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Different Ways to Improve Natural Ester Oils

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Abstract

The issue of natural esters as a substitution for mineral oils is more complicated than it seems. The first impulse for this substitution rose up as a demand for environment-friendly transformer oil. The case of fault of the transformer with mineral oil represents severe damage to the surrounding area. This would be minimized with the usage of biodegradable natural ester oil.

The category of natural esters offers a wide range of possibilities. These oils have an advantage of local manufacturing by the available local oil plant. In our area it is sunflower and rapeseed oil. Research presented in this article covers various areas concerning the development process of new biodegradable liquid usable in distribution transformers. This includes the process of choosing the base oil, testing of operation conditions of its properties, finding ways to improve imperfect properties through additives like antioxidants and possible benefits of the addition of nanoparticles. Various problems in this area were tackled and detailed results (mostly of electrical but also chemical parameters) are presented with basis on the chemical composition of tested materials.

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Keywords: natural ester; insulation oil; fatty acids; oxidation; antioxidants; nanoparticles

1. Introduction

Historical development of transformer fluids began at the end of the nineteenth century. This development was tied with the power rise of the transformers that needed some insulation that could serve also as a heat dissipation medium. Thus arose the insulation oil on a petroleum base that eventually evolved into mineral oil that we know today. Typical

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representatives are Shell Diala S3 and Nynas Nytro Taurus. Their datasheet values compared to the representative of natural ester oil FR3 are presented in Table 1. [1]

Table 1. Datasheet values of insulating oils.

	Shell Diala	Nynas Nytro Taurus	Cargill FR3 [2]
Fire point [°C]	138	152	350
Pour point [°C]	-60	-48	-18
Viscosity at 40, -30 °C [cSt]	8; 720	10; 1000	35; -
Breakdown voltage [kV/2.5mm]	>70	>70	73
Dissipation factor tan δ	0.001	0.080	0.02

These oils even though have perfect dielectric and other parameters are insufficient when it comes to environmental protection like biodegradability for example. The contamination in the case of an accident is very extensive and means to eliminate this accident very costly. This became a huge factor and therefore the search for alternative transformer fluid began. Some progress was made in the area of synthetic esters but even they are not fully biodegradable and thus still provide a threat to the environment.

The attention turned its way towards natural esters in the last decade of the 20th century [3,4]. These vegetable oils are available in plenty of variety across the world. That provides an economic benefit as the source plant is not located at once place as it is with source material for mineral oil. But this variety is also the source of weakness – the properties of natural esters are dependent on the content of fatty acids and they vary between the types of plant crops. [5] This means that more research is needed for the improvement of their parameters. Several ways are possible, one would be focused on the composition of natural ester, other would be the addition of some sort of additives like antioxidants or nanoparticles.

2. Chemical Composition of Natural Esters

Natural esters are composed of a glycerol backbone bonded with three fatty acid groups. This structure is illustrated in Fig.1. These fatty acids determine the properties of the oil. There are three types of fatty acids – saturated, mono unsaturated and poly unsaturated. The biggest difference is in the content of C=C double bonds. [6]

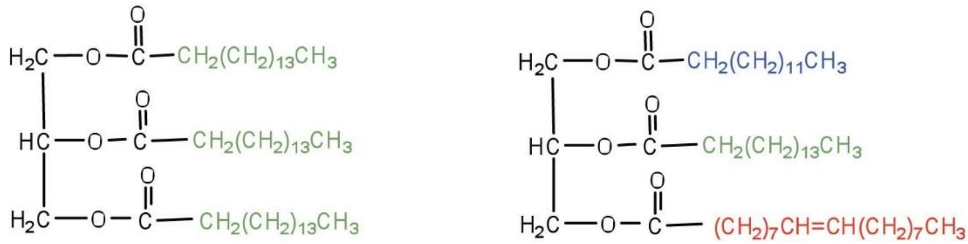

Fig. 1. Structures of natural esters

The composition of fatty acids gives us the idea about the overall physical properties of the oil, namely state, viscosity and oxidation stability. We can see some common vegetable oils and their fatty acid content in Table 2. Bigger the content of unsaturated fatty acids (right part of the Table 2) is in oil, more liquid the oil would be (and contrary bigger content of saturated more solid it would be). This is linked with oxidation stability – saturated acids make oil more oxidation stable and in that regard, the unsaturated make it more unstable. [6]

