

On Increasing the Efficiency of Amine Antioxidant

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ABSTRACT: The amine antioxidant, Neozon D, was treated to increase its effectiveness in suppressing oxidation of polyethylene in contact with copper. It was found that this antioxidant becomes more efficient after interaction with a copper substrate. These experimental results show that the role of substrate is to catalyze oxidation transforma-

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Key words: oxidation; amine; antioxidant; polyethylene; copper

INTRODUCTION

The problem of polymer interaction (oxidation) when in contact with metals has been extensively studied during the last several decades.^{1–4} We have been examining the inhibition of polymer oxidation when in adhesional contact with metals.^{5–7} It was found that when choosing an antioxidant (AO), it is important to take into consideration both the inhibiting property of the antioxidant towards the polymer and the possibility of interaction between the AO and the metal being a component of the adhesional joint.^{8–10} The results of using an AO, therefore, can be most unexpected. It was found, for example, that contact between polyethylene films and copper substrates accelerated the consumption of phenolic AO thioalcofene MBP (bis-[2-oxy-5-methyl-3-(α -methyl benzyl) phenyl] sulfide). It means that its efficiency dropped.⁶ When polyethylene oxidation was inhibited with an amine AO, for example, Neozon D (phenyl- β -naphthyl amine), in polymer/copper joints, a different (opposite) result was obtained, namely, the efficiency of the AO increased. This was exhibited in the fact that the induction period of oxidation (IPO) of the films on copper substrates was longer than the IPO of the films on inert substrates, for example, glass.⁸ Probably, copper influences the efficiency of both phenolic and amine antioxidant through a direct interaction between the AO and the copper substrate. This study was undertaken to understand whether the increased efficiency of amine AO results from its interaction with copper.

EXPERIMENTAL

Materials

The materials used in our experiments were as follows: powdered high density polyethylene of density 0.950–0.959 g/cm³; melt flow index (MFI) 0.5 g/10 min; molecular weight between 150,000 and 200,000; PE Grade 20,306–05, GOST 16,338–85 (Polimir Co., Novopolotsk, Belarus). To compare the inhibiting efficiency of the antioxidant, two types of them were tested: (1) an amine AO, phenyl- β -naphthyl amine (Neozon D, GOST 39–79, Zavolzhsk, Russia), and (2) a phenolic AO (Irganox XP 620, Ciba Specialty Chemicals, Switzerland).¹¹ The substrates were in the form of copper foil of thickness 100 μ m (Grade M1, Precious Metal-Processing Plant, St. Petersburg, Russia) and glass plates of thickness 3mm (GOST 111–90, Glasswear, Gomel, Belarus). Copper powder of particle size between 5 and 10 μ m (Grade M1, Precious Metal-Processing Plant, St. Petersburg, Russia) was used as a filler for the amine AO. Acetone (dimethylketone, GOST 2603–79, Orgsintez, Kazan, Russia) served as the solvent for the two antioxidants.

Sample preparation

To make inhibited polyethylene films, powdered PE was mixed with one of the two antioxidants (Neozon D or Irganox XP 620). Then acetone was added to the mixture, and it was stirred for 5–7 min in the magnetic mixer to obtain a homogenous suspension. Then the solvent (acetone) was removed by natural evaporation at room temperature during 24 h in a vent hood.

Some experiments were run with Neozon D that had been modified before mixing with the polymer (PE). The modification was carried out as follows. First, the antioxidant (Neozon D) was heat treated at

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150°C for different lengths of time (between 1 and 20 h) in ovens following two schemes:

- I. The antioxidant was poured into a layer 2 mm thick onto the copper substrate (foil). For comparison, a similar layer of the antioxidant was formed on the glass substrate (plate).
- II. The antioxidant was dry mixed with the copper powder (the copper powder made 1 wt % of the mixture), and a layer 2 mm thick was formed on the glass substrate (plate).

After the thermal treatment was complete, the antioxidants on their substrates were removed from the ovens and cooled in air to room temperature. Thus, modified antioxidants were added to the powdered polyethylene in the amounts of 0.1 wt %. The mixture of AO and copper powder (Scheme II of the thermal treatment) was either added to PE as a whole, or the copper powder was first separated from the antioxidant and only the AO was added to PE. In both cases the concentration of AO in the polymer was 0.1 wt %. The copper powder was separated from the antioxidant according to the following procedure. The cooled mixture of AO and copper was removed from the glass plate and poured into a glass vessel, acetone was added in the ratio 1 : 3; the mixture was kept for 15–20 min, and then stirred thoroughly with a glass rod. The solution was then filtered under vacuum using the equipment consisting of Büchner funnel, Bunsen flask (cone), safety funnel, and vacuum pump.¹²

The resultant filtrate (the soluble portion) was put into the vent hood for 48 h at room temperature to remove (evaporate) the solvent (acetone).

