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The Influence of Antioxidants on the Resistance of Rapeseed Oil of High-Voltage Electrical Equipment to Oxidation

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Abstract—This paper analyzes the influence of various types of antioxidants on the resistance of rapeseed oil to oxidation at high temperatures. The experimental data have been compared with the specifications of MIDEL eN 1204 transformer fluid. Processes stipulating oil aging are described.

Keywords: high-voltage equipment, rapeseed oil, resistance to oxidation, antioxidants

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The use of mineral transformer oil is dangerous for ambient environment due to their resistance to decomposition by microorganisms. In addition, mineral oils are characterized by moderate flash and combustion points and, hence, high explosion and fire hazard.

This stipulates the relevance of development of alternative dielectric fluids characterized by higher flash and combustion points, as well as rapid decomposition in the presence of microorganisms.

Some vegetable oils comply with most requirements for transformer fluids. Herewith, the main issue is their low resistance to oxidation; as a consequence, such oils rapidly lose their properties, requiring additional measures for replacement and periodic monitoring of oil quality.

Vegetable oils are 94–96% comprised of mixtures of triglycerides of higher fatty acids [1]. Their properties vary only as concerns their fatty acids, which differ in the following parameters:

— chain length (number of carbon atoms);

— number and position of double bonds; and

— position in triglyceride molecule.

Variation of these properties stipulate chemical and physical differences of oils.

Vegetable oils in comparison with mineral fluids are exposed to more intensive oxidation under the impact of air oxygen. Rancidification of vegetable oils is caused by their oxidation and characterized by occurrence of an unpleasant taste and a specific odor. The resistance of oil to oxidation depends on the number of double bonds in fatty acids. At the first stage of oxidation, upon interaction of molecular oxygen with carbon residues of both saturated and nonsaturated fatty acids, peroxide radicals are formed. The oxidation is catalyzed by compositions that are capable of forming free radicals (peroxides, transition metals), as well as by physical impacts in the form of heat and light. Peroxide radicals initiate nonbranching and branching chain reactions, as well as being decomposed with the formation of a series of secondary derivatives: hydroxy acids, epoxides, ketones, and aldehydes [2]. Aldehydes and ketones cause changes in oil taste and odor. Oils with predominant fatty acids are characterized by the formation of ketones (ketone rancidification), oils with a high content of nonsaturated acids are characterized by aldehyde rancidification. To inhibit and prevent chemical rancidification, the inhibitors of radical reactions are used, as well as compounds forming complexes with heavy metals [2].

Differential scanning calorimetry (DSC) was applied as a method of thermal analysis of resistance of vegetable oils. This method was used for analysis of concentration of various natural antioxidants on thermal stability of nonsaturated edible oils [3].

This article is devoted to studying the influence of various antioxidants/mixtures of antioxidants on the resistance to oxidation of rapeseed oil. The following compounds were used as inhibitors of oil oxidation:

— Mannich base (Agidol-3) (TU Specifications 38.103368-94 with modifications) 1-5, 2,6-di-tert-butyl-4-[(dimethylamino-)methyl] phenol (hereinafter, OM), which can be applied as an inhibitor of polymerization [4], well soluble in fats;

— Agidol-2 antioxidant (*GOST* (State Standard) R 55065-2012) 6,6'-methylene-bis (2-(tert-butyl)-4-methyl-phenol) (hereinafter, AG-2), which, in addition to antioxidizing properties, can accept metals of

Table 1. Results of testing rapeseed oil for resistance to oxidation

Oil type	AO content, %	Content of volatile low molecular acids, mg KOH/1 g oil	Acid number, mg KOH/1 g oil	Sediment content, %
Refined rapeseed oil w/o antioxidants	–	5.99	5.105	0.277
MIDEL eN 1204 transformer fluid, CAS 68956-68-3	*	3.63	3.84	0.0054
Rapeseed oil with AO: OM AG-2 BF-5	 0.083 0.083 0.083	4.635	4.2	0.0306
Rapeseed oil with AO: OM AG-2 BF-5	 0.167 0.167 0.167	2.87	3.665	0.0008
Rapeseed oil with AO: OM AG-2 BF-5	 0.333 0.333 0.333	3.15	3.75	0
Rapeseed with AG-2	0.5	3.79	4.19	0
Rapeseed with OM	0.5	2.74	3.66	0.0072
Rapeseed with BF-5	0.5	2.22	3.29	0.0009
Rapeseed with TTBFF	0.5	3.06	3.57	0.0424

* Content and type of the used antioxidant are unavailable.

various valence [5]; this property of AG-2 is important, since copper wire is used in transformer coils;

— bis-phenol-5(4,4'-bis(2,6-di-tert-butyl-phenol)) [6] (TU Specifications 205956-005-44178696-2022) with 99.9 wt % purity (hereinafter, BF-5); and

— tris(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propyl)phosphite (hereinafter, TTBFF), which is characterized by high antioxidant activity under the conditions of accelerated thermal oxidation of paraffinic and mineral oils; the antioxidant is synthesized according to the method in [7].

