Т. 88, № 4 **ЖУРНАЛ ПРИКЛАДНОЙ СПЕКТРОСКОПИИ** ИЮЛЬ — АВГУСТ 2021

V. 88, N 4 **JOURNAL OF APPLIED SPECTROSCOPY** JULY— AUGUST 2021

THERMAL AND SPECTROSCOPIC STUDIES OF THE THERMAL-OXIDATION STABILITIES OF LUBRICANTS**

P. Wang [1], Y. Wang [1*], Y. Sun [1], Z. Cao [1], W. Zhu [1], H. Wang [2*]

[1] State Key Laboratory of Intelligent Manufacturing of Advanced Construction Machinery,
Jiangsu Xuzhou Construction Machinery Research Institute, Xuzhou Construction Machinery Group,
Xuzhou 221004, China; e-mail: wangyuexing@163.com
[2] Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, School of Chemistry
& Materials Science at Jiangsu Normal University, Xuzhou 221116, China; e-mail: wanghy@jsnu.edu.cn

The influence of aromatic antioxidants 2,6-di-tert-butyl-4-methylphenol (BHT) and diphenylamine (DPA) on the thermal–oxidative degradation of base oils 150N was studied by using the hot oil oxidation test (HOOT) with temperatures varying from 100 to 200°C and times ranging from 1–24 h. Qualitative as well as quantitative analyses of the base oils and their fractions were done using gas chromatography-mass spectrometry (GC-MS) and spectroscopic (FTIR, UV–visible) techniques to gain a better understanding of their compositional and structural details. Oxidization processes were also studied and structural changes resulting from thermal oxidation were identified. The results indicate that the addition of antioxidants causes an obvious enhancement in the resistance of base oils to thermal–oxidative degradation. Moreover, the mixture of antioxidants shows better thermal–oxidative resistance than the phenolic or diphenylamine antioxidants alone.

Keywords: *base oil, oxidation, Infrared spectroscopy, gas chromatography-mass spectrometry, thermal stability, antioxidants.*

ИССЛЕДОВАНИЕ ТЕРМООКИСЛИТЕЛЬНОЙ СТАБИЛЬНОСТИ СМАЗОЧНЫХ МАТЕРИАЛОВ И ИХ СПЕКТРОСКОПИЧЕСКИЙ АНАЛИЗ

P. Wang [1], Y. Wang [1*], Y. Sun [1], Z. Cao [1], W. Zhu [1], H. Wang [2*]

УДК 543.42

[1] Научно-исследовательский институт строительной техники Цзянсу,
Сюйчжоу 221004, Китай; e-mail: wangyuexing@163.com
[2] Школа химии и материаловедения Университета Цзянсу,
Сюйчжоу 221116, Китай; e-mail: wanghy@jsnu.edu.cn

(Поступила 10 августа 2020)

Влияние ароматических антиоксидантов 2,6-ди-трет-бутил-4-метилфенола (BHT) и дифениламина (DPA) на термоокислительную деструкцию базовых масел 150N изучено с помощью теста на окисление горячим маслом (HOOT) при температурах 100–200 °С и времени в диапазоне 1–24 ч. Качественный и количественный анализ базовых масел и их фракций проведен с использованием газовой хроматографии–масс-спектрометрии (GC-MS) и спектроскопических методов (FTIR, UV-vis) для лучшего понимания их композиционных и структурных деталей. Изучены процессы окисления и выявлены структурные изменения, возникающие в результате термического окисления. Показано, что добавление антиоксидантов приводит к повышению устойчивости базовых масел к термоокислительной деградации. Смесь антиоксидантов проявляет лучшую термоокислительную стойкость, чем только фенольные или дифениламиновые антиоксиданты.

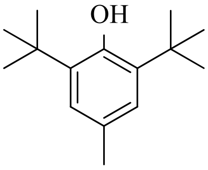
Ключевые слова: *базовое масло, окисление, инфракрасная спектроскопия, газовая хроматография–масс-спектрометрия, термостабильность, антиоксиданты.*

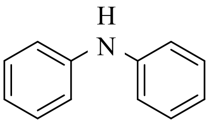
** Full text is published in JAS V. 88, No. 4 (http://springer.com/journal/10812) and in electronic version of ZhPS V. 88, No. 4 (http://www.elibrary.ru/title_about.asp?id=7318; sales@elibrary.ru).