The original dry powdered PE and simultaneously dry mixtures of PE and antioxidants were hot molded into test films. The press temperature was 150°C; the length of molding was between 30 and 90 s. The film thickness was 100 μm . These films were used in the experiments.

Testing

To study the oxidation, the prepared films were oxidized on copper substrates (foil) and on KBr plates (these are transparent in the IR-region of the spectrum). The samples were oxidized in air in ovens at 150°C. Maximum exposure lasted 90 h.

To estimate the degree of polymer oxidation, the test samples (i.e., PE films on KBr glass substrates and self-supported films that had been separated (peeled off) from the copper foil) were subjected to IR-spectroscopy analysis. The optical density of the absorption band at 1720 cm^{-1} that refers to carbonyl groups was the measure of oxidation of the samples. The variations in the optical density of the band at 1720 cm^{-1} served as the measure of the length of the IPO of

the samples as well as of the antioxidant's efficiency, as the length of action of the AO coincides approximately with the induction period of polymer oxidation. The IR-spectra were taken using Specord-75 IR (Carl Zeiss, Jena, Germany). The optical density was determined using the baseline procedure.

The IR-spectroscopy technique was also used to understand chemical changes taking place in the molecules of the amine AO in the course of its thermal treatment in contact with the copper substrate. These experiments were conducted with the films prepared as follows. First, mixtures were prepared of PE and an antioxidant (original AO, AO heat treated on copper foil, and AO heat treated on glass substrate); the concentration of the antioxidant in each mixture was 12 wt %. These mixtures were hot molded into films of thickness 50 μm . IR-spectra of the self-supported films were taken, and the variations in the intensity of absorption bands referring to the AO were analyzed.

In the course of testing, the content of copper in the filtrate obtained from the mixtures of AO and copper powder was determined. To do this, the resultant AO powder was ashed (burned) in the muffle furnace; the ash residue was cooled and used in the polarography analysis. Greater details of the analysis can be found elsewhere.¹³

Five samples of every type were tested in every experiment; the relative errors of measurements did not exceed 7%.

RESULTS AND DISCUSSION

Increase in the inhibiting power of amine antioxidant

Results on accumulation of carbonyl groups in the polyethylene films oxidized on catalytically active (copper) and on catalytically inert (KBr) substrates are shown in Figure 1. The uninhibited polyethylene was found to oxidize earlier and the oxidation proceeded faster in contact with copper than in contact with glass (KBr) (Fig. 1, curves 1 and 2). When an antioxidant (either Neozon D or Irganox XP 620) was introduced into the polymer, the IPO increased (Fig. 1, curves 3–6). However, the copper substrate influenced differently the variations in the length of IPO depending on the type of the AO. For the films containing Irganox XP 620, the contact with copper caused the IPO to decrease (Fig. 1, curves 5 and 6), while the films containing Neozon D (amine antioxidant) showed an increased IPO (Fig. 1, curves 3 and 4). In other words, the amine AO introduced (present) in the films oxidized on copper becomes a more effective AO.

It was mentioned above that the interaction between the amine AO and copper substrate can result in a higher efficiency of the AO. To verify this hypothesis, experiments were conducted. The amine AO had been

