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SYNERGISM OF STABLE NITROXYL RADICALS AND AMINES DURING THE OXIDATION PROCESS OF MOTOR FUELS AND OILS AT INCREASED TEMPERATURES

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Алкілфенольні основи Манніха (ОМ), перспективні антиокисиданти паливно-мастильних матеріалів, синтезовано конденсацією 2,6-ди-трет-бутилфенолу з формальдегідом і амінами, а також алкілфенолів з діетилентриаміном. Для ОМ і стабільних нітроксильних радикалів методом поглинання кисню встановлено, що при інгібованому окисненні вуглеводнів за високих температур все ще спостерігається синергізм дії стабільних нітроксильних радикалів з нітрогеновмісними сполуками, що мають групи –NH або β-CH< по відношенню до Нітрогену

Ключові слова: основа Манніха, присадка, добавки до палива та мастил; антиоксидант, стабільні нітроксильні радикали

Алкилфенольные основания Манниха (ОМ), являющиеся перспективными антиокисидантами горюче-смазочных материалов (ГСМ), синтезированы конденсацией 2,6-ди-трет-бутилфенола с формальдегидом и аминами и алкилфенолов с диетилентриамином. Для ОМ и стабильных нитроксильных радикалов методом поглощения кислорода установлено, что при ингибированном окислении углеводородов при высоких температурах по-прежнему наблюдается синергизм действия стабильных нитроксильных радикалов с азотсодержащими соединениями, имеющими группы –NH или β-CH< по отношению к азоту

Ключевые слова: основание Манниха, присадка, добавки к топливам и маслам, антиокидант, стабильные нитроксильные радикалы

1. Introduction

Trends in the automobile industry, aimed at reducing the size of machines and mechanisms, as well as environmental problems of motor transport, result in an increase of the requirements for the level of the functional efficiency of fuels and lubricants. Thus, the usage of the special additives and, first of all, oxidation inhibitors (antioxidant substances) is the most progressive and profit-proved way of obtaining high-quality fuels and lubricants, as well as their long-term storage.

The following types of compounds have been most commonly used among the antioxidant additives to fuels and lubricants: dithiophosphates and dithiocarbonates of metals (mainly zinc dithiophosphates), secondary aromatic amines, and hindered alkylphenols. However, each of these types of additives has both advantages and disadvantages. In particular, dithiophosphates and dithiocarbonates of metals together with the antioxidant properties also have anticorrosion and antiwear properties. But these compounds, especially dithiophosphates, have insufficient thermal stability and, consequently, when they are decomposed at increased temperatures (for example, in the area of the piston rings while they are used in motor oils) they lead to the formation of undesirable sediments and deposits.

An essential advantage of alkylphenol and amine antioxidants is that they belong to the ashless additives. And alkylphenol Mannich bases (MB), which are obtained by condensation of the hindered alkylphenols with carbonyl compounds and different amines, are the most promising among the high-temperature oxidation inhibitors of fuels and lubricants. In the composition of such compounds, there are both hindered phenols and amine groups that can significantly enhance antioxidant activity. This fact is important because the Mannich reaction is very simple from the technological point of view and, if necessary, the industrial production of the target products can be arranged on its basis.

Consequently, the study of the influence of the Mannich bases on the processes of fuels and lubricants oxidation and the establishment (at high temperatures) of the synergetic effect of the interaction of stable nitroxyl radicals with amines that contain groups of –NH or β-CH< in relation to Nitrogen is an urgent task. The possibilities of synthesis on the basis of the available reagents of the effective antioxidants for fuels and lubricants that have antioxidant properties at high temperatures (that is, under the normal operating conditions in the engine) are also described in the paper. These results can be used to create new materials (additives to fuels and lubricants), as well as technologies for their manufacture.

2. Literature review and problem statement

Mixtures of nitrogen oxide compounds with aliphatic amines (or alcohols) have been widely used in the processes of the thermo-oxidative inhibition of polyolefins [1]. Nitroxyl radicals (>NO•) mixed with piperidine are extremely effective stabilizers of polymers [2]. Today, nitroxyl radicals very often attract attention of scientists and experts [3]. So, the main areas of their application will be considered. For example, the role of nitroxyl radicals in the radical oxidation of polypropylene was investigated in [4], and in [5] the processes of the microcrystalline cellulose transformation in the presence of these radicals were studied.