The antioxidants were added to samples by dissolution of predetermined amount during heating to 75°C.

The catalytic oxidation of rapeseed oil, content of volatile low-molecular acids, acid number, and residue were determined in accordance with *GOST* (State Standard) 981-75 at 130°C for 4 h. Copper and iron were used as catalysts.

In the case of polyolefins, tests for determination of the induction time of oxidation (ITO) were standardized both in terms of the recommended flow rate of oxidizing gas (oxygen) and in terms of the temperature of isothermal segment [8, 9]. Such standards are unavailable for vegetable oils. The procedure of ITO determination was developed on the basis of published data available for the closest molecular analogs [10]. The induction period of non-catalytic oxidation of antioxidants in rapeseed oil was determined by differential scanning calorimetry using a DSC 214 Polyma (NETZSCH) instrument. Heating to the test temperature was carried out at a rate of 10 K/min under continuous purging by inert gas (argon). DSC thermograms were recorded in oxygen environment at 150°C and an oxygen flow rate of 60 mL/min. The thermal analysis was performed in aluminum crucibles with the capacity of 25 μL, and the sample weight was 1.5–2.5 mg. The experimental results obtained in the form of graphical and table data were processed using the Proteus 7.0 software.

The results of catalytic oxidation of oils are summarized in Table 1.

It follows from Table 1 that the oil with addition of three types of antioxidants with total content of 0.5 wt % and the Mannich base individually with the content of 0.5 wt % was characterized by comparable performances with regard to reference specimens. Upon catalytic oxidation the highest antioxidizing activity is demonstrated by BF-5 with the purity of 99.9%. When analyzing stabilization of polypropylene and SKI-3

Table 2. Results of testing rapeseed oil with various content of DFKh in BF-5 for resistance to oxidation

Oil type	AO content, wt %	Content of DFKh, wt % of AO	Content of volatile low molecular acids, mg KOH/1 g oil	Acid number, mg KOH/1 g oil	Sediment content, %
Oil with BF-5	0.5	0	2.22	3.29	0.0009
		1	2.06	3.14	0
		5	3.4	4.38	0.0308
		25	3.735	4.76	0.0436
Oil with DFKh	0.5	100	5.66	5.38	0.048

rubber [6], the increase in antioxidizing activity was observed upon addition to BF-5 of the product of its oxidation: 3,3',5,5'-tetra-tret-butyl-4,4'-diphenoquinone (hereinafter, DFKh). In this regard, the influence of DFKh in BF-5 and without it on the oil resistance to oxidation was studied.

The results (Table 2) evidence that, with an increase in the DFKh content, the antioxidant activity of BF-5 decreases.

Therefore, the highest decrease in the catalytic oxidation of rapeseed oil is achieved by adding 0.5 wt % BF-5 antioxidant with a DFKh content of no higher than 1 wt %.

The induction period of noncatalytic oxidation of rapeseed oil was determined by differential scanning calorimetry. The obtained results are illustrated in Figs. 1–3.

It can be seen in Fig. 1 that an increase in the content of antioxidant mixture higher than 0.5% does not result to further significant growth of the resistance of rapeseed oil. However, the resistance of the oil with 1 wt % AO is higher in comparison with that of the oil with 0.5 wt % AO.