Introduction. Thermal–oxidative degradation is one of the most important problems of lubricants. This degradation is the primary cause of increases in viscosity, pour point, sludge formation, lacquer formation and engine corrosion [1–4]. The autoxidation of lubricants takes place in the presence of heat and dissolved oxygen, producing hydroperoxides or other reactive intermediates; these can be transformed into various harmful oxygenated products, such as acids, aldehydes, ketones, esters, and lactones [5–7], which always have many unfavorable consequences for the lubricant system. The widely accepted mechanistic routes suggest the occurrence of free radical reactions, including chain initiation, propagation and termination steps [5]. To increase the thermo-oxidative stability and to provide the stability required during transport and storage, antioxidants (AOs) are used to delay the fuel degradation process [8–14]. To date, many different classes of antioxidants applied in the field of lubricants are commercially available or have been described in the literature [15–20]. However, there is still much ongoing research designed to develop more effective, efficient, and ecofriendly systems.

In the case of base oils, sterically hindered phenolic compounds and amine derivatives are commonly employed [5, 8, 21, 22]. Often, both classes are part of the lubricant formulation since they exhibit significant homosynergism. Numerous tests have been conducted to select the proper base oil and additives for formulating oils for a particular service and determining whether the used fluid is fit for continued use [15, 20, 23–27].

The antioxidant characteristics of base oils were evaluated via changes in temperatures for the different oxidation stages occurring during the course of oxidation. The oxidative degradation processes were estimated via thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) and the changes in the base oils before and after thermal oxidation were detected by infrared and ultraviolet–visible spectroscopies. Gas chromatography-mass spectrometry (GC-MS) was employed to monitor the changes in the chemical composition of the base oil samples. These studies contribute to obtaining information on the thermal behavior of lubricants under an ambient atmosphere and estimating the stability of antioxidants. In addition, this work can help in the development of new lubricant formulations, and particularly of new antioxidants, which requires information on the oxidation behavior of the formulations.





2,6-di-tert-butyl-4-mathylphenol (BHT) diphenylamine (DPA)

Data and methods. *Materials.* The base oil used in this work was a kind of mineral base oils (150N) supplied by the Formosa Plastic Group. According to the American Petroleum Institute (API), 150N belongs to group II. Commercial antioxidants BHT and DPA were purchased from Energy Chemical Reagent Company (Shanghai, China).

Thermal-oxidation tests. All the fuel samples were thermally oxidized in an isothermal apparatus according to reference [28]. For thermal degradation, base oils were heat-treated at 100, 120, 140, 160, 180, and 200°C. Samples were withdrawn at times that varied from 1 to 24 h.

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG). The experiments were performed on 5±0.5 mg samples using a TA-Q50 thermogravimetric instrument. The experiments were carried out under a continuous nitrogen flow of 60 mL/min. The mass losses were recorded at temperatures ranging from 30 to 500°C.

Spectroscopic analyses. A Bruker Tensor 27 Fourier transform infrared spectrometer was used to observe the changes in organic functional groups in the fuel samples and the deposits, using KBr pellets, and the region 400–4000 cm^{-1}.

The UV–vis absorbance measurements were determined for wavelengths ranging from 255 to 450 nm, on a PerkinElmer Lambda 365 UV/VIS spectrophotometer equipped with 1.0 cm quartz cells, to track the color changes of each fuel sample during its thermal-oxidation process. To ensure that the absorbance did not exceed the photometric intensity limit, deeply oxidized base oils were studied after appropriate dilution with the unoxidized fuel. The original oils used as reference solution. 2.4 Gas chromatography-mass spectrometry (GC-MS) Analysis

Gas chromatography-mass spectrometry (GC-MS) analysis. GC-MS was used to characterize the base oils XG-1, XG-2, and XG-3. A trace GC-MS system (Agilent 6890A) was used for the analysis. The instrument was set up to perform GC-electron impact ionization (EI) MS. Positive ions were generated by electron impact ionization (EI) with 70 eV electron energy. A 30 m long, 0.25 mm inner diameter stationary phase column coated with a 0.25 μm thick layer of VF-5MS provided component separation. A 1 μL injection volume was used under the following conditions: the temperature was held at an initial temperature of 60°C, with a hold time of 3 min, ramped at 10°C/min to a final temperature of 230°C/min, and held at this temperatures for 10 min. Helium was used as a carrier gas.

