



STUDY OF THE PRESENCE OF PRO-OXIDATIVE PROPERTIES IN PHENOLIC OXIDATION INHIBITORS IN RELATION TO MODERN TRANSFORMER OILS

Garifullin M.Sh.¹, Slobodina Y.N.¹, Bikzinurov A.R.¹, Giniatullin R.A.², Chernyshov V.A.³

¹Kazan State Power Engineering University, Kazan, Russia

²Kazan National Research Technological University, Kazan, Russia

³Oryol State University named after I.S. Turgenev, Oryol, Russia

ORCID: <http://orcid.org/0000-0001-6026-9923>, g_marsels@mail.ru

yulya_slobodina@mail.ru

mr.azat780@mail.ru

g_ruslan7@mail.ru

ORCID: <http://orcid.org/0000-0002-5955-5540>, blackseam78@mail.ru

Abstract: ACTUALITY. In the community of Russian specialists servicing oil-filled transformers, there is an established opinion that when the concentration of the phenolic oxidation inhibitor Ionol (DBPC) in the oil drops below 0.1% (wt.), the transformer oil begins to oxidize faster than in the absence of Ionol. This is the so-called "pro-oxidizing effect" described in 1968. Modern hydrocracking transformer oils differ significantly from the former oils in terms of hydrocarbon composition, but the opinion about the pro-oxidizing properties of Ionol remains, despite the lack of such information in foreign studies. OBJECTIVE. To reveal the presence or absence of pro-oxidative action of phenolic antioxidants, Ionol and 2,6-DTBP, when their concentration in transformer oil is reduced. METHODS. Two series of oil samples were prepared for the study: with Ionol and 2,6-DTBP additive. The concentration of additives: 0; 0.05; 0.1 and 0.2 % (wt.). VG grade oil produced by hydrocracking technology was used as a base mineral oil. All oils were subjected to accelerated thermal degradation at elevated temperature. Destructive changes in the hydrocarbon base of oils were analyzed by IR absorption spectra. Changes in the relative content of degradation products dissolved in the oil were analyzed using UV-visible absorption spectra. RESULTS. On the basis of the analysis of optical spectra of both series of oils, it was obtained that as the initial concentration of any of the phenolic oxidation inhibitors in the oil decreases, the intensity of thermodestructive changes in the hydrocarbon composition of the oils consistently increases. It is shown that in transformer oils produced by hydrocracking technology both additives in the concentration range of 0.05÷0.1 % do not show pro-oxidizing properties. It is concluded that the widespread idea about pro-oxidizing effect of Ionol at its concentration in transformer oil less than 0.1 % should be considered as not corresponding to reality.

Keywords: mineral transformer oil; oxidation inhibitor; butylated hydroxytoluene (BHT); Ionol; pro-oxidation properties; IR spectroscopy; UV-VIS spectroscopy.

For citation: Garifullin M.Sh., Slobodina Y.N., Bikzinurov A.R., Giniatullin R.A., Chernyshov V.A. Study of the presence of pro-oxidative properties in phenolic oxidation inhibitors in relation to modern transformer oils. *Power engineering: research, equipment, technology*. 2024; 26 (6): 30-41. doi:10.30724/1998-9903-2024-26-6-30-41.

ИССЛЕДОВАНИЕ НАЛИЧИЯ ПРООКИСЛИТЕЛЬНЫХ СВОЙСТВ У ФЕНОЛЬНЫХ ИНГИБИТОРОВ ОКИСЛЕНИЯ В ОТНОШЕНИИ СОВРЕМЕННЫХ ТРАНСФОРМАТОРНЫХ МАСЕЛ

Гарифуллин М.Ш.¹, Слободина Ю.Н.¹, Бикзинуров А.Р.¹, Гиниатуллин Р.А.², Чернышов В.А.³

¹Казанский государственный энергетический университет, г. Казань, Россия

²Казанский национальный исследовательский технологический университет, г. Казань, Россия

³Орловский государственный университет имени И.С. Тургенева, г. Орел, Россия

ORCID: <http://orcid.org/0000-0001-6026-9923>, g_marsels@mail.ru

yulya_slobodina@mail.ru

mr.azat780@mail.ru

g_ruslan7@mail.ru

ORCID: <http://orcid.org/0000-0002-5955-5540>, blackseam78@mail.ru

Резюме: АКТУАЛЬНОСТЬ исследования заключается в получении достоверных сведений об изменении эффективности фенольных ингибиторов окисления применительно к современным минеральным трансформаторным маслам, производимым по технологии гидрокрекинга, при снижении концентрации их в масле от 0.2 % до нуля. ЦЕЛЬ. Исследовать с помощью оптической спектроскопии характер изменений в углеводородной основе трансформаторных масел, подвергнутых искусственной термодеструкции, в зависимости от исходной концентрации в маслах одной из антиокислительных присадок: 1) 2,6-ди-трет-бутил-4-метилфенол (Ионол) и 2) 2,6-ди-трет-бутилфенол (2,6-DTBP). Определить, существуют ли признаки наличия проокислительных свойств у данных фенольных антиоксидантов при их массовой доле в масле менее 0.1 %. МЕТОДЫ. Для исследования были подготовлены 2 серии образцов масел с различным содержанием в них одной из присадок – Ионол и 2,6-DTBP. Исходная концентрация присадок в маслах: 0; 0.05; 0.1 и 0.2 % (масс.). В качестве базового минерального масла использовалось масло марки ВГ, производимое по технологии гидрокрекинга. Все масла были подвергнуты ускоренной термодеструкции при повышенной температуре. Анализ глубины деструктивных изменений в углеводородной основе масел осуществлялось по ИК спектрам поглощения. Анализ изменений относительного содержания растворенных в масле продуктов деградации осуществлялся с помощью спектров поглощения в УФ-видимом диапазоне. РЕЗУЛЬТАТЫ. На основе анализа оптических спектров обеих серий масел было получено, что по мере снижения в масле исходной концентрации любого из фенольных ингибиторов окисления интенсивность термодеструктивных изменений в углеводородном составе масел последовательно возрастает. Показано, что в трансформаторных маслах, производимых по технологии гидрокрекинга, обе присадки в диапазоне концентраций 0.05÷0.1 % не проявляют проокислительных свойств. Сделан вывод, что распространенное представление о проокислительном действии Ионола при его концентрации в трансформаторном масле менее 0.1 % следует считать не соответствующими действительности.

Ключевые слова: минеральное трансформаторное масло; ингибитор окисления; ионол; проокислительные свойства; ИК-спектроскопия; спектроскопия УФ-видимого диапазона.