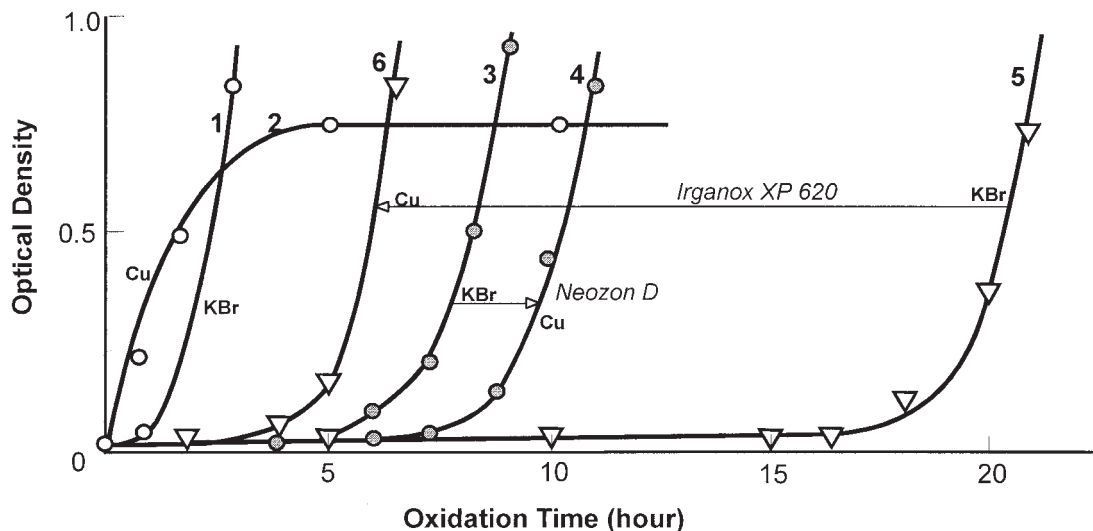


Figure 1 Variations in optical density at 1720 cm^{-1} in IR-spectra of uninhibited polyethylene films (1 and 2) and PE films containing 0.1 wt % of Neozon D (3 and 4) and 0.1 wt % of Irganox XP 620 (5 and 6) versus oxidation time at 150°C in contact with copper (2, 4, and 6) and KBr (1, 3, and 5) substrates.

heat treated in contact with copper foil (substrate) or separately in contact with copper powder (in "Experimental" section, the Schemes I and II, respectively).

Thermal treatment of amine AO on copper substrate (foil)

The results of research into oxidation of polyethylene containing the amine AO that had been heat

treated in contact with copper foil (Scheme I of heat treatment) are shown in Figure 2. The experimental data indicated that the heat treatment of the AO in contact with copper could significantly increase the inhibiting power of the AO. For example, after the AO had been heated for 15 h, the IPO of the polyethylene increased about 7 times (Fig. 2, curves 1 and 4). Longer heating (20 h) of the AO in contact

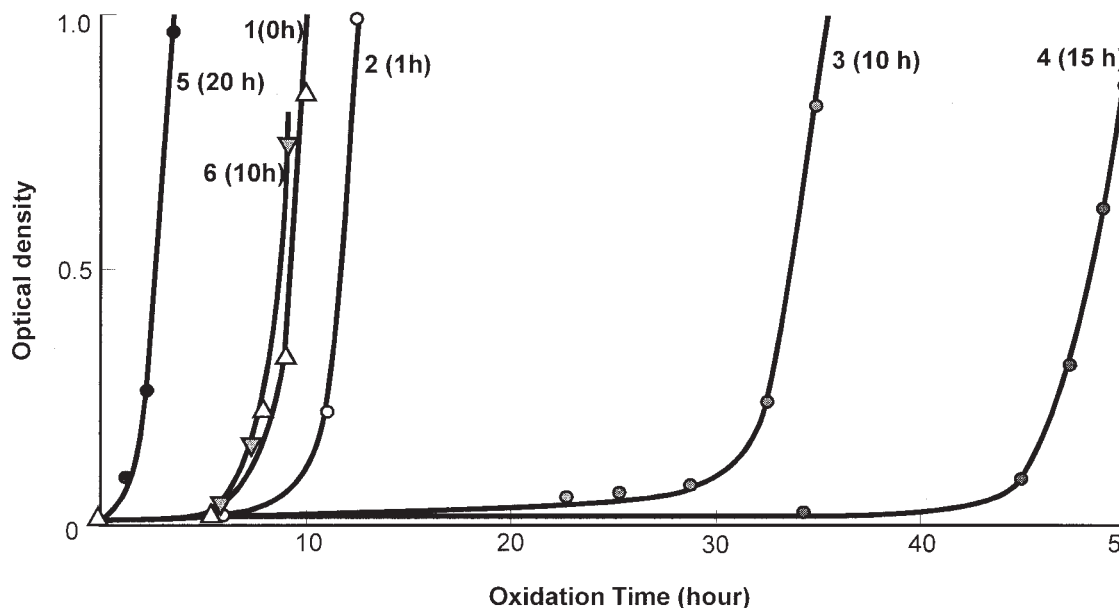


Figure 2 Variations in optical density at 1720 cm^{-1} in IR-spectra of PE films containing 0.1 wt % of Neozon D versus oxidation time at 150°C in contact with KBr substrate. Curve 1, the films contained original AO. Curves 2–5, the films contained AO preliminarily heat treated in contact with copper substrate. Curve 6, the films contained AO preliminarily heat treated in contact with glass substrate. The lengths of heat treatment in hours for AO in contact with substrates at 150°C are indicated on the curves.