The oxidation-reduction potential (redox potential) of nitroxyl radicals was theoretically researched in [6]. In particular, the authors found that nitroxyl radicals of the piperidine series in the oxidation of amines that contain groups –NH or β-CH< in relation to Nitrogen are effective reusable antioxidants due to the possibility of their regeneration [7]. The effect of autocatalysis of nitroxyl radicals in the oxidation of polypropylene [8] was also determined, and in [9] the efficiency of their antioxidant activity in the mixtures with hydroxylamines was shown.

In order to inhibit undesirable radical processes in the cross-polymerization reactions, the authors of the patent [10] used alkoxyamines and hydroxylamine. The basis of the method is the ability of these compositions to form stable nitroxyl radicals during heating (under the conditions of polymerization processes). But this approach cannot be realized when nitroxyl radicals are used in motor fuels and oils, since in this case greater thermal stability of the additives-inhibitors is required.

Nitroxyl radicals (>NO•) are free radical acceptors [11], and, consequently, the possibility of their regeneration is conditioned by the ability of the α-aminoperoxide radical $>N-\overset{|}{C}OO\bullet$ to have oxidation-reduction properties [12]. That is

$$>C(OO\bullet)-NH+>NO\bullet\rightarrow>NOH+>C{=}N-+O_2. \tag{1}$$

$$>CH-CH(OO\bullet)-N<+>NO\bullet\rightarrow>NOH+>C{=}CH-N<+O_2. \tag{2}$$

$$ROO\bullet+>NOH\rightarrow ROOH+>NO\bullet.$$

In order to be able to exhibit regenerative properties (reactions 1 and 2), the ROO• radical must have the –NH or β-CH– groups relative to Nitrogen. Thus, the compositions of stable nitroxyl radicals with amines can be a kind of “repository” of the stabilizers of the oxidation reaction [2].

Similar to amines, phenols can be included in the compositions with nitroxyl radicals. In particular, in the patent [13], in order to block radical reactions in the polymerization processes, it was proposed to use the compositions of hindered phenols with nitroxyl radicals. However, the use of such compositions as additives to fuels and lubricants is considered inappropriate because they have insufficient thermal stability.

Amines, especially in combination with hindered phenols, have good antioxidation properties; for example, in the patent [14] in order to stabilize polyolefins, it was proposed to use a special composition that consists of an antioxidant substance, a stabilizer containing Phosphorus, and an acidic stabilizer containing metal salts. At the same time, the antioxidant is a derivative of the hindered alkylphenol, which composition includes an amino-group. However, this composition also has a significant disadvantage because it is ashy due to the presence of salts of organic acids. In turn, in [15] it was proposed to use macromolecules (alkylated derivatives of phenols and amines) as antioxidants for polymers, fuels and lubricants.

Consequently, according to the information given above, it is appropriate to investigate the influence of stable nitroxyl radicals with amines as additives to motor fuels and oils at increased temperatures that are common when fuels and lubricants are used in internal combustion engines.

3. The aim and objectives of the study

The aim of the research is to determine and study the synergetic effect of stable nitroxyl radicals and amines during the fuels and lubricants oxidation at increased temperatures (~150–200 °C), which are the operating temperatures in internal combustion engines.

So, in order to achieve the research aim, the following tasks were set:

– to synthesize the alkylphenol Mannich bases by condensation of 2,6-di-*tert*-Butylphenol with formaldehyde, ammonia, *n*-toluidine and dibenzylamine;

– to synthesize Mannich bases by condensation of alkylphenols with paraform and diethylenetriamine;

– to determine the induction periods during the oxidation of hydrocarbons of fuels and lubricants at increased temperatures (~200 °C) in the presence of the synthesized tributylamine additives and stable nitroxyl radicals.

4. The investigation of the synergetic phenomenon of stable nitroxyl radicals and amines

4. 1. Objects of research

As the research objects, the following nitroxyl radicals were used: 2,2,6,6-tetramethyl-4-oxopiperidin-1-oxyl (R•) with a melting temperature (t_{mlt}) of 36 °C and di-(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl)-isophthalate (•R•) with t_{mlt}=163 °C [3] (Fig. 1).

