	0.2	0.1	0.0	2.0	25.4	59.6	1.2	0.4	0.0
Linseed	0.0	0.0	5.5	0.0	0.0	0.0	3.5	19.1	15.3	56.6	0.0	0.0
Olive	0.0	0.0	13.7	1.2	0.0	0.0	2.5	71.1	10.0	0.6	0.9	0.0
Palm	1.0	0.0	44.4	0.2	0.1	0.0	4.1	39.3	10.0	0.4	0.3	0.0
Soybean	0.1	0.0	11.0	0.1	0.0	0.0	4.0	23.4	53.2	7.8	0.3	0.0
Sunflower	0.0	0.0	6.1	0.0	0.0	0.0	3.9	42.6	46.4	1.0	0.0	0.0
High oleic	0.0	0.0	6.4	0.1	0.0	0.0	3.1	82.6	2.3	3.7	0.2	0.4

B

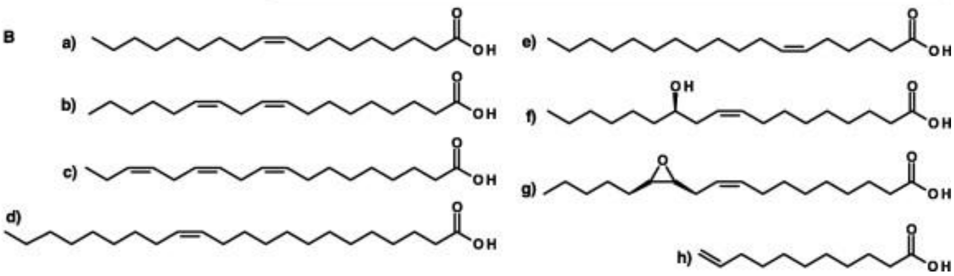


Figure 1: (A) General triglyceride structure and fatty acid percentage composition of common plant oils (x:y stands for chain carbon atoms:number of unsaturations). (B) Fatty acids commonly used in polymer chemistry: (a) oleic acid, (b) linoleic acid, (c) linolenic acid, (d) erucic acid, (e) petroselinic acid, (f) ricinoleic acid, (g) vernolic acid, (h) 10-undecenoic acid. [2]

1.3. RHEOLOGICAL AND DIELECTRICAL PROPERTIES

Important rheological properties use in electrical engineering are viscosity and density, which affect the behavior of liquid in dependence to changes in operating temperature. If these parameters are taken into account, it can lead to poor lubrication of moving parts, loss or leakage liquid from the transformer. Viscosity is a measure of fluidity of liquids can be divided into two types: kinematic and dynamic. Kinematic viscosity is influenced by gravitational force and its conversion to dynamic it is necessary to know the density of the liquid at a given temperature. The density of liquids can be measured in standard laboratory conditions.

For the correct selection of electrical insulating liquids is necessary to know these dielectric properties: dielectric constant and loss number. Another relevant parameter is the influence of temperature on the change of parameters. Oils are tested in laboratory conditions using various accelerated aging tests in order to monitor changes in parameters over time. The changes are mainly influenced by the oxidative stability of oil.

The conductivity of liquid insulators is influenced by concentration of free carriers of electric charge that may be due to ionization of neutral molecules, molecular dissociation own liquid, dissociation of molecules of matter, electron emission from the cathode in strong electric fields and thermal excitation of electrons. Temperature dependence of the mobility of free carriers of electric charge causes a strong dependence of conductivity on the temperature of insulating liquid. Technically pure liquids with conductivity in the order of 10^{-11} to 10^{-12} $S \cdot m^{-1}$ The mobility of free carriers affects the viscosity, which is a rheological parameter. The relationship between conductivity and dynamic viscosity can be described Walden's law [3].

2. EXPERIMENTAL PART

2.1. RHEOLOGICAL PROPERTIES

For find the densities the density of different types depending on the temperature of oil were the following oils: synthetic ester (Midel 7131 - natural and synthetic esters and transformer oils), natural (rapeseed oil), methyl ester rapeseed oil (FAME) and one mineral Renolin Eltec T. The waveform in Fig. 2 is showing the density in dependence on temperature in the inverse temperature interval from 250 to 370 K. The lowest values were found in mineral oils and methyl ester rapeseed oil.