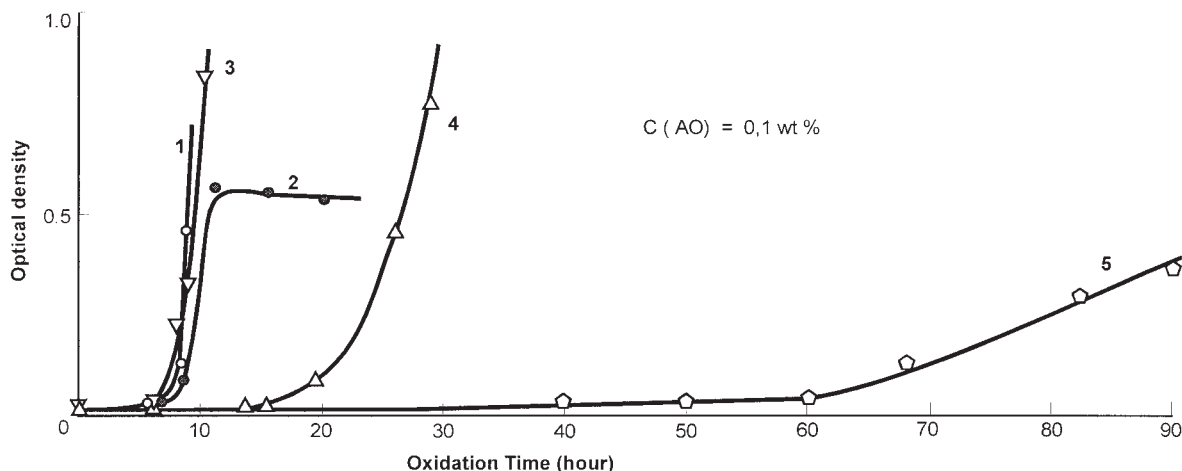


Figure 3 Variations in optical density at 1720 cm^{-1} in IR-spectra of PE films containing 0.1 wt % of Neozon D versus oxidation time at 150°C in contact with KBr substrate. Curve 1, the films contained original AO. Curve 2, the films contained original AO and 10 wt % of copper powder. Curve 3, the polymer contained a mixture of Neozon D/1 wt % copper powder. Curve 4, the polymer contained a mixture of Neozon D/1 wt % copper powder that had been preliminarily heat treated at 150°C for 10 h. Curve 5, the latter mixture was added to the polymer after the copper powder had been removed.

with copper gave an opposite result, that is, the IPO reduced (Fig. 2, curves 1 and 5). Comparing the data in Figure 2, one can see that the dependence of IPO on the length of heat treatment of AO in contact with copper is described by a curve with a maximum.

The heat treatment of the amine AO in contact with glass did not in fact change the length of IPO (Fig. 2, curve 6). Curves 1 and 6 in Figure 2 almost coincide (overlap). We conclude, therefore, that the described variations in IPO (Fig. 2, curves 1–5) are due to chemical changes in the AO when in contact with copper.

Thermal treatment of amine AO in contact with copper powder

We found that the efficiency of Neozon D could be increased by preliminarily treating it when mixed with copper powder (Scheme II of treatment), Figure 3. For example, Neozon D containing 1 wt % of copper powder treated at 150°C for 10 h became much more effective than the original AO; the IPO increased more than two times (Fig. 3, curves 1 and 4). That the inhibiting power of Neozon D did not increase in this case can be explained by the small surface area of the copper particles that had been introduced into the polymer. At 10^{-3} wt % of the copper powder in the polymer (this amount corresponds to 1 wt % of copper in the mixture of copper powder and AO), the specific surface area of the particles (the ratio of surface of the copper particles to the polymer weight) is 10^{-4} – 10^{-5} times smaller than the ratio of the area of the copper foil (substrate) to the polymer weight in the film that didn't contain copper. When the concentration of copper powder (filler) in the polymer containing 0.1 wt %