Results and discussion. *Thermal stability of XG-1, XG-2, and XG-3 with antioxidants.* The addition of antioxidants can restrain the oxidative processes of base oils and reduce the generation of oxidative products that are always of low weight and easily evaporate or decompose at elevated temperatures. As shown in Fig 1, similar TGA and DTG curves indicating the homologous thermal–oxidative degradations of XG-1, XG-2, and XG-3, which contain 1 wt% phenolic, diphenylamine or a mixture of these antioxidants (BHT:DPA =1:1), were obtained with heating rates of 10°C/min in an air atmosphere.

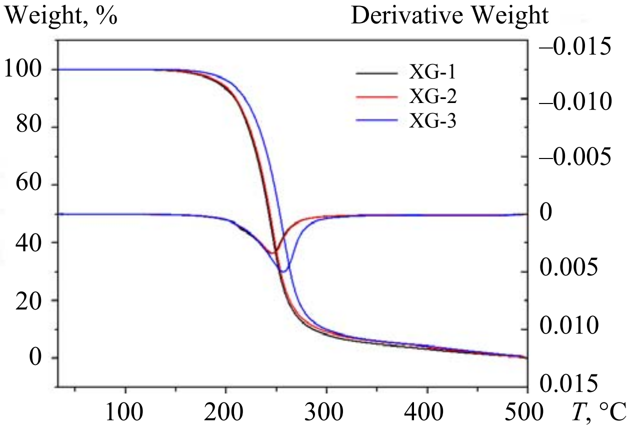


Fig. 1. TGA and DTG curves of XG-1, XG-2, and XG-3.

The decomposition temperature (T_d) which is used to indicate the resistance of the base oils to thermal–oxidative degradation is designated from the intersection of the extrapolated baseline and the tangent line of the curve with maximum slope (TGA curve). The T_d of base oils is increased to different levels with the addition of different antioxidants [29]. The T_d values of XG-1and XG-2 are 217 and 218°C with the single addition of BHT or DPA, respectively. However, XG-3, with the introduction of mixed antioxidants (BHT:DPA = 1:1), exhibited an improved T_d of 228°C. All these data demonstrate that the addition of antioxidants causes an obvious enhancement in the thermal–oxidative resistance of base oils, and mixed antioxidants result in better thermal–oxidative resistance than phenolic or diphenylamine antioxidants alone.

The maximum degradation temperature (T_m) is defined as the degradation temperature corresponding to the maximum weight loss rate in the DTG curve (Table 1). It can be observed that the TGA curves shifted toward higher temperatures as the heating rate increases for XG-1, XG-2, and XG-3 with 1 wt% antioxidants. The T_d temperatures of all the samples also increased with increasing heating rate (Fig. 2). This can be attributed to the fact that the sample spends a longer time at a certain temperature with lower heating rates, in other words, with a longer residence time at a particular temperature, more degradation will occur before the sample reaches the next temperature zone [20, 28].

TABLE 1. TGA and DTG results of XG-1, XG-2, and XG-3

Heating rate, °C/min	XG-1		XG-2		XG-3	
	T_d	T_m	T_d	T_m	T_d	T_m
10	217	245	218	245	228	255
20	233	264	224	252	234	264
30	253	285	225	253	237	271