Для цитирования: Гарифуллин М.Ш., Сlobодина Ю.Н., Бикзинуров А.Р., Гиниатуллин Р.А., Чернышов В.А. Исследование наличия проокислительных свойств у фенольных ингибиторов окисления в отношении современных трансформаторных масел // Известия высших учебных заведений. ПРОБЛЕМЫ ЭНЕРГЕТИКИ. 2024. Т. 26. № 6. С. 30-41. doi: 10.30724/1998-9903-2024-26-6-3041.

Introduction

An oil-filled power transformer is one of the most important elements in any power system. The ability of these transformers to operate at high power levels is due to the use of a liquid dielectric, transformer oil, which effectively dissipates the heat from the active part of the transformer into the external environment [1].

The traditional type of transformer oil, used in the very first oil-filled transformers, is mineral transformer oil, produced from petroleum. The main disadvantages of mineral oil are related to fire safety problems, as well as the possibility of environmental contamination in case of oil leaks. A promising alternative to mineral oils at present are ester-based oils - synthetic oils (Midel 7131, Envirottemp 360) [2, 3] as well as those produced from vegetable raw materials (MIDEL eN, FR3, etc.) [4-6].

Despite certain advantages, there are a number of factors that will not allow transformer oils based on esters to displace mineral oils in the near future. The main reason is the high cost of ester oils, especially the synthetic version. For example, Midel 7131 is more than an order of magnitude more expensive than GC, one of the best Russian oils. As a result, Midel 7131 oil in

domestic practice has found a niche use, for example on transformers of nuclear power plants, where economic aspects go into the background.

For vegetable-based oils, the main disadvantages are the higher viscosity and pour point values. Therefore, replacement of mineral oil with vegetable oil always leads to an increase in temperature inside the transformer, which can lead to unacceptable overheating of the equipment. At the same time, the geography of use of such oils is limited to a minimum winter temperature of -30°C .

A similar situation is typical for countries with developing economies, where due to the high rate of expansion of electrical networks the need for transformer oils is particularly high, but the economic aspect tilts the scales towards the traditional mineral oils [7].

At the same time, the addition of synthetic [8, 9] and natural esters [10, 11] to traditional mineral oils seems promising, which will increase the operational properties of the resulting oil mixtures without a significant increase in financial costs.

Based on the above, we can conclude that mineral transformer oil will remain the main type of liquid dielectric for oil-filled transformer electrical equipment in the foreseeable future. Therefore, research aimed at improving the efficiency of operation and diagnostics of the condition of mineral transformer oils continues to be relevant.

At one time, R.A. Lipstein made a great contribution to the development of the theory of mineral oils. The results of the research conducted under his supervision are presented in the twice republished monograph [6], which is still a table book for specialists in operation and diagnostics of oil-filled electrical equipment.

It should be noted that most of the research results presented in this monograph were conducted more than half a century ago. Since then, there have been significant changes in the production of oils. Firstly, Baku oils, which served as the main raw material for the production of transformer oils, have now been completely replaced by domestic paraffinic oils. Secondly, and more importantly, modern high-quality transformer oils are produced using hydrocracking technology, which has significantly changed their structural group composition. In particular, the content of aromatic, resinous-asphaltene and unsaturated compounds in oils has decreased. In this regard, some provisions on the properties and characteristics of transformer oils as applied to modern oils may need to be corrected or may be erroneous at all.

One such provision is the idea of the pro-oxidizing properties of the antioxidant additive Butylated hydroxytoluene (BHT). This additive is the most widely used oxidation inhibitor for transformer oils. According to the structural formula, the BHT additive belongs to the class of spatially hindered mononuclear phenols – Figure 1. Other common names for this additive are 2,6-di-tert-butyl-4-methylphenol or 2,6-di-tert-butyl-p-cresol (DBPC). In Russia, as well as in a significant part of the post-Soviet space, the additive has a well-established name – Ionol. Further in this article we will use the name Ionol along with BHT.

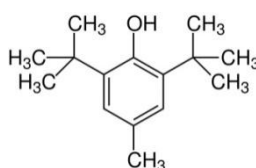


Fig. 1. Structural formula of the antioxidant additive Ionol (BHT) Рис. 1. Структурная формула антиокислительной присадки Ионол (БНТ)

*Источник: Составлено авторами Source: compiled by the author.

The mechanism of antioxidant action of this type of additives is to interact with the radicals $\dot{\text{R}}$ and $\text{RO}_2\dot{\text{}}$ formed at the initial stage of oxidation, preventing further development of the oxidation process [13]. During the oil operation the concentration of ionol in it decreases. According to the industry standard STO 34.01-23.1-001-2017, the residual concentration of ionol is a regularly monitored parameter and should not fall below 0.1 % (wt.). It is generally accepted that when the concentration of ionol drops below this limit, transformer oil begins to oxidize faster than in the absence of ionol. This phenomenon has been called "pro-oxidative effect of ionol" [12, 14] and is now a deeply rooted idea of the properties of ionol additive among domestic specialists. As a result, the mention of ionol's prooxidative properties not only occurs regularly in domestic scientific publications [15], but also entered a number of normative documents on transformer oils, as well as reference literature [16].

At the same time in the international standard IEC 60296 [17] the minimum level of ionol for operational transformer oils is set at 0.08 % (wt), and there is no information about the presence of prooxidative effect of ionol at low concentrations.

In addition to ionol in foreign practice for stabilization of oils the additive 2,6-di-tert-butylphenol (2,6-DTBP), also belonging to the class of spatially hindered mononuclear phenols, is used. The structural formula of 2,6-DTBP is shown in Figure 2. The mechanism of action of this additive is similar to ionol, so one would expect both additives to have similar properties at concentrations below 0.1 % as well.

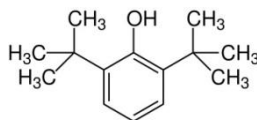


Fig. 2. Structural formula of the antioxidant additive 2,6-DTBP Рис. 2. Структурная формула антиокислительной присадки 2,6-DTBP

*Источник: Составлено авторами Source: compiled by the author.

Based on the above, it was interesting to find the presence of prooxidative action of ionol and 2,6-DTBP additives at their concentration of less than 0.1 % in modern mineral oil, produced using hydrocracking technology, which was the main purpose of the study. For this purpose the depth of thermal-oxidative degradation of oils was determined at different initial concentrations of the specified oxidation inhibitors in them.