of Neozon D was increased up to 10 wt %, the kinetic curve of accumulation of carbonyl groups clearly showed an increased IPO as compared with the polyethylene, containing the same amount of AO but free of copper powder (Fig. 3, curves 1 and 2). At equal concentrations of Neozon D (0.1 wt %), the IPO of the polyethylene containing 10 wt % of the copper powder and oxidized in contact with KBr substrate was almost of the same length as the IPO of the initial (unfilled) polymer oxidized in contact with copper substrate (foil) (Fig. 1, curve 4; Fig. 3, curve 2). In both these cases the specific areas of contact between the copper and the polymer are almost the same. The results of our research showed that direct contact between Neozon D and copper powder (preliminary heat treatment of the AO/copper powder mixture) is a more effective way of increasing the inhibiting power of the amine AO as compared with indirect contact (the AO/copper powder mixture is added to the polymer without any preliminary heat treatment).

The efficiency of the antioxidant could be increased still more if the AO was separated from the metal after the AO (Neozon D) copper powder mixture had been heat treated (the procedure of separation of copper powder from AO is described in the "Experimental" section). It was found that the Neozon-D-based antioxidative additive containing 1 wt % of copper as a filler showed higher inhibiting properties after it had been heat treated and the copper powder had been removed from it. The IPO of the polymer was increased here more than three times (Fig. 3, curves 4 and 5). In this case, we explain the variation in the IPO of tested stabilized films by the catalytic effect of copper on polymer oxidation. By removing the copper

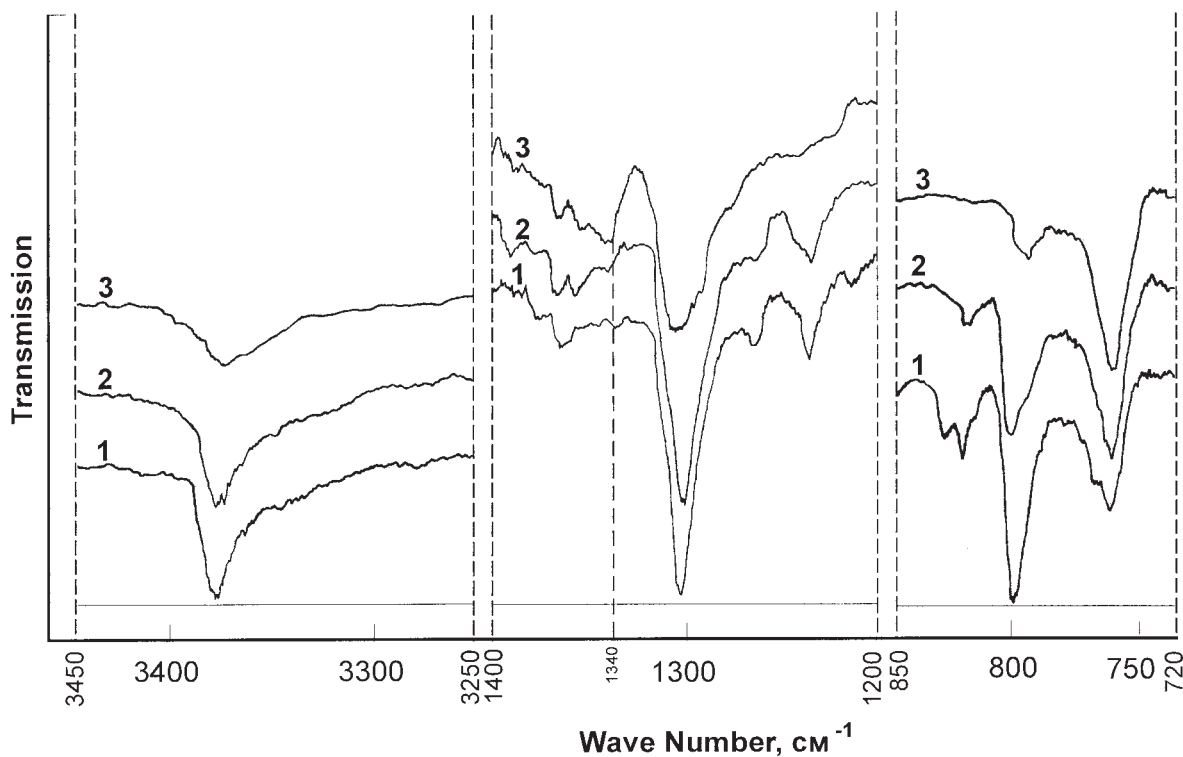


Figure 4 IR-spectra of PE films containing 0.1 wt % of: Neozon D original substance (1); Neozon D was preliminarily heat-treated on glass substrate (2) and on copper substrate (3). The duration of heat treatment was 15 h at 150°C.