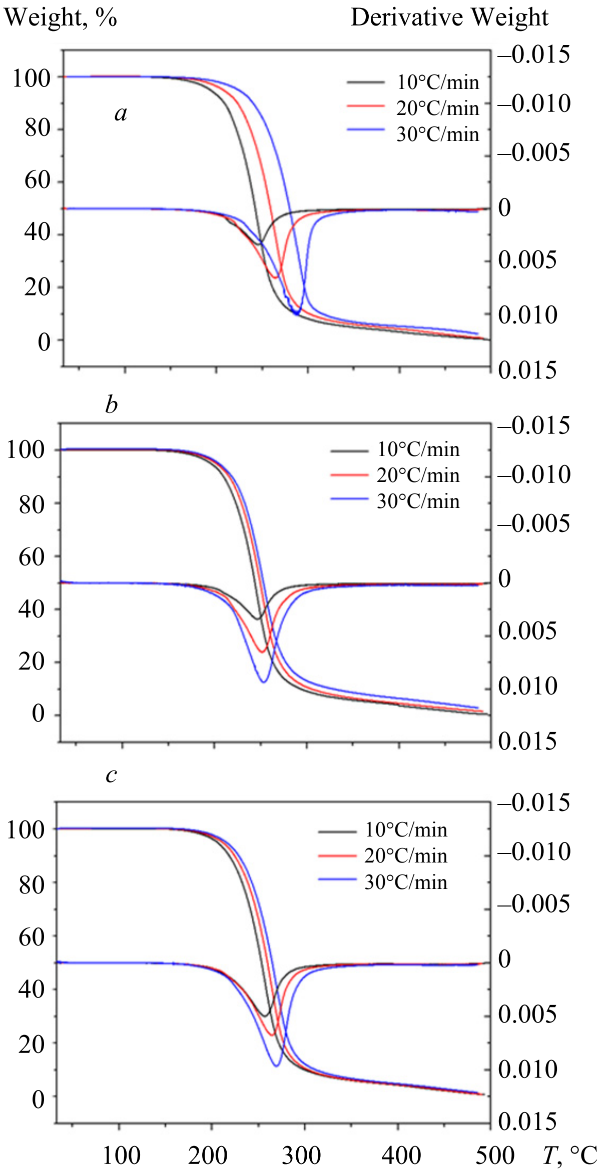


Fig. 2. TGA and DTG curves for XG-1 (a), XG-2 (b), and XG-3 (c) at different heating rates.

Infrared spectroscopy analyses. The FT-IR spectra for oxidation of the samples at different temperatures are shown in Fig. 3. Here, the absorption at 2924 and 2854 cm^{-1} was assigned to stretching vibrations and the bands at 1463 and 1377 cm^{-1} correspond to the deformation vibrations of the CH_3 and CH_2 groups. The absorption at 722 cm^{-1} is due to the rocking vibration of the long alkane chain [30, 31]. Accordingly, it is confirmed that the main components in the base oils are alkanes with long molecular chains. The absorptions at 1295 and 1156 cm^{-1} was attributed to the stretching vibration of C–O bonds. As a characteristic peak of oxidation, the strong ν(C=O) stretching vibration centered at 1716–1720 cm^{-1} was accompanied by another peak centered at 1780 cm^{-1}, which emerged obviously and increased rapidly after XG-1, XG-2, and XG-3, respectively. The appearance of the peak at 1716–1720 cm^{-1} was likely due to the formation and accumulation of aldehydes and ketones, while the 1780 cm^{-1} peak was ascribed, to a large extent, to further oxidized carboxylic acids, esters, lactones, etc. [23, 32].

Therefore, the base oil samples underwent a series of autoxidation reactions in the presence of oxygen. The oxidation processes accelerated with increasing temperature, and the colors of the base oils changed from colorless to orange.