The principle of density measurements using principle Archimedes' law takes into account the gravity and buoyancy force acting on the plunger (calibrated glass weights) with a defined volume (V_{pl}). For calculate the density is necessary to know the weight of the plunger calibrated (calibrated glass weight) weighed in air (m_A) and immersed in liquid (m_L). The density of the liquid can be calculated according to equation:

$$\rho = \frac{m_A - m_L}{V_{pl}} \quad (1)$$

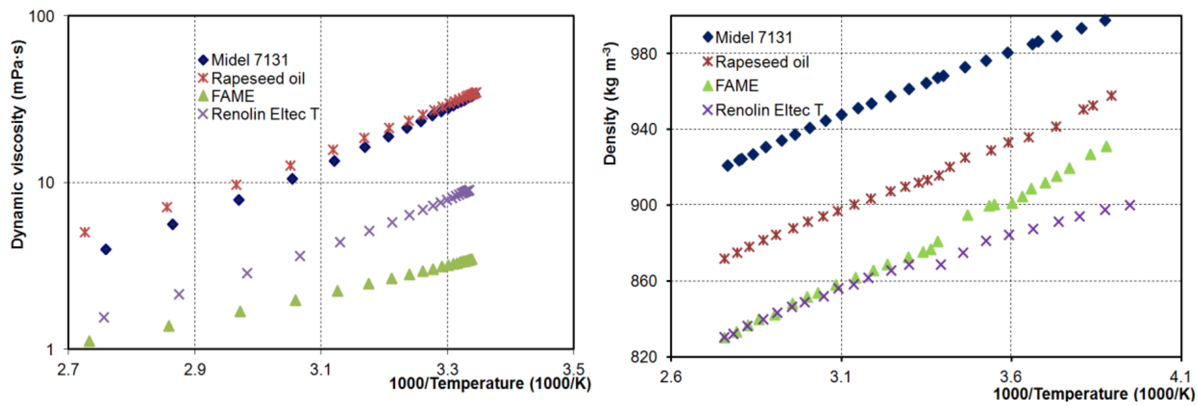


Figure 2: Plot of density and dynamic viscosity *vs.* reciprocal temperature for different oils

2.2. DIELECTRICAL PROPERTIES

The temperature dependence of relative permittivity showed the following changes of values in the temperature interval 283 – 363 K for samples: methyl laureate (Fig.3) from 3.0 to 2.4, methyl oleate from 3.1 to 2.5. In an analogous manner, permittivity of methyl stearate slowly decreased in the temperature interval 323 – 363 K from 2.7 to 2.4.

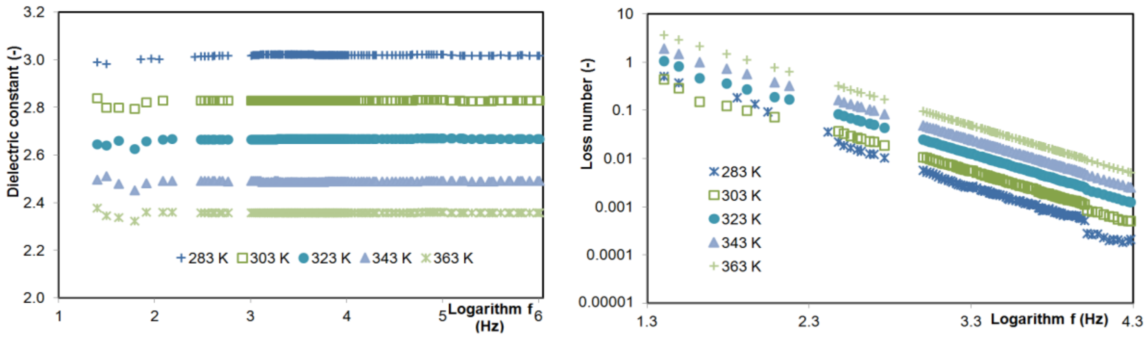


Figure 3: Frequency dependence of dielectric constant and loss number (methyl laureate)

2.3. CONDUCTIVITY AND ACTIVATION ENERGY

The external electric field in insulating liquids may cause the ions, but the state can also occur when the ion captures the molecule, forming a single unit. Effect of temperature can cause separation of ions from the molecule to overcome some potential barriers to energy E_A, called the activation energy. For calculate the activation energy can be used temperature dependence of ionic conductivity according to the equation:

$$\sigma = \sigma_0 e^{-\frac{E_A}{kT}} . \qquad (2)$$

To Fig. 4 can see rapeseed oil. The highest conductivity is of 15 $nS \cdot m^{-1}$ at frequency 1 MHz is shown in rapeseed oil. Conductivity values of the other samples are given for frequency of 10 kHz. The second highest conductance 4 $nS \cdot m^{-1}$ had FAME. Methyl esters had the lowest conductivity of these values: methyl laurate 0.087 $nS \cdot m^{-1}$ and methyl oleate 0.097 $nS \cdot m^{-1}$ For methyl conductivity values were at frequencies above 30 kHz useless because the values are close to the threshold of resolution LCR meter Agilent 4284 instrument, that were loss factor lower than 0.00001 (-).