Spectral methods are traditionally used to identify the features of changes in the chemical composition of different materials. For mineral oils, among all spectral methods, optical spectroscopy is the most convenient tool. Therefore, a comparative assessment of the depth of destructive changes in oxidized mineral oils was based on changes in their optical spectra. For the analysis we measured absorption spectra of oils in ultraviolet (UV) – visible and infrared (IR) ranges.

Materials and methods

For the study were prepared 2 Series samples of mineral transformer oil with different concentrations of oxidation inhibitor of one of two types: *a*) Ionol (BHT) and *b*) 2,6-DTBP.

Fresh VG grade oil (PJSC "Lukoil") produced using hydrocracking technology and containing no oxidation inhibitors was used as a base mineral oil. The acid number of the base oil was 0.003 mg KOH/g oil.

The required concentration of the relevant inhibitor was achieved by adding it to the base oil in the required amount. The inhibitor concentrations in each series are shown in Table 1.

Table 1

| Oxidation inhibitor concentrations in two oil series | | | | | |
|--|-------------|---|------|-----|-----|
| Series | Inhibitor | Inhibitor concentration in series oils, % (wt.) | | | |
| <i>a</i> | Ionol (BHT) | 0 | 0.05 | 0.1 | 0.2 |
| <i>b</i> | 2,6-DTBP | 0 | 0.05 | 0.1 | 0.2 |

*Источник: Составлено авторами Source: compiled by the author.

Both series of oils were subjected to thermo-oxidative degradation according to GOST 981-75 at elevated temperature with oxygen barbotage. Thermal oxidation was carried out with the help of apparatus APSM-1. Thermal oxidation conditions are presented below.

Oxidation temperature: 150C;
 Oxidation time: 14 hours;
 Oxygen feed rate: 200 ml/min;
 Catalyst: copper plate.

Since only 6 samples can be oxidized simultaneously in the APSM-1 device, the oxidation of the prepared oil samples was performed in 2 stages: 4 samples of Series *a*) were oxidized on one day; 4 samples of Series *b*) on another day. Thermal destruction resulted in samples of oils with different degrees of oxidation and different degrees of degradation of the hydrocarbon base.

We designate the samples of oxidized oils derived from Series *a*) oils as follows: Ia; IIa; IIIa; IVa in order of increasing initial concentration (before oxidation) of ionol in the oils, according to Table 1.

Accordingly, samples of oxidized oils derived from Series *b*) oils will be designated as Ib; IIb; IIIb; IVb, in order of increasing the initial concentration (before oxidation) of DBPC in the oils, according to Table 1.

For all samples of oils the acid number was determined by titration method, according to GOST-5985-79.

To assess the degree of degradation of the hydrocarbon base of the oxidized oil samples were measured optical absorption spectra in the UV-visible and in the infrared (IR) range.

Absorption spectra in the UV-visible region were measured using a spectrometer "Cary-100" in the spectral range of 360÷600 nm with a resolution of 1 nm. Measurements were made in a quartz cuvette with thickness (optical path length) of 10 mm.

A TENSOR-27 FT-IR spectrometer was used to measure infrared absorption spectra. IR spectra were measured with a resolution of 1 cm⁻¹ in two spectral ranges. A 10-mm-thick cuvette was used to measure spectra in the 4800÷4500 cm⁻¹ wave number region. In the 6000÷5600 cm⁻¹ wave number region, IR spectra were measured in a 2 mm cuvette. The window material of both cuvettes was CaF₂.

UV and IR spectra of basic VG oil, not subjected to thermal oxidation, were also measured. Hereafter, the spectra of this oil will be referred to as "Fresh Oil".

Results and discussions

As noted above, the oxidation of oils with Ionol (Series *a*) and with 2,6-DTBP (Series *b*) was performed separately. It should be taken into account that the APSM-1 unit has an error of ±10% in maintaining the stability of the oxygen flow rate. Therefore, the oxygen consumption (instantaneous and integral) during oxidation of Series *a*) oils differed from the oxygen consumption during oxidation of Series *b*) oils. Therefore, the comparative analysis of oil samples is performed separately for each Series. For the same reason, the comparative effectiveness of Ionol and 2,6-DTBP additives is not discussed in this work.

Table 2 and Table 3 show the values of acid numbers in the oxidized samples of Series *a*) and Series *b*) oils, respectively.

Table 2

Values of the acid number in the samples of Series *a*) (oxidation inhibitor – Ionol (BHT))

| Sample | Ionol concentration before oxidation, % (wt.) | Acid number, mg KOH/g oil |
|--------|---|---------------------------|
| Ia | 0 | 25.40 |
| IIa | 0.05 | 19.59 |
| IIIa | 0.10 | 5.29 |
| IVa | 0.20 | 0.017 |

*Источник: Составлено авторами Source: compiled by the author.

Table 3

Values of the acid number in the samples of Series *b*) (oxidation inhibitor – 2,6-DTBP)

| Sample | Concentration of 2,6-DTBP before oxidation, % (wt.) | Acid number, mg KOH/g oil |
|--------|---|---------------------------|
| Ib | 0 | 26.30 |
| IIb | 0.05 | 20.79 |
| IIIb | 0.10 | 8.76 |
| IVb | 0.20 | 0.17 |

*Источник: Составлено авторами Source: compiled by the author.

As can be seen from the tables, in both series, the acid number of the oils consistently increases as the initial concentration of the oxidation inhibitor decreases. Characteristically, the samples of oils Ia and Ib, which had no oxidation inhibitor before oxidation, have significantly higher acid numbers than the oils with the addition of 0.05 % of any of the inhibitors. Thus, judging by the acid number of the oils, both inhibitors had no prooxidative effect when their concentration in the oil was less than 0.1 %.

To identify changes in the chemical composition of oxidized oils, consider the optical absorption spectra in the spectral range of 360÷600 nm, relating to the UV-visible range – Figures 3 and 4.

In the spectral region under consideration, the decrease in the intensity of radiation passing through the oils is due to both molecular absorption by the polyaromatic and asphaltene compounds present and formed during oil degradation [18] and scattering on colloidal particles formed from oil degradation products [19]. As can be seen from the presented spectra, the absorption intensity increases as the initial concentration of the oxidation inhibitor in the oil decreases, which leads to a shift of the spectra to the longwave region.

For quantitative comparison, according to 14 ASTM D 6802-02, it is necessary to determine the areas under the analyzed spectra in the range 360÷600 nm. In the case under consideration, the content of degradation products in oxidized oils turned out to be so high that in

the short-wave part of the spectrum the values of optical densities of oils exceeded the sensitivity of the instrument (except for sample IVa). Therefore, a correct numerical integration to determine the value of the area under the spectra was impossible.