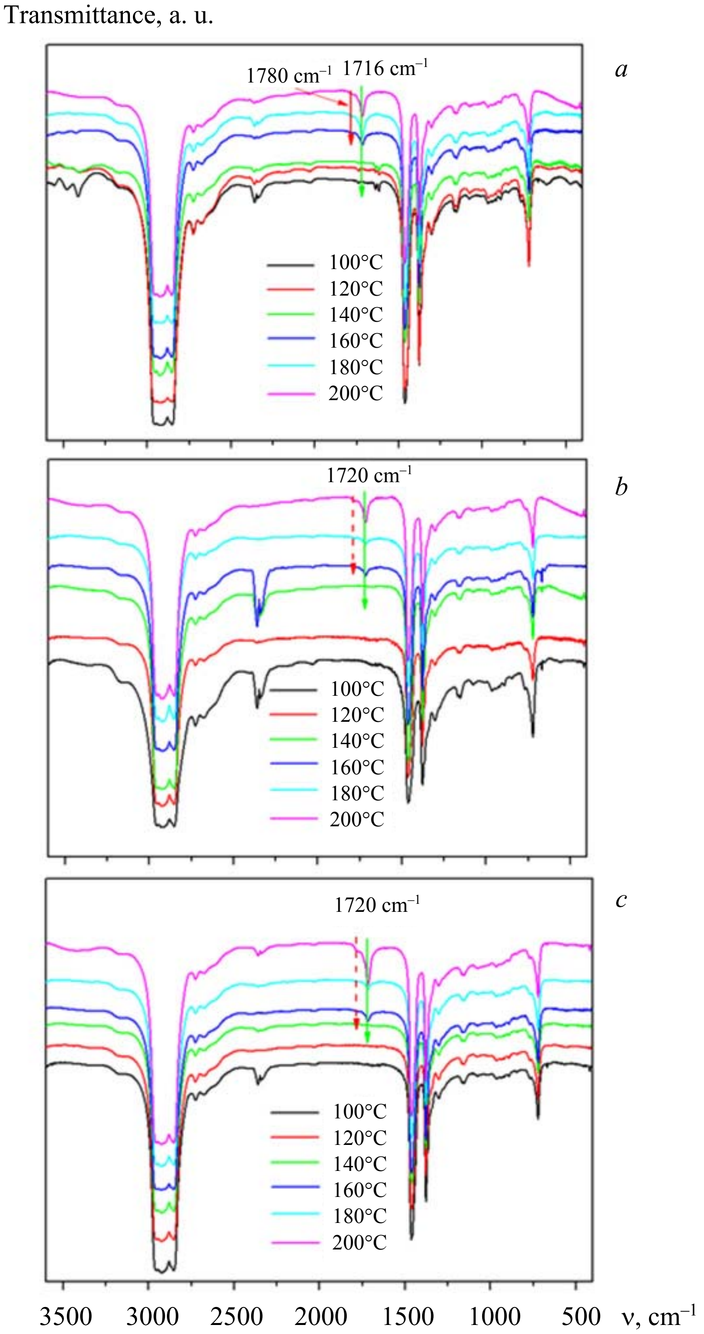


Fig. 3. FT-IR spectra of XG-1 (a), XG-2 (b), and XG-3 (c) after 24 h at different temperatures.

UV–vis spectroscopy analyses. The color changes with temperature for the oxidized base oils of XG-1, XG-2, and XG-3 were analyzed by UV–vis spectroscopy as shown in Fig. 4. The absorption bands at 280–400 nm is characteristic of the n-π^* transition of the carbonyl C=O bonds formed as a result of thermal-oxidation [8]. The intensity of the absorption became stronger at longer oxidation times. With increasing oxidation temperature, the absorption edge shifted slightly to longer wavelengths, and the maximum absorption also underwent a redshift. The color changes of the fuels and the formation of hydroperoxides are both results of autoxidation. It is clearly demonstrated that the UV-vis spectral changes resulted from differences in the extent of oxidation of the oils [33].