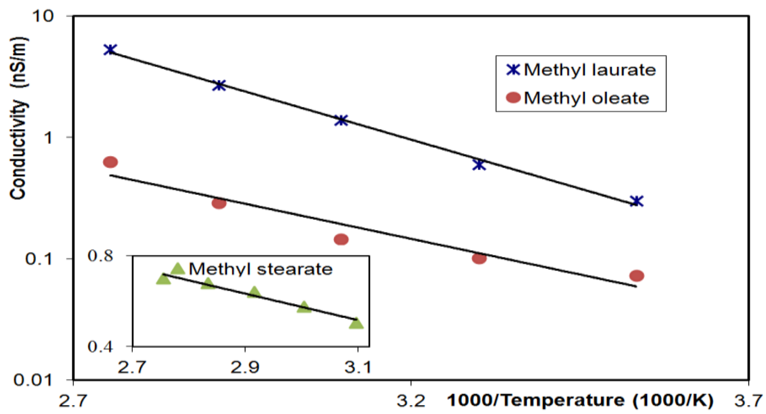


Figure 4: Conductivity of methyl esters vs. inverse temperature

In Table 1 is see the comparison of the activation energy E_A calculated for different types of oils: synthetic MIDEL 7131, rapeseed oil, rapeseed oil methyl ester (FAME - methyl esters of unsaturated fatty acids of vegetable origin) and mineral oil RENOLIN Eltec T. The highest value of activation energy of 30.3 $MJ \cdot kmol^{-1}$ was calculated for oil MIDEL 7131 and the lowest 14.8 $MJ \cdot kmol^{-1}$ for FAME. In the second column are calculated to compare the activation energy of methyl esters of three acids found in rapeseed and other oils. The rapeseed oil with methyl oleate occurs in approximately 60% of the composition and its activation energy was determined 22.8 $MJ \cdot kmol^{-1}$. Rapeseed oil had the activation energy of 26.3 $MJ \cdot kmol^{-1}$. The difference is due to other fatty acids contained in oil. Representation of the ratio of fatty acids in natural oils differ in genetic intervention in the growing of plants (canola, soybean, peanut, sunflower, elaeis oleifera, etc.), both the composition of the soil in which plants were grown. The proportion and type of fatty acids influences the solidification temperature, which is not common in natural oils significantly below 0 °C as in mineral and synthetic oils.

The activation energy E_A of different types of oils		**The activation energy E_A of fatty acids**	
Midel 7131 (*synthetic oil*)	30.3 $MJ\cdot kmol^{-1}$	Methyl laurate	30.2 $MJ\cdot kmol^{-1}$
Rapeseed oil (*natural oil*)	26.3 $MJ\cdot kmol^{-1}$	Methyl oleate	22.8 $MJ\cdot kmol^{-1}$
Fame	14.8 $MJ\cdot kmol^{-1}$	Methyl stearate	8.7 $MJ\cdot kmol^{-1}$
Renolin Eltec T (*mineral oil*)	24.1 $MJ\cdot kmol^{-1}$		

Table 1: Size of the activation energy for different oils and three compounds of natural esters

3. CONCLUSION

Properties of natural oils can vary depending on the gene structure of the given tribe (rape, sunflower, soybean, corn), but also on the place of growth in the same regions on the grounds that is conducted sowing field on one every four years of higher returns. Mineral oils (Midel 7131, Renolin Eltec T, Trafo N, etc.) from the same raw material may have different composition parameters from different manufacturers. Experimental measurement of rheological (viscosity, density) and dielectric properties (dielectric constant and loss number) of various types of oils showed differences between species, as known fact that mineral oils are less dense. The activation energy has been calculated for different types of oils. The activation energies were also calculated for the three methyl esters of fatty acids found in natural oils (Fig. 1). The highest activation energy E_A 30.3 $MJ\cdot kmol^{-1}$ was calculated for synthetic oil Midel 7131 and 30.3 $MJ\cdot kmol^{-1}$ methyl laurate. The lowest activation energy was methyl ester: methyl oleate and 8.7 $MJ\cdot kmol^{-1}$.

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