However, even a qualitative analysis of the presented spectra suggests that adding any of the considered oxidation inhibitors at a concentration of 0.05% to the oil leads to a decrease in the amount of dissolved degradation products, compared to uninhibited oil. Thus, according to the content of degradation products dissolved in the oil, both oxidation inhibitors have no prooxidative effect.

Further consider the IR spectra of absorption of oils, analysis of which changes allows to assess the degradation of the hydrocarbon base of the mineral oil. For carrying out researches the near infra-red region was chosen, researches in which possess a number of advantages before average and far IR regions.

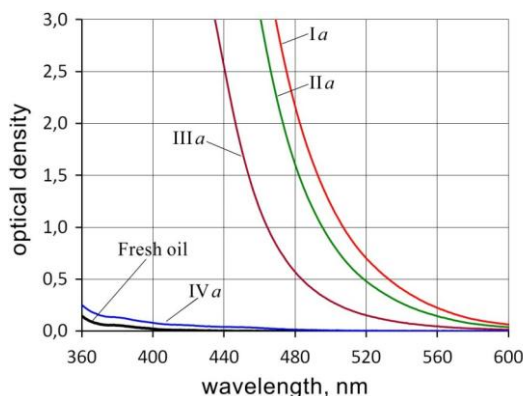


Fig. 3. UV-Visible absorption spectra of fresh and oxidized oils of Series a) (with Ionol). Cuvette thickness is 10 mm. Designation of sample oils according to Table 2.

Рис. 3. Спектры поглощения в УФ-видимом диапазоне свежего и окисленных масел Серии а) (с Ионолом). Толщина кюветы – 10 мм. Обозначение образцов масел согласно Таблице 2.

*Источник: Составлено авторами Source: compiled by the author.

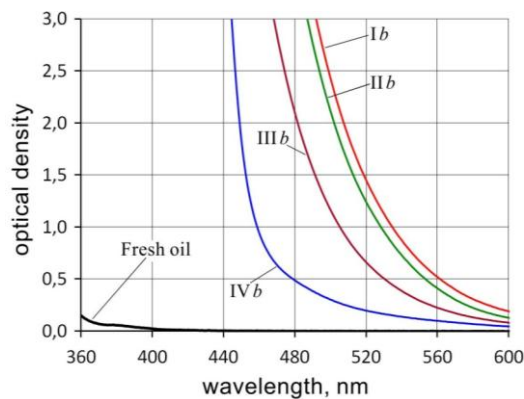


Fig. 4. UV-Visible absorption spectra of fresh and oxidized oils of Series b) oils (with 2,6-DTBP). Cuvette thickness is 10 mm. Designation of sample oils according to Table 3.

Рис. 4. Спектры поглощения в УФ-видимом диапазоне свежего и окисленных масел Серии b) (с 2,6-DTBP). Толщина кюветы – 10 мм. Обозначение образцов согласно Таблице 3.

*Источник: Составлено авторами Source: compiled by the author.

Consideration will begin with the spectral range in the region of wave numbers $6000 \div 5600 \text{ cm}^{-1}$ (about $1.67 \div 1.79 \text{ }\mu\text{m}$). IR absorption spectra of both Series of oils are shown in Figures 5 and 6. In this region of the spectrum there are absorption bands belonging to the first overtones of the valence C-H vibrations in the methyl ($-\text{CH}_3$) and methylene ($-\text{CH}_2-$) groups of hydrocarbon molecules of the oils. A 2-mm-thick cuvette was used to measure the IR spectra.

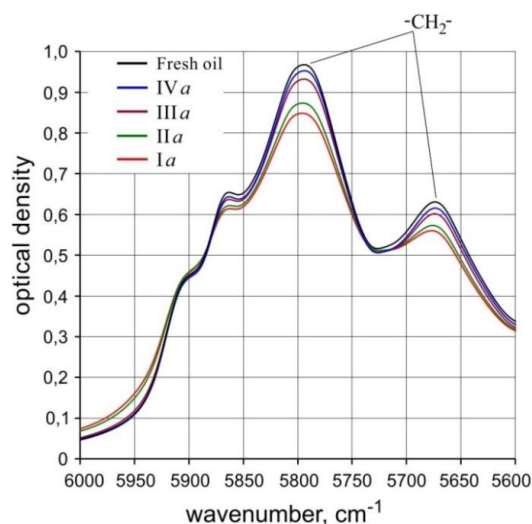


Fig. 5. IR absorption spectra of fresh and oxidized oils of Series a) in the region of 6000÷5600 cm^{-1} . Cuvette thickness is 2 mm. Designation of samples according to Table 2. Рис. 5. ИК спектры поглощения свежего и окисленных масел Серии а) в области 6000÷5600 cm^{-1} . Толщина кюветы – 2 мм. Обозначение образцов согласно Таблице 2.

*Источник: Составлено авторами Source: compiled by the author.

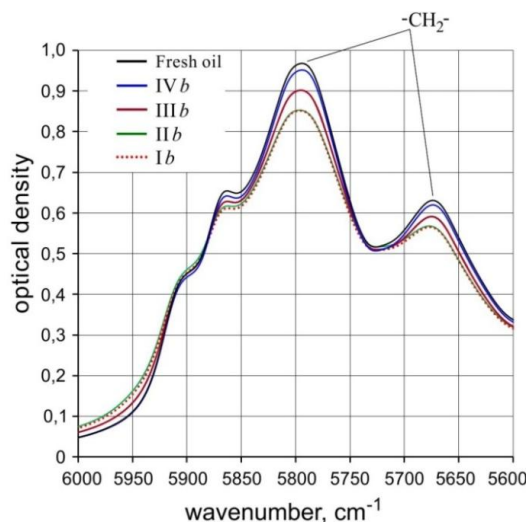


Fig. 6. IR absorption spectra of fresh and oxidized oils of Series b) in the region of 6000÷5600 cm^{-1} . Cuvette thickness is 2 mm. Designation of samples according to Table 3. Рис. 6. ИК спектры поглощения свежего и окисленных масел Серии б) в области 6000÷5600 cm^{-1} . Толщина кюветы – 2 мм. Обозначение образцов согласно Таблице 3.

*Источник: Составлено авторами Source: compiled by the author.