As amines, tributylamine (TBA) and alkylphenol Mannich bases were used because nitrogen-containing derivatives of the hindered alkylphenols have been known for a long time as effective antioxidants, including for the use in motor fuels and oils [16]. The choice of the alkylphenol Mannich bases was also conditioned by their effectiveness as high-temperature oxidation inhibitors for fuels and lubricants [17].

The high temperature of the fuels and lubricants usage in internal combustion engines accelerates undesirable oxidation and corrosion processes, which, in turn, reduces the working life of the friction units of mechanisms and causes other technological and environmental problems. Therefore, it is important to create effective compositions of additives, especially those with high-temperature antioxidant properties.

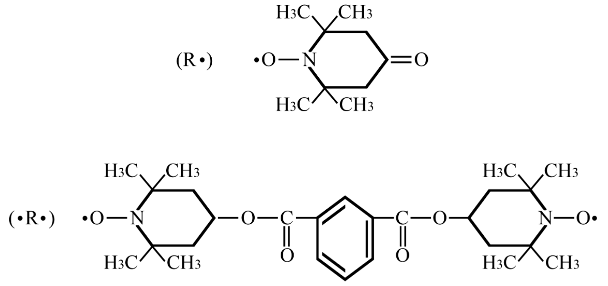

Fig. 1. The chemical formulae of the nitroxyl radicals: 2,2,6,6-tetramethyl-4-oxopiperidin-1-oxyl (R•) and di-(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl)-isophthalate (•R•)

Thus, nitrogen-containing derivatives of 2,6-di-*tert*-Butylphenol and alkylphenols with alkyl radicals C_8–C_{12} have been investigated, namely:

– N-(4-methylphenyl)-N,N-bis-(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine (MB-MPh); melting temperature t_{mlt}=198–199 °C;

– N,N-dibenzyl-N-(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine (MB-DBA); t_{mlt}=90–91 °C;

– tris-(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine (MB-T); t_{mlt}=235 °C [18] (Fig. 2);

– a mixture of condensation products of alkylphenols with paraform and diethylenetriamine (Fig. 3).

As alkylphenols, the following substances were used: 2,6-di-*tert*-Butylphenol (white crystalline needles, melting temperature t_{mlt}=40 °C, boiling temperature (t_{boil}) is 120 °C at the pressure of 2 mm of mercury) and alkylphenols with alkyl radicals C_8–C_{12} that had such isomeric composition, %: paraffin-olefins – 6.0, 2,6-dialkylphenols – 13.0, 2,4-and 2-alkylphenols – 50.0, 4-alkylphenols – 30.0.

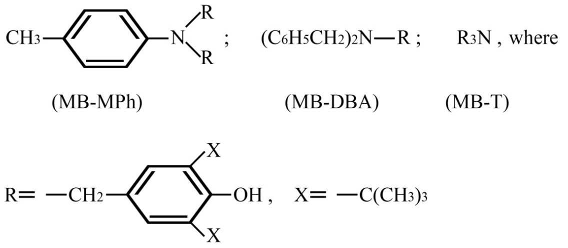

Fig. 2. The chemical formulae of the nitrogen-containing derivatives of 2,6-di-*tert*-Butylphenol and alkylphenols with alkyl radicals C_8–C_{12}: N-(4-methylphenyl)-N, N-bis-(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine (MB-MPh); N,N-dibenzyl-N-(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine (MB-DBA) and tris-(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine (MB-T)

Compounds with *n*-toluidine (MB-MPh) and dibenzylamine (MB-DBA) were synthesized by the method of 2,6-di-*tert*-Butylphenol condensation with formaldehyde and amines [19]; Mannich bases with Ammonia (MB-T) – according to the method [18]. Structures of the synthesized compounds were confirmed by the elemental analysis, as well as by proton magnetic resonance and infrared (IR) spectra.