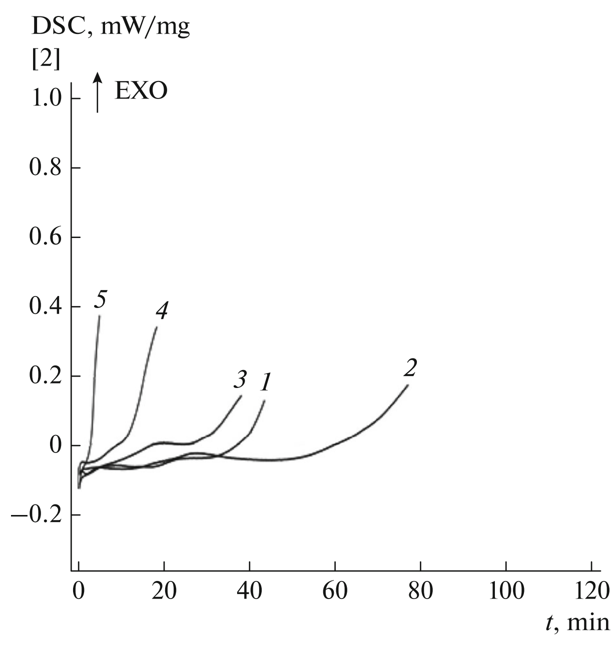

Fig. 1. Induction period of the noncatalytic oxidation of rapeseed oil in the presence of antioxidant mixtures: (*1*) oil in combination with 0.5 wt % AO (OM, 0.167 wt %; AG-2, 0.167 wt %; BF-5, 0.167 wt %), (*2*) oil in combination with 1 wt % AO (OM, 0.333 wt %; AG-2, 0.333 wt %; BF-5, 0.333 wt %), (*3*) oil in combination with 0.25 wt % AO (OM, 0.083 wt %; AG-2, 0.083 wt %; BF-5, 0.083 wt %), (*4*) MIDEL eN 1204 transformer fluid, and (*5*) nonstabilized rapeseed oil. Induction period of oxidation, min: (*1*) 39.9, (*2*) 69.0, (*3*) 30.8, (*4*) 4.6, and (*5*) 2.9.

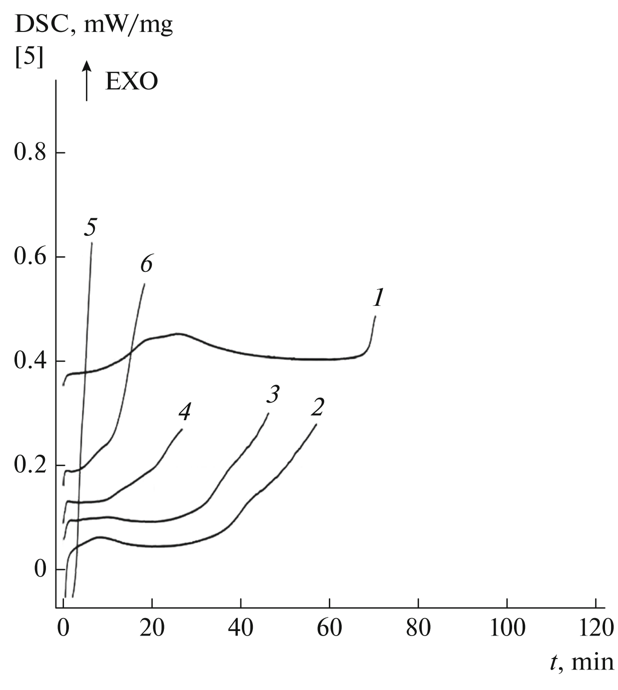

Fig. 2. Comparison of the induction period of noncatalytic oxidation of rapeseed oil in the presence of individual antioxidants: (*1*) oil with 0.5 wt % BF-5(p), (*2*) oil with 0.5 wt % OM, (*3*) oil with 0.5 wt % TTBFF, (*4*) oil with 0.5 wt % AG-2, (*5*) nonstabilized rapeseed oil, and (*6*) MIDEL eN 1204 transformer fluid. Induction period of oxidation, min: (*1*) 68.3, (*2*) 11.5, (*3*) 11.2, (*4*) 6.3, (*5*) 2.9, and (*6*) 4.6.