According to the theory of hydrocarbon oxidation, methyl groups are the most resistant to the oxidation process [20]. Oxidation of methylene $-\text{CH}_2-$ groups occurs relatively easily by the introduction of oxygen through C-H bonds [21, 22]. In addition, a decrease in the number of methylene groups occurs during the formation of double $\text{C}=\text{C}$ and triple $\text{C}\equiv\text{C}$ bonds, as well as the breaking of carbon chains. Consequently, oxidative degradation of the hydrocarbon base of mineral oil is always accompanied by a decrease in its content of methylene $-\text{CH}_2-$ groups, which leads to a decrease in the intensity of the corresponding absorption bands. In the spectra under consideration, the methylene group corresponds to the most intensive absorption band with a peak near 5795 cm^{-1} , as well as a weaker one with a peak near 5673 cm^{-1} [23, 24].

From the spectra shown in Figures 5 and 6, it can be seen that the intensity of both $-\text{CH}_2-$ absorption bands decreases as the initial concentration of the oxidation inhibitor decreases. Consequently, the depth of degradation of the hydrocarbon backbone of the oil also increases as the initial concentration of oxidation inhibitor in the oil decreases.

And if the effect of 2,6-DTBP additive at its concentration in oil of 0.05 % is not so noticeable compared to uninhibited oil (spectra of samples Ib and IIb in Figure 6), the addition of Ionol at a concentration of 0.05 % showed a distinct change in IR spectra (spectra of samples Ia and IIa in Figure 5).

Thus, the addition of any of the considered inhibitors at a concentration of 0.05 % reduces the depth of degradation of the hydrocarbon base of the oil compared to uninhibited oil.

Next, let us consider the spectral range $4800\div4500\text{ cm}^{-1}$ (about $2.08\div2.22\text{ }\mu\text{m}$). Absorption bands of various compounds with unsaturated $\text{C}=\text{C}$ bonds [25] are located in this region. The main advantage of using this spectral range is that there are no absorption bands of other mineral oil compounds here. For example, in the spectral range $2000\div1600\text{ cm}^{-1}$ in addition to absorption bands related to double $\text{C}=\text{C}$ bonds, there are intensive absorption bands of carbonyl groups $\text{C}=\text{O}$ of various oil oxidation products (aldehydes, ketones, acids), as well as absorption bands of aromatic compounds, which makes analysis of changes in the content of unsaturated compounds in oils difficult.

Since the studied absorption bands are very weak, a cuvette with a thickness of 10 mm was used to measure the IR spectra, which is a sufficiently large value for IR spectroscopy.

The absorption bands with peaks around 4600 and 4665 cm^{-1} , which refer to the vibrations of $=\text{C}-\text{H}$ and $\text{C}=\text{C}$ groups of unsaturated hydrocarbons, act as analytical bands in this range [23]. Figures 7 and 8 show absorption spectra of oxidized oils of Series a) and b), respectively, as well as of fresh oil.

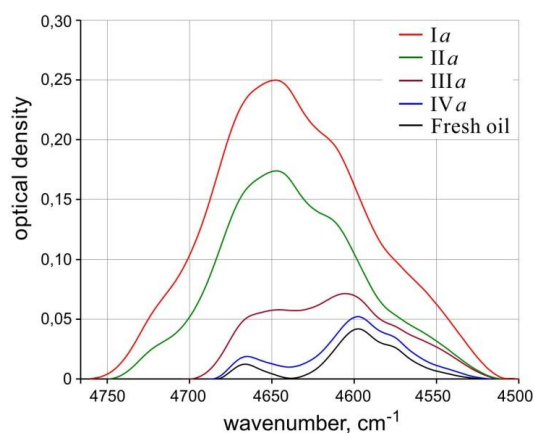


Fig. 7. IR absorption spectra of fresh and oxidized oils of Series a) in the region of $4800\div4500\text{ cm}^{-1}$. Cuvette thickness is 10 mm. Designation of samples according to Table 2.

Рис. 7. ИК спектры поглощения свежего и окисленных масел Серии а) в области $4800\div4500\text{ cm}^{-1}$. Толщина кюветы – 10 мм. Обозначение образцов согласно Таблице 2.

*Источник: Составлено авторами Source: compiled by the author.

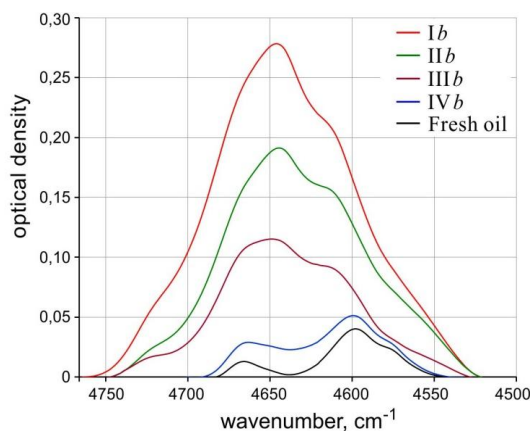


Fig. 8. IR absorption spectra of fresh and oxidized oils of Series b) in the region of $4800\div4500\text{ cm}^{-1}$. Cuvette thickness is 10 mm. Designation of samples according to Table 3.

Рис. 8. ИК спектры поглощения свежего и окисленных масел Серии б) в области $4800\div4500\text{ cm}^{-1}$. Толщина кюветы – 10 мм. Обозначение образцов согласно Таблице 3.

*Источник: Составлено авторами Source: compiled by the author.

As can be seen from the spectra, the process of thermal oxidation, which is the main mechanism of degradation of oils in the equipment, leads to an increase in the content of unsaturated compounds containing $\text{C}=\text{C}$ double bonds. The unsaturated compounds are also present in fresh mineral oil, as evidenced by the presence in the spectrum of this oil of both absorption peaks under consideration, but of low intensity.

With increasing degree of oxidation of oils (according to Tables 2 and 3) absorption intensity in the region of the peak 4665 cm^{-1} increases faster than in the region of 4600 cm^{-1} . As a result, there is a change in the shape of the spectrum. This effect can be explained by a significant increase in the proportion of unsaturated hydrocarbons containing carbonyl C=O group, which in turn affects the change in intensity and position in the IR spectrum of some absorption bands. It should be noted that operational transformer oils have a much lower degree of oxidation, so in their IR spectra absorption in the area of the 4600 cm^{-1} peak is always more intense [26, 27].

Based on the analysis of changes in the intensities of the considered absorption bands, it can be argued that the presence of an oxidation inhibitor in oil, even in a small amount - 0.05 % - leads to a significant slowdown in the formation of unsaturated compounds.