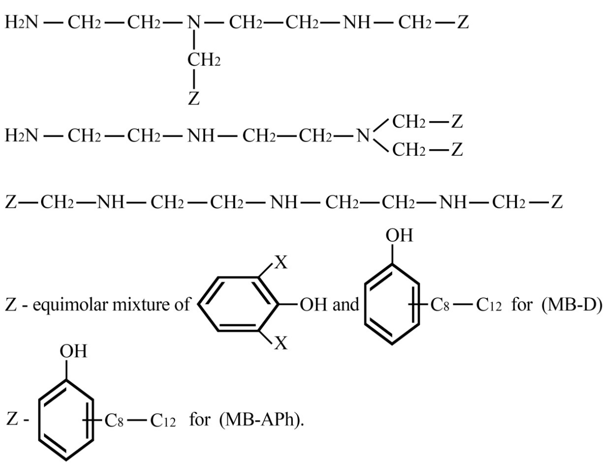

Fig. 3. The chemical formulae of the compounds included in the mixture of the condensation products of alkylphenols with paraform and diethylenetriamine

Consequently, the infrared spectrum for the MB-MPh (tablets of KBr, υ, cm^{-1}) is: 3648 (–OH); 2875–3005 (–CH_2–); 2958 (–CH_3); 1623 (aromatic ring Ar); 756–780 (substituted 1,2,3,5 aromatic ring). In this case, there were no characteristic bands for $ArNH_2$, Ar–NH–R.

Proton magnetic resonance spectrum (in CCl_4 solution), δ, ppm (number of protons, multiplicity, group): 1.41 (36H, s, t-Bu–); 2.25 (3H, s, –CH_3); 3.68 (4H, s, >N–CH_2); 4.89 (2H, s, –OH); 7.12 (4H, s, –Ar); 6.52–7.28 (4H, m, >C_6H_4). Infrared spectra were recorded on the UR-20 spectrometer; proton magnetic resonance spectra – on the Tesla BC-477 spectrometer (60 MHz, internal standard – hexamethyldisilane $C_6H_{18}Si_2$, HMDS).

4. 2. Mannich bases synthesis at the molar ratio of diethylenetriamine:2,6-di-*tert*-Butylphenol (2,6-DTB): alkylphenol C_8–C_{12}:paraform=1:1:1:2 (MB-D)

The method of the target product synthesis was as follows: 20.6 g (0.2 mole) of diethylenetriamine and 41.4 g (0.2 mole) of 2,6-DTB were heated to 60 °C; then 6 g (0.2 mole) of paraform was added in portions. The reaction mixture was thoroughly blended. Then the temperature of the reaction mixture was raised to 120 °C and it was kept in a nitrogen stream for 1 hour. After that, the temperature was raised to 150 °C and the reaction mixture was kept under such conditions for 1 more hour.

The reaction mixture was cooled to 90 °C, 46 g (0.2 mole) of alkylphenol was added and then, while blending and nitrogen barbotage, 6 g (0.2 mole) of paraform was added in portions. The mixture was kept for 2 hours at a temperature of 120 °C and 2 hours – at a temperature of 150 °C. The reaction mixture was vacuumed for 15 minutes at a temperature of 150 °C and a pressure of 2–3 mm of mercury. As a result of the reaction, a transparent, red and brown and very viscous mass was obtained. By the elemental analysis, it was found that % *N*=7.0. Taking into account the molecular weights of 2,6-DTB and alkylphenol, respectively, 207 and 233, it was calculated that % *N*=7.4.

4. 3. Mannich bases synthesis at the molar ratio of diethylenetriamine:alkylphenol:paraform=1:2:2 (MB-APh)

For the Mannich base synthesis, a mixture of 20.6 g (0.2 mole) of diethylenetriamine and 93.2 g (0.4 mole) of alkylphenol was heated to 60–65 °C. Then 12.1 g (0.4 mole) of paraform was added during intensive blending. After that, the temperature of the reaction mixture was raised to 120 °C and the mixture was kept under these conditions for 2 hours. Then the reaction mixture was bubbled by nitrogen, the temperature was increased to 150 °C; the mixture was kept for 2 hours with Dean-Stark attachment (in order to control the reaction by the amount of released water). The reaction mixture was vacuumed for ~0.5 hour (under such conditions: 150 °C, 2–3 mm of mercury). By the elemental analysis, it was found that % *N*=6.8.