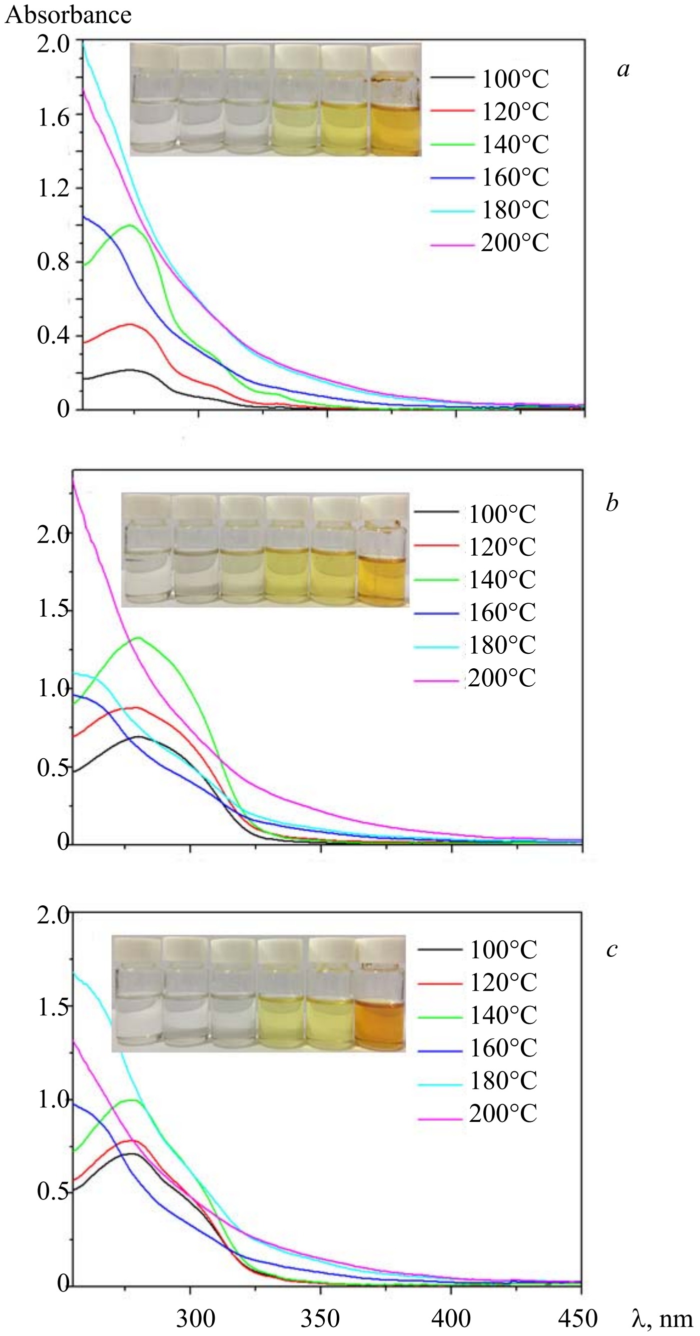


Fig. 4. UV-spectra of XG-1 (a), XG-2 (b), and XG-3 (c) after 24 h at different temperatures.

Gas chromatography mass spectrometry (GC-MS) analysis. GC-MS can indicate the presence of additives and serve as an indicator of additive depletion or decomposition [12, 13, 17, 34–37]. The actual antioxidative stabilization of the base oils XG-1, XG-2, and XG-3 were determined. The GC-MS analysis results clearly show that these base oils are complicated mixtures with hundreds of hydrocarbons. By means of the exact masses and the obtained EI-MS spectra, one phenolic and one amine stabilizer could be identified in Fig. 5. For the phenolic compound, a comparison of the obtained EI-MS spectrum with that from a BHT standard indicates substances with the same constitution. This could be confirmed by the determination of the exact mass, which revealed the molecular formula $C_{15}H_{24}O$. For the aminic antioxidants the structures were suggested by an EI spectral library (Fig. 5) and could be confirmed subsequently with the exact masses obtained from EI-MS measurements.