Summarizing the results of the study of IR absorption spectra of oxidized oils, we can conclude that neither Ionol nor 2,6-DTBP at a concentration of 0.05 % lead to an increase in the depth of degradation of the hydrocarbon base of oils as compared to uninhibited oils.

Conclusions

The presence of phenolic oxidation inhibitor in mineral transformer oil, as expected, slows down the process of its oxidation and degradation of the hydrocarbon basis. The results of the study lead to the conclusion that neither Ionol (BHT) nor 2,6-DTBP in concentrations below 0.1 % (wt.) show pro-oxidative properties against modern mineral transformer oils, at least in the concentration range of 0.05÷0.1 %. Thus, the representation about the prooxidative effect of Ionol at its concentration in the mineral transformer oil less than 0.1 % should be considered as not corresponding to reality.

The minimum concentration of Ionol in oil established by the standard at the level of 0.1 % significantly slows down the process of thermal-oxidative degradation of oil. However, as demonstrated by the results of the study, bringing the concentration of Ionol to the level of 0.2 % allows to almost completely prevent the process of oil oxidation over a long period of time. This is relevant, because the periodicity of control of the content of Ionol in transformer oil is 2 years. In this regard, it seems advisable not to allow the concentration of Ionol in operating oils to decrease below 0.2% (wt.).

It should also be noted that in practice there is a problem of separate determination in oil of both additives – Ionol and 2,6-DTBP. The traditional method of solving this problem involves the use of gas-liquid chromatography with flame ionization detector [28]. It is also possible to use IR spectroscopy [29, 30], however, the practical realization of this approach has both algorithmic and instrumental difficulties, since the main IR absorption bands of these additives coincide. It seems promising to use the near infrared spectral region [31], studies in which can be carried out in the form of express analysis. The results obtained in solving this problem will be presented in the next paper.

In conclusion, it should also be noted that the presented in this work optical methods of controlling the degradation of hydrocarbon base in the UV-visible and near-infrared spectral regions can be realized using small-size spectrophotometers in which the radiation detector is a multielement CCD photodetector [32]. The use of spectrometers of this type, in particular, with cooled CCD photodetectors, will not only significantly simplify and reduce the cost of measurements, but also make it possible to conduct studies in the field.

The study was carried out within the activities of the Problematic Working Group PWG D1.1 “Determination of Degradation Markers of Mineral Transformer Oils by Infrared Spectroscopy” of the National Research Committee D1 of the Russian National Committee of CIGRE.

References

1. Lukenda N. Not all mineral oils are equal. *Transformers Magazine*. 2019. 6(4):112-117.
2. MIDEL 7131 - premium performance since the 1970s. – URL: <https://www.midel.com/midel-range/midel-7131/> (дата обращения: 01.09.2024)
3. Rozga P., Beroual A., Przybylek P., Jaroszewski M. et al. A Review on Synthetic Ester Liquids for Transformer Applications. *Energies*. 2020; 13(23):6429. <https://doi.org/10.3390/en13236429>
4. Rapeseed natural ester dielectric fluid. – URL: <https://www.cargill.com/bioindustrial/dielectric-fluids/fr3r-fluid> (дата обращения: 01.09.2024).
5. Rao U.M., Fofana I., N'cho J.S. On Some Imperative IEEE Standards for Usage of Natural Ester Liquids in Transformers. *IEEE Access*. 2020;8:145446-145456. doi: 10.1109/ACCESS.2020.3014600.
6. Shen Z., Wang F., Wang Z., Li J. A critical review of plant-based insulating fluids for transformer: 30-year development. *Renewable and Sustainable Energy Reviews*. 2021;141. 110783. <https://doi.org/10.1016/j.rser.2021.110783>
7. Transformer oils market. Analytical review. URL: <https://www.marketsandmarkets.com/Market-Reports/transformer-oil-market-967.html/> (дата обращения: 01.09.2024)