5. Methods and results of the investigation of the synergetic effect of stable nitroxyl radicals and amines

The antioxidant properties of the obtained compounds were studied in vaseline oil at a temperature of 200 °C by the method of oxygen absorption. The antioxidant activity of the compounds was estimated by the induction periods in the oxygen absorption kinetics. The induction period of oxidation of the oil with the inhibitor was determined as the time from the beginning of the experiment to the point when the rate of the oxygen absorption reached the initial rate of the uninhibited oil oxidation. This moment was controlled both by the slop angle change of the oxygen absorption kinetic curve and by the sharp temperature change (jump) by several degrees of the oxidizing medium. The kinetics of the oxygen absorption was studied by the manometer with an automatic compensation and recording of spent oxygen [20].

The magnitude of the synergetic effect (f) was calculated by the formula:

$$f = \frac{\tau_{12}}{\tau_1 + \tau_2},$$

where τ_{12}, τ_1 and τ_2 – periods of oxidation induction with a mixture of inhibitors and with each inhibitor separately, min.

The periods of induction of the vaseline oil oxidation at a temperature of 200 °C in the presence of various concentrations of nitroxyl radicals and amines are shown in Table 1.

Table 1

Vaseline oil oxidation in the presence of the inhibitors at a temperature of 200 °C

Experiment number	Oxidation inhibitor	Inhibitor concentration, % mass	Oxidation induction period τ_1, τ_2^*, min.	Oxidation induction period τ_{12}, min.	Synergetic effect magnitude *f*
1	•R•	0.25	33	–	–
2	•R•	0.5	65	–	–
3	R•	0.5	8	–	–
4	MB-MPh	0.25	50	–	–
5	•R•+MB-MPh	0.25+0.25	–	92	1.1
6	MB-DBA	0.25	45	–	–
7	•R•+MB-DBA	0.25+0.25	–	80	1.0
8	MB-T	0.5	65	–	–
9	R•+MB-T	0.5+0.5	–	68	0.9
10	MB-D	0.25	24	–	–
11	•R•+MB-D	0.25+0.25	–	87	1.5
12	MB-APh	0.25	8	–	–
13	MB-APh	0.5	12	–	–
14	•R•+MB-APh	0.25+0.25	–	78	1.9
15	•R•+MB-APh	0.5+0.5	–	160	2.1
16	Tributylamine (TBA)	1.25–10.0	0	–	–
17	•R•+TBA	0.25+10.0	–	40	1.2
18	•R•+TBA	0.25+5.0	–	107	3.2
19	•R•+TBA	0.25+2.5	–	57	1.7
20	•R•+TBA	0.25+1.25	–	23	0,7
21	R•+TBA	0.5+5.0	–	40	5,0

Note: the average values of the induction periods from 3 experiments are given

So, according to the experimental data, there is a synergetic effect of the alkylphenol Mannich bases and TBA with nitroxyl radicals of different structure. However, the magnitude of this effect depends both on the concentration of the substances-inhibitors and on their ratio. For example, for the mixture of •R•+TBA there is an optimum (experiment 18); at the same time, alkylphenol Mannich bases have synergetic effects at much lower concentrations than TBA, in particular, 0.25–0.5 % for Mannich bases and 1.25–10.0 % for TBA.

6. Discussion of the results of the investigation of stable nitroxyl radicals and amines synergy during fuels and lubricants oxidation

In order to confirm the appropriateness and importance of the investigation of antioxidant and synergetic effects of the alkylphenol Mannich bases with amines to create effective compositions of additives to fuels and lubricants (in particular, to motor fuels and oils), the Table 1 data will be analyzed.

It should be noted that synergism was observed only with alkylphenol Mannich bases that contain the group –NH or β-CH< in relation to Nitrogen (experiments 11, 14, 15). However, no synergetic effect was found for Mannich bases that are highly effective oxidation inhibitors because of the hindered phenol group but do not contain the –NH and β-CH< groups (experiments 5, 7, 9).