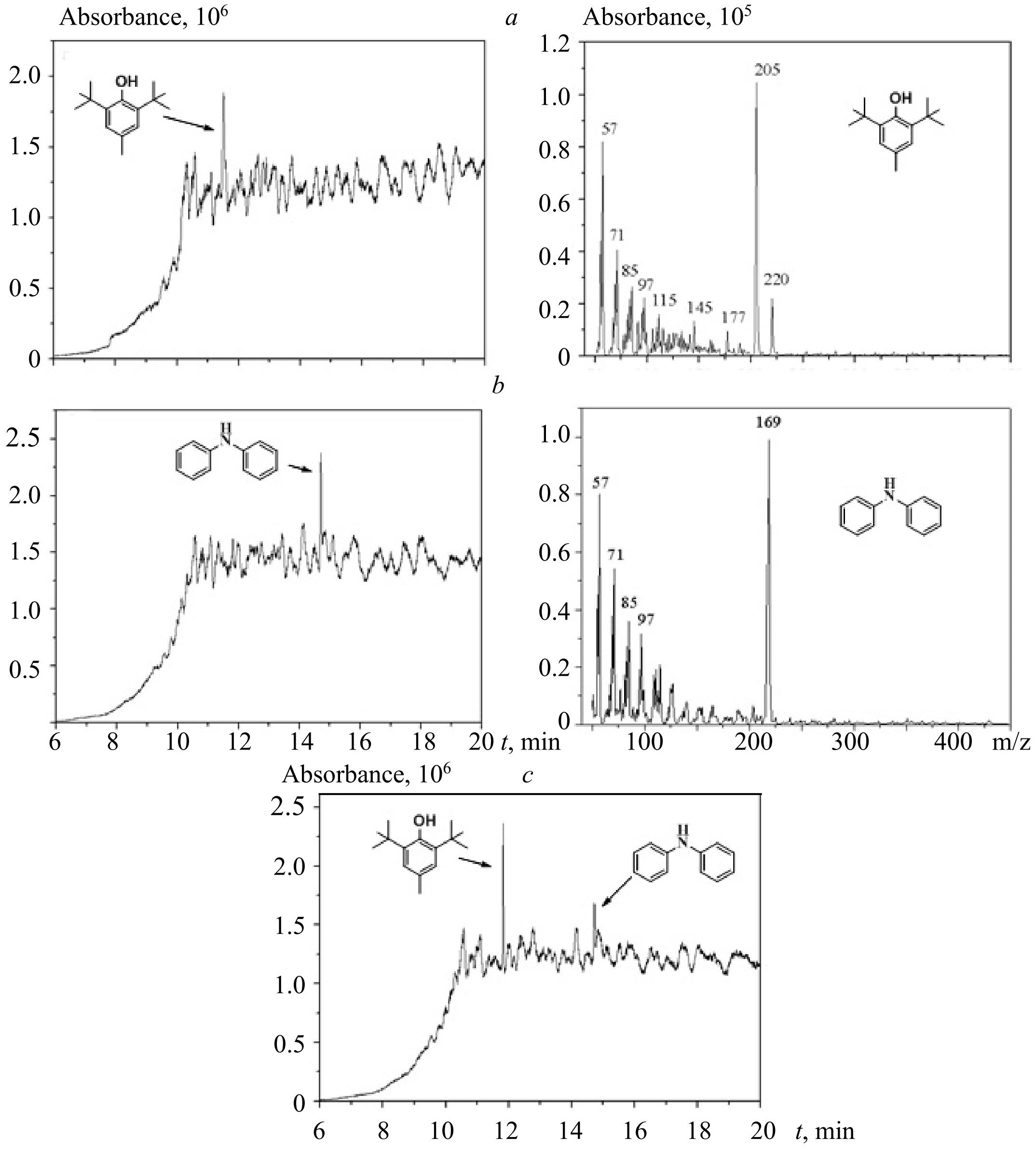


Fig. 5. GC-MS spectra of XG-1 (a), XG-2 (b), and XG-3 (c).

The chemical protection mechanism for primary antioxidants results from their ability to act as hydrogen donors. This enables them to trap alkyl and peroxy alkyl radicals, formed in the oil due to oxidation under standard-usage conditions and therefore inhibits the oxidative degradation of the oil. This reaction leads to the transformation of the phenolic (or aminic) compound to the corresponding phenoxyl (or amino) radical [15].

Conclusions. In this work, the thermal–oxidative degradation behaviors of the base oil 150N with aromatic antioxidants 2,6-di-tert-butyl-4-methylphenol (BHT) and diphenylamine (DPA) were studied. The antioxidant character of the base oil 150N was used to evaluate via reaction temperatures and the different oxidation stages observed during the course of oxidation. The oxidation processes monitored by UV–vis absorption spectra, infrared spectroscopy and GC-MS. The oxygenated products formed in the oxidized oils indicated that hydroperoxides, as the intermediates of the autoxidation reactions, have substantial impacts on the thermal-oxidation stability of oils.