8. Lyutikova M.N., Korobeynikov S.M., Rao U.M. Fofana I. Mixed Insulating Liquids With Mineral Oil for High-Voltage Transformer Applications: A Review. *IEEE Transactions on Dielectrics and Electrical Insulation*. 2022;29(2):454-461. doi: 10.1109/TDEI.2022.3157908.
9. Lyutikova M., Korobeynikov S., Konovalov A. Evaluation of the Properties of Mixtures of Aromatic Mineral Oil and Synthetic Ester for High-Voltage Equipment. *IEEE Transactions on Dielectrics and Electrical Insulation*. 2021; 28(4):1282-1290. doi: 10.1109/TDEI.2021.009636
10. Rouabeh J., M'barki L., Hammami A., et. al. Studies of different types of insulating oils and their mixtures as an alternative to mineral oil for cooling power transformers. *Heliyon*. 2019;5(3). doi: 10.1016/j.heliyon.2019.e01159.
11. Hao J., Zhang J., Ye W., et. al. Development of Mixed Insulation Oil as Alternative Liquid Dielectric: A Review. *CSEE Journal of Power and Energy Systems*. 2024; 10(3):1242-1258. doi: 10.17775/CSEEJPES.2023.05960
12. Lipshtein R.A., Shakhnovich M.I. *Transformatornoe maslo*. Moscow: Ehnergoatomizdat, 1983. (In Russ).
13. Roginskii V.A. *Fenol'nye antioksidanty: Reaktsionnaya sposobnost' i effektivnost'*. – Moscow: Nauka; 1988. (In Russ).
14. Lipshtein R.A. O mekhanizme deistviya ingibitorov okisleniya. *Prisadki k maslam: Trudy Vtorogo Vsesoyuznogo nauch.-tekhn. soveshchaniya*. Moscow: Khimiya Publ., 1968. 169-177. (In Russ).
15. S.P. Vysogorets, "Improvement of the methodology of physical and chemical diagnostics of oil-filled transformer equipment": D. thesis for the degree of Doctor of Technical Sciences. 05.14.12, St. Petersburg, 2020. 423 p.
16. Lizunov SD, Lokhanin AK, editors. *Silovye transformatory. Spravochnaya kniga*. Moscow: Energoatomizdat; 2004. (In Russ).
17. Atanasova-Höhlein I. IEC 60296 (Ed. 5) – a standard for classification of mineral insulating oil on performance and not on the origin. *Transformers magazine*. 2021; 8(1):86-91.
18. Turanov A.N. Analiz metodov diagnostiki doli aromatischeskikh grupp v sostave transformatornykh masel. *Elektrichestvo*. 2022; 4: 72-77. (In Russ).
19. N'cho J.S., Fofana I., Hadjadj Y., et al. Review of Physicochemical-Based Diagnostic Techniques for Assessing Insulation Condition in Aged Transformers. *Energies*. 2016;9(5):367. doi: <https://doi.org/10.3390/en9050367>
20. Emanuel' N.M., Denisov E.T., Maizus Z.K. *Tsepnye reaktsii okisleniya uglevodorodov v zhidkoi faze*. M.: Nauka; 1965. (In Russ).
21. Ivanov K.I. *Provezhutochnye produkty i promezhutochnye reaktsii avtookisleniya uglevodorodov*. M.;-L.: Gostoptekhizdat; 1949. (In Russ).
22. Waters W.A. *Mechanism of oxidation of organic compounds*. New York: Wiley, 1964. (Russ. ed.: Uoters U.A. Mekhanizm okisleniya organicheskikh soedinenii. Moscow: Mir Publ., 1966; 175 p.)
23. Krishchenko V.P. *Blizhnyaya infrakrasnaya spektroskopiya*. Moscow: KRONA-PRESS; 1997. (In Russ).
24. Jerry Workman, Jr. *The Handbook of Organic Compounds: NIR, IR, Raman, and UV-Vis Spectra Featuring Polymers and Surfactants*. 1st ed. Elsevier; 2000.
25. Garifullin M.Sh. Ispol'zovanie metodov opticheskoi spektroskopii dlya diagnostiki mineral'nykh izolyatsionnykh masel. *Fundamental'nye issledovaniya*. 2013;10: 3299-3304. (In Russ).
26. Garifullin M.Sh., Solobodina Y.N., Bikzinurov A.R., et al. Control of the degradation of the mineral transformer oils hydrocarbon base. *E3S Web of Conferences*. 2020;216(01055). DOI: <https://doi.org/10.1051/e3sconf/202021601055>
27. Garifullin M.Sh., Slobodina Y.N., Bikzinurov A.R., et al. Investigation of the content of unsaturated hydrocarbons in transformer oils using IR spectroscopy. *Power engineering: research, equipment, technology*. 2023;25(5):3-19. (In Russ). doi: <https://doi.org/10.30724/1998-9903-2023-25-5-3-19>
28. Lyutikova M.N., Nekhoroshev S.V., Kuklina V.M., et al. Identification of Impurities of Unknown Composition in Insulating Oil by Gas Chromatography-Mass Spectrometry (GC-MS). *Power Technology and Engineering*. 2020;54(4). doi: 10.1007/s10749-020-01257-0.
29. Ågren P., Lillhonga T., Melzer L. Identification and Improved Quantification of Inhibitors in Mineral Insulating Oils using FTIR Spectroscopy and Partial Least Squares Regression: 48 *CIGRE Session*; 23-28 Aug 2020; Paris, France; 2020. Paper D1-103.
30. Muratova V.M., Nekhoroshev S.V., Gadzhieva A.S., et al. Determination of phenolic-type antioxidant additives in fresh insulating oils by IR spectrometry on a liquid express analysis attachment. *Analytics and Control*. 2023; 27(2):113-121. (In Russ). doi: 10.15826/analitika.2023.27.2.005
31. Lyutikova M.N., Konovalov A.A., Korobeinikov S.M., et al. Control of the Antioxidant Additive (Ionol) Content in Liquid Insulation of High-Voltage Equipment in Electric Grid Companies Using Modern Instrumental Methods. *Power Technology and Engineering*. 2019;53(1): 118-125.
32. Garifullin M.Sh., Kozlov V.K. Pribor dlya spektral'nykh issledovaniy izolyatsionnykh masel v diapazone 600-1100 nm. *Power engineering: research, equipment, technology*. 2001; 9-10: 114-116. (In Russ).

Authors of the publication

Marsel Sh. Garifullin – Kazan State Power Engineering University, Kazan, Russia.

Yulia N. Slobodina – Kazan State Power Engineering University, Kazan, Russia.

Azat R. Bikzinurov – Kazan State Power Engineering University, Kazan, Russia.

Ruslan A. Giniatullin – Kazan National Research Technological University, Kazan, Russia.

Vadim A. Chernyshov – Oryol State University named after I.S. Turgenev, Oryol, Russia.

Литература

1. Lukenda N. Not all mineral oils are equal // Transformers Magazine. 2019. Vol. 6, №4. pp. 112-117.
2. MIDEЛ 7131 - premium performance since the 1970s. – URL: <https://www.midel.com/midel-range/midel-7131/> (дата обращения: 01.09.2024)
3. Rozga P., Beroual A., Przybylek P., Jaroszewski M., et al. A Review on Synthetic Ester Liquids for Transformer Applications // Energies. 2020. Vol. 13. Iss. 23. 6429. <https://doi.org/10.3390/en13236429>
4. Rapeseed natural ester dielectric fluid. – URL: <https://www.cargill.com/bioindustrial/dielectric-fluids/fr3r-fluid> (дата обращения: 01.09.2024).
5. Rao U.M., Fofana I., N'cho J.S. On Some Imperative IEEE Standards for Usage of Natural Ester Liquids in Transformers. // IEEE Access. 2020. Vol. 8. pp. 145446-145456. doi: 10.1109/ACCESS.2020.3014600.
6. Shen Z., Wang F., Wang Z., Li J. A critical review of plant-based insulating fluids for transformer: 30-year development // Renewable and Sustainable Energy Reviews. 2021. Vol.141. 110783. <https://doi.org/10.1016/j.rser.2021.110783>
7. Рынок трансформаторных масел. Аналитический обзор. – URL: <https://www.marketsandmarkets.com/Market-Reports/transformer-oil-market-967.html/> (дата обращения: 01.09.2024)
8. Lyutikova M.N., Korobeynikov S.M., Rao U.M., Fofana I. Mixed Insulating Liquids With Mineral Oil for High-Voltage Transformer Applications: A Review // IEEE Transactions on Dielectrics and Electrical Insulation. 2022. Vol. 29. N. 2. pp. 454-461. doi: 10.1109/TDEI.2022.3157908.
9. Lyutikova M., Korobeynikov S., Konovalov A. Evaluation of the Properties of Mixtures of Aromatic Mineral Oil and Synthetic Ester for High-Voltage Equipment // IEEE Transactions on Dielectrics and Electrical Insulation. 2021. Vol. 28. N. 4. pp. 1282-1290. doi: 10.1109/TDEI.2021.009636
10. Rouabeh J., M'barki L., Hammami A., et. al. Studies of different types of insulating oils and their mixtures as an alternative to mineral oil for cooling power transformers. Heliyon. 2019. Vol. 5, N3. doi: 10.1016/j.heliyon.2019.e01159.
11. Hao J., Zhang J., Ye W., et. al. Development of Mixed Insulation Oil as Alternative Liquid Dielectric: A Review // CSEE Journal of Power and Energy Systems. 2024. Vol. 10. N.3. pp.1242-1258. doi: 10.17775/CSEEJPES.2023.05960
12. Липштейн Р.А., Шахнович М.И. Трансформаторное масло. М.: Энергоатомиздат, 1983. 296 с.
13. Рогинский В.А. Фенольные антиоксиданты: Реакционная способность и эффективность. М.: Наука, 1988. 247 с.
14. Липштейн Р.А. О механизме действия ингибиторов окисления // Присадки к маслам: Труды Второго Всесоюзного науч.-техн. совещания. М.: «Химия», 1968. С. 169-177.
15. Высогорец С.П. Совершенствование методологии физико-химического диагностирования маслonaполненного трансформаторного оборудования.: диссертация на соискание ученой степени докт. техн. наук. 05.14.12 / Высогорец Светлана Петровна. Санкт-Петербург, 2020. 423 с.
16. Силовые трансформаторы. Справочная книга / Под. ред. С.Д. Лизунова, А.К. Лоханина. – М.: Энергоатомиздат, 2004. 616 с.
17. Atanasova-Höhlein I. IEC 60296 (Ed. 5) – a standard for classification of mineral insulating oil on performance and not on the origin // Transformers magazine. 2021. Vol. 8, Iss. 1. pp. 86-91.
18. Туранов А.Н. Анализ методов диагностики доли ароматических групп в составе трансформаторных масел // Электричество. 2022. № 4. С. 72-77.
19. N'cho J.S., Fofana I., Hadjadj Y., et al. Review of Physicochemical-Based Diagnostic Techniques for Assessing Insulation Condition in Aged Transformers // Energies. 2016. Vol. 9, N5. 367. <https://doi.org/10.3390/en9050367>
20. Эмануэль Н.М., Денисов Е.Т., Майзус З.К. Цепные реакции окисления углеводов в жидкой фазе. М.: Наука, 1965. 375 с.