Table 2. Fatty acid composition (%) of vegetable oils

Oil fatty acid	Saturated fatty acid		Mono-unsaturated	Poly-unsaturated	
	Palmitic acid C16:0	Stearic C18:0	Oleic C18:1	Linoleic C18:2	Linolenic C18:3
Palm oil	45	4	40	10	-
Olive oil	11	3	71	10	1
Rapeseed oil	4	2	62	22	10
Sunflower oil	7	5	19	68	1

3. Oxidation and Effect of Antioxidants

Oxidation is a process between molecules of unsaturated fatty acids and oxygen. The weak spot is the C=C double bond in unsaturated fatty acids (that is why their high content means poor oxidation stability). During the oxidation process the highly reactive free radicals are created and released into the oil in which they further react. The oxidation is a slow process but can be accelerated by the presence of metal oil particles, heat, and light. Oxidation can be slowed down with the addition of antioxidants. These additives react with free radicals and other oxidative products and make them unable to further react thus reducing the oxidation speed.

The example below gives insight into how different antioxidants affect rapeseed oil. This was shown on a test of oxidation stability (TOS) by IEC 61125. That includes thermal ageing of samples at 150 °C for 164 hours and measurement of dissipation factor (see Fig. 2) that serves as an indicator of the desired effect. Sample No.1 is clear rapeseed oil, other samples represent different antioxidants at 1 wt%.

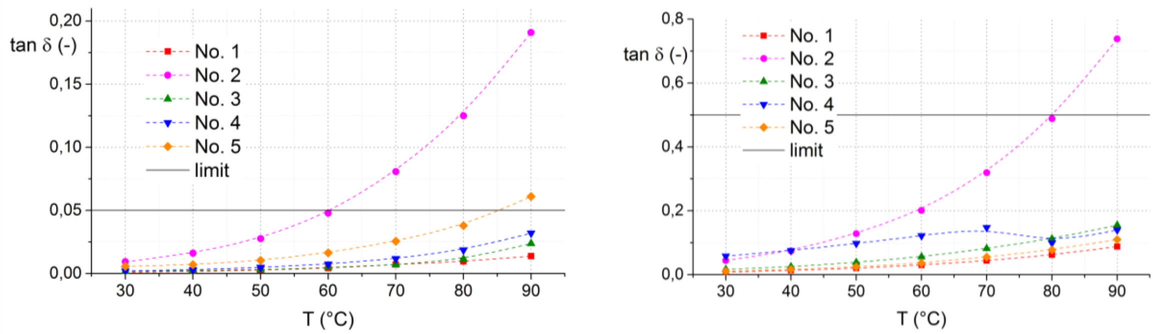

Fig. 2 Temperature dependencies of dissipation factor before (a) and after (b) test of oxidation stability

The evaluation of tan δ at 90 °C was made by comparison of values before and after TOS (see Tab. 3) via the oxidation speed coefficient. Lower the coefficient value is than for No.1 the better effect the antioxidant have. In this example we can clearly see the problem with natural esters – lack of proper limit values as the effective antioxidant (sample No. 5) exceeds the limit value after its addition.

Table 3. Results of the test of oxidation stability

Sample No.	1	2	3	4	5
tan δ before TOS	0.0138	0.1910	0.0238	0.0032	0.0610
tan δ after TOS	0.0881	0.7380	0.1550	0.1400	0.1100
Oxidation speed Coefficient	6.38	3.86	6.51	4.37	1.80

4. The Effect of Nanoparticles in Natural Ester Oil

The current trend of using nanoparticles to improve the dielectric properties of transformer oil started around 2006. In this context, nanoparticles represent metal particles (mostly metal oxides like TiO_2, Al_2O_3, ZnO, SiO_2 …) the size of 1-100 nm. Nanoparticles can vary in size, conductivity (conductive, semi- or non-conductive) and also in their concentration in oil. Their positive effect on dielectric performance (enhancement of breakdown voltage, resistivity, and dissipation factor) was proved by several authors [7,8,9]. What is yet unknown is long term behaviour in a transformer in contact with paper insulation. Another factor to consider is the agglomeration and sedimentation of nanoparticles dispersed in oil. Only the complex study of these phenomena can guarantee the long term usability of such a transformer fluid.