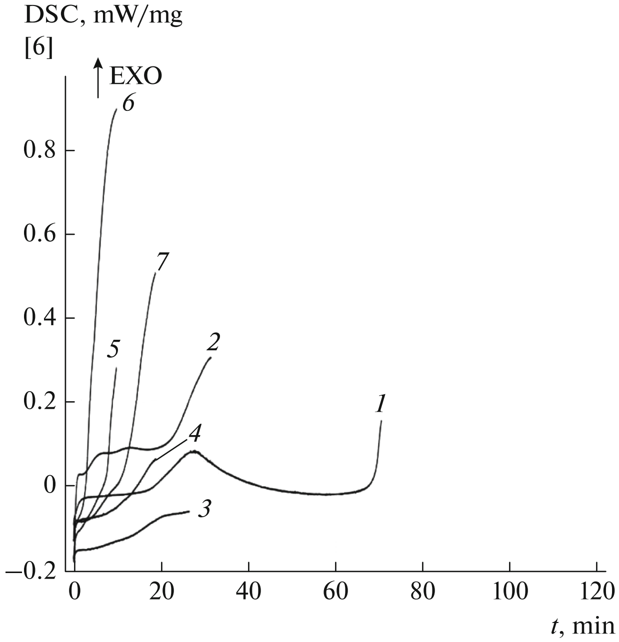

Fig. 3. Comparison of the induction period of noncatalytic oxidation of rapeseed oil with various content of DFKh in BF-5: (*1*) oil with 0.5 wt % BF-5(p), (*2*) oil with 0.5 wt % BF-5 (1% DFKh of AO weight), (*3*) oil with 0.5 wt % BF-5 (5% DFKh of AO weight), (*4*) oil with 0.5 wt % BF-5 (25% DFKh of AO weight), (*5*) oil with 0.5 wt % DFKh, (*6*) nonstabilized rapeseed oil, and (*7*) MIDEL eN 1204 transformer fluid. Induction period of oxidation, 150°C, min: (*1*) 68.3, (*2*) 23.4, (*3*) 11.6, (*4*) 16.4, (*5*) 7.4, (*6*) 2.9, and (*7*) 4.6

As can be seen in Fig. 2, the highest resistance is demonstrated by rapeseed oil with 0.5 wt % of BF-5.

It can be seen in Fig. 3 that the resistance of rapeseed oil decreases with increase in the weight content of DFKh in BF-5. Presumably, DFKh enters into an oxidation reaction of residue of unsaturated acid in the oil, thus accelerating oxidation. Correspondingly, when using BF-5 as an antioxidant additive to transformer fluid, the use of BF-5 with the minimum added content of DFKh is the most reasonable.

The experimental results of dielectric properties of transformer fluids on the basis of rapeseed oil are summarized in Table 3. It can be seen that the specimen 1 stabilized by an antioxidant mixture is comparable with the MIDEL eN 1204 transformer fluid.

A high tangent of a dielectric loss angle can be attributed to a rather high viscosity and higher setting point, the existence of high molecular triglycerides, and a high amount of polar products, as well as moisture.

Therefore, the following antioxidants are efficient for stabilization of rapeseed oil:

— 0.5 wt % BF-5; and

— 0.5 wt % AO mixture (OM, 0.167 wt %; AG-2, 0.167 wt %; BF-5, 0.167 wt %).

Table 3. Results of testing transformer fluids on the basis of rapeseed oil with 0.25 wt % AO mixture (OM, 0.083 wt %; AG-2, 0.083 wt %; BF-5, 0.083 wt %)—specimen 1 and MIDEL eN 1204 transformer fluid

Indicator, units of measurement	ND	Norm (prepared for filling in accordance with Regulations RD 34.45-51.300-97)	MIDEL eN 1204 transformer fluid	Specimen 1
Color, units	Visual control	1.5	1.5	1.5
Transparency	Visual control	Transparent		
Content of mechanical impurities (class of commercial purity)	*GOST* (State Standard) 17216-2001	12	12	12
Fire point in closed crucible, not lower than, °C	*GOST* (State Standard) 6356-75	135	Higher than 258.00	245
Acid number, mg KOH/g	*GOST* (State Standard) 5985-79	0.02	0.02	0.09
Content of water-soluble acids and alkalis, pH of water extract, not lower than	*GOST* (State Standard) 6307-75	No	No	6.6
Moisture content, g/t, not higher than	*GOST* (State Standard) R IEC 60814-2013	25.0	50.0	26.4
Breakdown voltage, kV, not lower than	*GOST* (State Standard) 6581-75	55.0	81.1	81.3
Tangent of dielectric loss angle at 90°C, %, not more than	*GOST* (State Standard) 6581-75	2.0	7.50	9.00

CONCLUSIONS

(1) It has been revealed that the resistance of rapeseed oil to oxidation decreases with an increase in the DFKh content in BF-5. Due to a rather high viscosity and high setting point and the existence of polar products, including water, the standard rapeseed oil does not comply with the norms of a product prepared for filling into equipment and, partially (in terms of tan δ), of the operational transformer fluid.

(2) The results obtained during analyzing oxidation of rapeseed oil can be used for development of preparation of transformer fluids based on vegetable raw material. Therefore, it becomes possible to substitute MIDEL eN 1204 transformer fluid for a domestic transformer fluid addition of BF-5 antioxidant.

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