21. Иванов К.И. Промежуточные продукты и промежуточные реакции автоокисления углеводов. М.;-Л.: Гостоптехиздат, 1949. 192 с.
22. Уотерс У.А. Механизм окисления органических соединений. М.: Мир, 1966. 175 с.
23. Крищенко В.П. Ближняя инфракрасная спектроскопия. М.: КРОНА-ИРЕСС, 1997. 638 с.
24. Jerry Workman, Jr. The Handbook of Organic Compounds: NIR, IR, Raman, and UV-Vis Spectra Featuring Polymers and Surfactants. 1st ed. Elsevier; 2000.
25. Гарифуллин М.Ш. Использование методов оптической спектроскопии для диагностики минеральных изоляционных масел // Фундаментальные исследования. 2013. №10. С. 3299-3304.
26. Garifullin M.Sh., Solobodina Y.N., Bikzinurov A.R., et al. Control of the degradation of the mineral transformer oils hydrocarbon base // E3S Web of Conferences. 2020. Vol. 216, 01055. DOI: <https://doi.org/10.1051/e3sconf/202021601055>
27. Гарифуллин М.Ш., Слободин Ю.Н., Бикзинуров А.Р. и др. Исследование содержания непредельных углеводородов в трансформаторных маслах с помощью ИК спектроскопии // Известия высших учебных заведений. ПРОБЛЕМЫ ЭНЕРГЕТИКИ. 2023. Т. 25(5). С. 3-19. <https://doi.org/10.30724/1998-9903-2023-25-5-3-19>
28. Lyutikova M.N., Nekhoroshev S.V., Kuklina V.M., et al. Identification of Impurities of Unknown Composition in Insulating Oil by Gas Chromatography-Mass Spectrometry (GC-MS) // Power Technology and Engineering. 2020. Vol. 54, N4. pp. 594-599. – DOI: 10.1007/s10749-020-01257-0.
29. Ågren P., Lillhonga T., Melzer L. Identification and Improved Quantification of Inhibitors in Mineral Insulating Oils using FTIR Spectroscopy and Partial Least Squares Regression: 48 CIGRE Session; 23-28 Aug 2020; Paris, France; 2020. Paper D1-103.
30. Муратова В.М., Нехорошев С.В., Гаджиева А.С. и др. Определение антиоксидантных присадок фенольного типа в свежих изоляционных маслах методом ИК-спектроскопии на приставке для экспресс-анализа жидкостей // Аналитика и контроль. 2023. Т.27, № 2. С. 113-121. DOI 10.15826/analitika.2023.27.2.005.
31. Lyutikova M.N., Konovalov A.A., Korobeinikov S.M., et al. Control of the Antioxidant Additive (Ionol) Content in Liquid Insulation of High-Voltage Equipment in Electric Grid Companies Using Modern Instrumental Methods // Power Technology and Engineering. 2019. Vol. 53, N1, pp. 118-125.
32. Гарифуллин М.Ш., Козлов В.К. Прибор для спектральных исследований изоляционных масел в диапазоне 600-1100 нм // Известия высших учебных заведений. ПРОБЛЕМЫ ЭНЕРГЕТИКИ. 2001. № 9-10. С. 114-116.

Авторы публикации

Гарифуллин Марсель Шарифьянович – д-р. техн. наук, профессор кафедры «Электроэнергетические системы и сети» Казанского государственного энергетического университета (КГЭУ).

Слободин Юлия Николаевна – магистр, выпускник кафедры «Электроэнергетические системы и сети» Казанского государственного энергетического университета (КГЭУ).

Бикзинуров Азат Рашитович – магистр, выпускник кафедры «Электроэнергетические системы и сети» Казанского государственного энергетического университета (КГЭУ).

Гиниятуллин Руслан Анатольевич – канд. техн. наук, доцент кафедры «Электропривода и электротехники» Казанского национального исследовательского технологического университета (КНИТУ).

Чернышов Вадим Алексеевич – канд. техн. наук, доцент кафедры «Электрооборудование и энергосбережение» Орловского государственного университета имени И.С. Тургенева (ОГУ им. И.С. Тургенева).

Шифр научной специальности: 2.2.8. Методы и приборы контроля и диагностики материалов, изделий, веществ и природной среды

Получено 21.10.2024 г.

Отредактировано 28.10.2024 г.

Принято 05.11.2024 г.