The examples of the influence of MgO nanoparticles in natural ester oil (in this case rapeseed oil as in the previous example) are illustrated below. Fig.3 (a) illustrates the effect of different concentration on dissipation factor. Sample N0 is clear rapeseed oil in both cases. Other samples represent different concentrations of MgO – N1 is 1 g/l, N2 is 1.5 g/l and N3 is 2 g/l. We can clearly state that the addition of MgO nanoparticles had a beneficial effect on the dissipation factor. Lower concentrations (1 and 1.5 g/l) lowered the tan δ value significantly. On the other hand higher concentration does not prove beneficial.

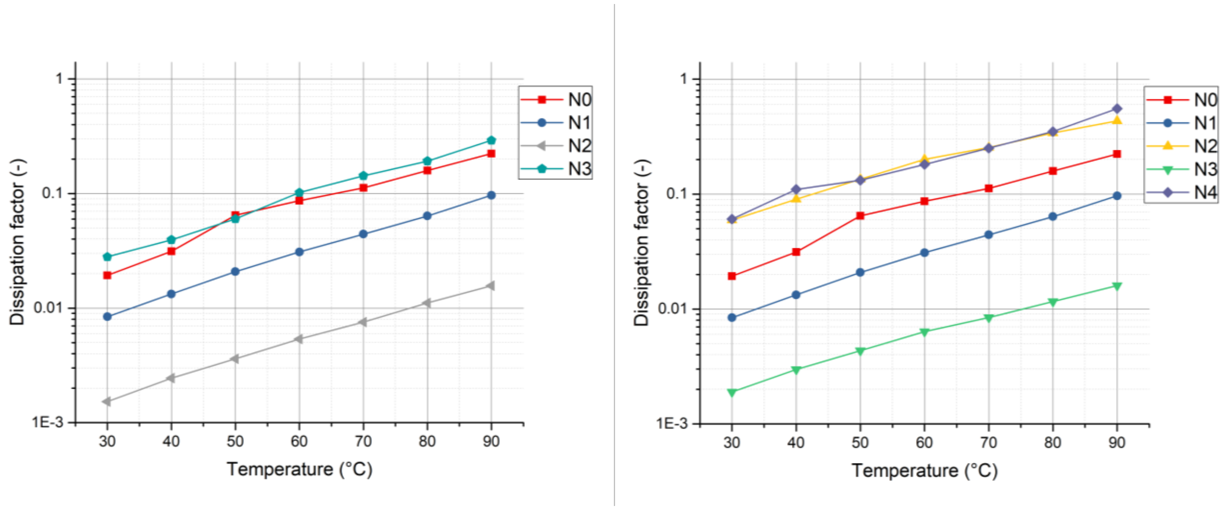

Fig. 3 Temperature dependencies of the dissipation factor of different concentrations of MgO (a) and a different surfactant of MgO (b)

The other case in Fig. 3 (b) shows the effect of different surfactant used on MgO nanoparticles. Again sample marked N0 is clear rapeseed oil. Samples N1-N3 represent the same concentration of nanoparticles (1 g/l) with 0.25 wt% of three kinds of surfactant. Sample N4 represents MgO nanoparticles without any surfactant applied. Right away the beneficial effect of surfactant is visible as samples N1 and N3 lowered the tan δ significantly. This might be due to better dispersion of nanoparticles in oil as there are fewer agglomerates. This is supported by N4 that shows the rise of dissipation factor compared to sample N0.

Conclusion

This paper presented an introduction to natural esters, their chemical composition, usage and possible means of improvement. The effect of antioxidants as a way of improvement of natural esters was shown along with some problems that were outlined. The other possible way to improve the dielectric properties of vegetable oils is the usage of nanoparticles. This brings great possible improvement (as presented in this paper) but also several problems with long term usage that were not discussed in this paper as is the effect of surfactant on agglomeration.

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