REFERENCES

1. L. R. Rudnick, *Lubricant Additives Chemistry and Applications*, 2nd ed., Taylor & Francis Group (2009).
2. J. M. Herdan, *Lubric. Sci.*, **9**, No. 2, 161–172 (1997).
3. X. Maleville, D. Faure, A. Legros, J. C. Hipeaux, *Lubric. Sci.*, **9**, No. 1, 3–60 (1996).
4. M. A. Keller, C. S. Saba, *Anal. Chem.*, **68**, 3489–3492 (1996).
5. K. U. Ingold, D. A. Pratt, *Chem. Rev.*, **114**, No. 18, 9022–9046 (2014).
6. A. Adhvaryu, S. Z. Erhan, I. D. Singh, *Lubric. Sci.*, **14**, No. 2, 119–129 (2002).
7. V. J. Gatto, W. E. Moehle, T. W. Cobb, E. R. Schneller, *J. Synth. Lubric.*, **24**, No. 2, 111–124 (2007).
8. G. Kreisberger, C. W. Klampfl, W. W. Buchberger, *Energy Fuels*, **30**, No. 9, 7638–7645 (2016).
9. A. Mustafa, J. J. Verendel, C. Turner, P. Wiklund, *Ind. Eng. Chem. Res.*, **53**, No. 49, 19028–19033 (2014).
10. M. Bernabei, G. B. R. Seclı, *J. Microcolumn Sep.*, **12**, No. 11, 585–592 (2000).
11. Y. Jin, H. Duan, L. Wei, B. Cheng, S. Chen, S. Zhan, J. Li, *Lubric. Sci.*, **31**, No. 6, 252–261 (2019).
12. I. Ahmad, J. Ullah, M. Ishaq, H. Khan, R. Khan, W. Ahmad, K. Gul, *Energy Fuels*, **31**, No. 7, 7653–7661 (2017).
13. M. del Nogal Sanchez, P. Glanzer, J. L. Perez Pavon, C. Garcia Pinto, B. Moreno Cordero, *Anal. Bioanal. Chem.*, **398**, No. 7-8, 3215–3224 (2010).
14. X. Qian, Y. Xiang, H. Shang, B. Cheng, S. Zhan, J. Li, *Friction*, **4**, No. 1, 29–38 (2016).
15. C. Miao, D. Yu, L. Huang, S. Zhang, L. Yu, P. Zhang, *Ind. Eng. Chem. Res.*, **55**, No. 7, 1819–1826 (2016).
16. L. Huang, C. Zhou, Y. Zhang, S. Zhang, P. Zhang, *Langmuir: the ACS J. Surfaces and Colloids*, **35**, No. 12, 4342–4352 (2019).
17. M. Frauscher, A. Agocs, C. Besser, A. Rögner, G. Allmaier, N. Dörr, *Energy Fuels*, **34**, No. 3, 2674–2682 (2020).
18. S. Yu, J. Feng, T. Cai, S. Liu, *Ind. Eng. Chem. Res.*, **56**, No. 14, 4196–4204 (2017).
19. A. Singh, R.T. Gandra, E.W. Schneider, S. K. Biswas, *J. Phys. Chem. C*, **117**, No. 4, 1735–1747 (2013).
20. J. Feng, H. Zhao, S. Yue, S. Liu, *ACS Sustain. Chem. Eng.*, **5**, No. 4, 3399–3408 (2017).
21. M. A. D. S. Rios, S. N. Santiago, A. A. L. S. Lopes, S. E. Mazzetto, *Energy Fuels*, **24**, No. 5, 3285–3291 (2010).
22. J. Barret, P. Gijsman, J. Swagten, R. F. M. Lange, *Polym. Degrad. Stab.*, **76**, 441–448 (2002).
23. F. Bär, H. Hopf, M. Knorr, J. Krahl, *Fuel*, **215**, 249–257 (2018).
24. R. P. Caramit, A. G. de Freitas Andrade, J. B. Gomes de Souza, T. A. de Araujo, L. H. Viana, M. A. G. Trindade, V. S. Ferreira, *Fuel*, **105**, 306–313 (2013).
25. J. Chýlková, O. Machalický, M. Tomášková, R. Šelešovská, T. Navrátil, *Anal. Lett.*, **49**, No. 1, 92–106 (2015).
26. S. Kerkering, W. Koch, J. T. Andersson, *Energy Fuels*, **29**, No.2, 793–799 (2015).
27. E. V. Frantsina, A. A. Grinko, N. I. Krivtsova, M. V. Maylin, A. A. Sycheva, *Pet. Sci. Technol.*, **38**, No. 4, 338–344 (2019).
28. J. C. O. Santos, I. M. G. d. Santos, A. G. Souza, E. V. Sobrinho, V. J. Fernandes, A. J. N. Silva, *Fuel*, **83**, No. 17-18, 2393–2399 (2004).
29. M. Chao, W. Li, X. Wang, *Thermochim. Acta*, **591**, 16–21 (2014).
30. D. Li, W. Fang, Y. Xing, Y. Guo, R. Lin, *Fuel*, **87**, No. 15-16, 3286–3291 (2008).
31. G. Geethanjali, K. V. Padmaja, R. B. N. Prasad, *Ind. Eng. Chem. Res.*, **55**, No. 34, 9109–9117 (2016).
32. Y. Gong, L. Guan, X. Feng, J. Zhou, X. Xu, L. Wang, *Energy Fuels*, **31**, 2501–2512 (2017).
33. J. Ma, Y. Fei, N. Wu, S. Sun, Y. Wang, *Asia–Pac. J. Chem. Eng.*, **14**, No. 1, 2273–2289 (2018).
34. R. e. L. Webster, D. J. Evans, P. J. Marriott, *Energy Fuels*, **29**, 2059–2066 (2015).
35. M. Antolovich, D. R. B. Jr, A. G. Bishop, D. Jardine, P. D. Prenzler, K. Robards, *J. Agric. Food Chem.*, **52**, 962–971 (2004).
36. D.W. Johnson, *Applications of Mass Spectrometric Techniques to the Analysis of Fuels and Lubricants*, IntechOpen Groups (2017).
37. T. N. Loegel, R. E. Morris, K. M. Myers, C. J. Katilie, *Energy Fuels*, **28**, No. 10, 6267–6274 (2014).