As can be seen (experiments 14 and 15), the effect of the inhibitors mixture increases significantly with the increase in the concentration of the Mannich base and nitroxyl radical. In particular, for tributylamine, which has no inhibitory effect within the concentration of 1.25–10.0 % during the vaseline oil oxidation at a temperature of 200 °C (experiment 16) in the mixture with nitroxyl radicals (experiments 17–21), the maximum synergetic effect was observed when its concentration was 5 % (experiments 18, 21).

At the same time, an increase in the TBA concentration to 10 % leads to the decrease of the synergetic effect (experiment 17). Perhaps this is due to the fact that the TBA oxidation rate at increased temperatures is sufficiently high and therefore only a part of the α-aminoperoxide radicals is involved in the reduction of the nitroxyl radicals, while the other part continues to participate in the chain oxidation process. The obtained results can be explained by the theory of the action mechanisms of stable nitroxyl radicals, which is presented and discussed in [3].

Thus, the determined synergetic effect makes it possible to create effective antioxidant additives for fuels and lubricants in order to inhibit hydrocarbons oxidation processes and save the original properties of motor fuels and oils. The conducted investigation confirmed the possibility of obtaining synergetic mixtures of nitroxyl radicals and amines, which are Mannich bases. Such mixtures can have antioxidant properties at high temperatures.

The conducted investigations do not allow establishing clear patterns of the influence of the structure and component concentration of Mannich bases on their antioxidant ability. In order to answer these questions, wider investigations that should include more products and experiments with different component ratios are needed. The data from such studies can be used for the development of industrial antioxidants and their production technologies.

7. Conclusions

1. It was determined that during the vaseline oil oxidation at increased temperatures (200 °C), there is a synergetic effect of stable nitroxyl radicals with amines that contain –NH or β-CH< groups in relation to Nitrogen.

2. The magnitude of the synergetic effect for the Mannich bases reaches the value of 2, while for tributylamine – 5, and depends on the structure, concentration and ratio of the inhibitors.

3. The obtained results confirm the appropriateness of further investigations of the alkylphenol Mannich bases in order to create effective compositions of additives to fuel and lubricants (in particular for motor fuels and oils) because they have synergetic effects at significantly lower concentrations than TBA (0.25–0.5 % for Mannich bases versus 1.25–10.0 % for TBA).

References

1. Pat. No. 494396 USSR. A stabilized composition based on the polyolefin [Text] / Aleksandrov, A. L., Kovtun, G. A., Golubev, V. A., Berezin, M. P., Makhonina, L. I. – No. 2037113; declareted: 17.06.1974; published: 03.08.1976, Bul. No. 45.
2. Sakai, K. Effective 2,6-substitution of piperidine nitroxyl radical by carbonyl compound [Text] / K. Sakai, K. Yamada, T. Yamasaki, Y. Kinoshita, F. Mito, H. Utsumi // Tetrahedron. – 2010. – Vol. 66, Issue 13. – P. 2311–2315. doi: 10.1016/j.tet.2010.02.004
3. Rozantsev, E. G. Free iminoxyl radicals [Text] / E. G. Rozantsev. – Moscow: Khimiya, 1970. – 216 p.
4. Fairfull-Smith, K. E. A Novel Profluorescent Dinitroxide for Imaging Polypropylene Degradation [Text] / K. E. Fairfull-Smith, J. P. Blinco, D. J. Keddie, G. A. George, S. E. Bottle // Macromolecules. – 2008. – Vol. 41, Issue 5. – P. 1577–1580. doi: 10.1021/ma701944p
5. Coseri, S. One-shot carboxylation of microcrystalline cellulose in the presence of nitroxyl radicals and sodium periodate [Text] / S. Coseri, G. Biliuta, L. F. Zemljič, J. S. Srndovic, P. T. Larsson, S. Strnad et. al. // RSC Advances. – 2015. – Vol. 5, Issue 104. – P. 85889–85897. doi: 10.1039/c5ra16183e
6. Hodgson, J. L. One-Electron Oxidation and Reduction Potentials of Nitroxide Antioxidants: A Theoretical Study [Text] / J. L. Hodgson, M. Namazian, S. E. Bottle, M. L. Coote // The Journal of Physical Chemistry A. – 2007. – Vol. 111, Issue 51. – P. 13595–13605. doi: 10.1021/jp074250e
7. Kovtun, G. A. Oxidation of aliphatic amines by molecular oxygen. Message 4. Regeneration of inhibitors in the oxidizing tertiary amines [Text] / G. A. Kovtun, A. L. Aleksandrov // Izv. AN SSSR. Ser.: Himiya. – 1974. – Issue 6. – P. 1274–1279.

8. Denisov, E. T. Autocatalysis by the Nitroxyl Radical in the Cyclic Mechanism of Chain Termination in Polymer Oxidation [Text] / E. T. Denisov // Kinetics and Catalysis. – 2016. – Vol. 57, Issue 6. – P. 750–757. doi: 10.1134/s0023158416060057
9. Tikhonov, I. V. Stable nitroxyl radicals and hydroxylamines as inhibitors of methyl linoleate oxidation in micelles [Text] / I. V. Tikhonov, E. M. Pliss, L. I. Borodin, V. D. Sen', T. S. Kuznetsova // Russian Chemical Bulletin. – 2015. – Vol. 64, Issue 10. – P. 2438–2443. doi: 10.1007/s11172-015-1175-0
10. Pat. No. WO2009149001A1. Method for Inhibiting Scorch in Crosslinkable Compositions [Text] / Person T. J., Eaton R. F., Cogen J. M. – No. PCT/US2009/045808; declareted: 01.06.2009; published: 10.10.2009.
11. Stable Radicals: Fundamentals and Applied Aspects of Odd-Electron Compounds [Text] / R. G. Hicks (Ed.). – Chichester: John Wiley and Sons, 2010. – 588 p. doi: 10.1002/9780470666975
12. Bakhturidze, G. Sh. Oxidation of amines by molecular oxygen. Message 9. Liquid-phase oxidation of dimethylamine [Text] / G. Sh. Bakhturidze, A. L. Aleksandrov, I. L. Edilashvili // Izv. AN SSSR. Ser.: Himiya. – 1979. – Issue 3. – P. 515–519.
13. Pat. No. 7683144 B2 USA. Process for Chain Stopping of PVC Polymerization [Text] / Pfaendner R., Wegmann A., Wannemacher T., Braun D. – No. US 10/513,179; declareted: 23.03.2003; published: 23.05.2010.
14. Pat. No. 8008423 B2 USA. Stabilized Polyolefin Compositions [Text] / Kumar V., Kumar R., Dhawan A., Yang S., Cholli A. L. – No. US 12/789,832; declareted: 28.05.2010; published: 30.08.2011.
15. Pat. No. 8710266 B2 USA. Nitrogen and Hindered Phenol Containing Dual Functional Macromolecular Antioxidants: Synthesis, Performances and Applications [Text] / Kumar R., Yang S., Kumar V., Cholli A. L. – No. US 13/298,948; declareted: 17.11.2011; published: 29.04.2014.
16. Kachovec, J. Prehled komercnich antioxidantu. Dodatek k monografii [Text] / J. Kachovec, J. Pospišil // J. Pospišil: Antioxidanty. – 1968. – P. 10.
17. Anisimov, I. G. Fuels, lubricants, technical liquids. Assortment and application [Text]: handbook / I. G. Anisimov, K. M. Badyshtova, S. A. Bnatov et. al.; V. M. Shkol'nikov (Ed.). – izd. 2-e pererab. i dop. – Moscow: Izdatel'skiy tsentr "Tekhinform", 1999. – 596 p.
18. Pat. No. 3173952 USA. Tris-(3,5-Dialkyl-4-hydroxy-benzyl)amines [Text] / Ferrar M. W., Groves W. – published: 16.03.65.
19. Volod'kin, A. A. Spatially hindered phenols. Message 1. Synthesis of some 3,5-di-tert-butylphenol-4-oxybenzamines [Text] / A. A. Volod'kin, V. V. Ershov // Izv. AN SSSR. – 1962. – Issue 2. – P. 343–345.
20. Sanin, P. I. Installation for the oxidation of organic substances with the automatic compensation and registration of consumable oxygen [Text] / P. I. Sanin, L. F. Chernyavskaya, V. V. Sher et. al. // Neftehimiya. – 1966. – Vol. 6, Issue 1. – P. 112–114.