powder from the sample, we eliminated the catalytic action of copper upon polymer oxidation; as a result, the length of IPO increased. The experimental results also showed that the filtered solution of AO did not contain copper (i.e., the concentration of the metal in samples was beyond the sensitivity of the instrument, namely, 10^{-5} mg/mL). This indicates that the copper powder was not consumed in the reactions with Neozon D in the course of heat treatment of the mixture. We believe that the copper powder acted as a catalyst toward the oxidative transformation of the amine AO.

Figure 4 shows IR-spectra of polyethylene films containing original AO (Neozon D) and AO heat treated in contact with copper (foil) and glass (plate) substrates. The analysis of these IR-spectra suggests that contact between Neozon D and copper is accompanied by significant chemical transformations of the AO. Oxygen becomes detached from the amine group (the intensity of absorption bands at 800, 1300, 3300–3400 cm^{-1} that refer to valence vibrations of (N–H) bond in primary and secondary aromatic amines), while oxygen from the air becomes attached to the AO to form nitroxyl radicals (the intensity of the absorption band at 1340 cm^{-1} increases) (Fig. 4, IR-spectra 1 and 3). When Neozon D was heat treated in contact with glass, no such chemical changes took place in the AO, and the intensity of the absorption bands within the discussed region of IR-spectra remained constant (Fig. 4, IR-spectra 1 and 2). These results show that

copper, being an active catalyst for oxidative processes,¹⁴ catalyzes oxidative transformations in molecules of the amine AO, thus leading to nitroxyl radicals that possess a higher inhibiting power.¹⁵

CONCLUSION

It appears that increased efficiency of the amine AO (Neozon D) when polymer films were oxidized in contact with copper (foil or powder) is a result of interaction between the AO and the metal. The interaction between the amine AO and copper is catalytic in nature and takes place if these two substances are heat treated when in contact with each other. Therefore, direct contact between Neozon D and copper (the mixture of the AO and copper powder was preliminarily heat treated) seems a more effective way of increasing the inhibiting power of the AO as compared with indirect contact (when the AO/copper powder mixture was introduced into the polymer without preliminary heat treatment).

REFERENCES

1. Rusu, M.; Sofian, N.; Rusu, D. *Polymer Testing* 2001, 20, 409.
2. Arefi-Khonsari, F.; Kurdi, J.; Tatoulian, M.; Amouroux, J. *Surface and Coatings Technology* 2001, 142–144, 437.

3. Favre-Quattropani, L.; Groening, P.; Ramseyer, D.; Schlapbach, L. *Surface and Coatings Technology* 2000, 125, 377.
4. Yiu-gao, Y.; Han-sheng, L.; Min-lian, Zh. *Trans. Tianjin Uniu* 2000, 6, 1.
5. Lin, D. G. *J Appl Polym Sci* 1994, 54, 1789.
6. Lin, D. G.; Vorobieva, E. V. *J of Adhesions Science and Technology* 2003, 17, 179.
7. Lin, D. G.; Vorob'eva, E. V. *Russian J of Applied Chemistry* 2002, 75, 818.
8. Kiriyskin, S. G.; Kovaliov, I. B.; Panchenkov, G. M.; Chebotarevsky, A. E.; Shliapinkov, Y. A. *Plasticheskie massy (Russian Plastics J)* 1982, 5, 55 (in Russian).
9. Gugumus, F. *Polymer Degradation and Stability* 1999, 63, 41.
10. Wagner, H. *Stabilization of PE Against Copper-Catalyzed Thermal Oxidation; MACRO-87: 31st IUPAC Makromol. Symp.; Merseburg* 1987, 133.
11. *Material Safety Data Sheet Directive 91/155/EEC Irganox XP 620 The Simple Solution for Extra Performance; Ciba*; 1998.
12. Rachinsky, F. Y.; Rachinskaya, M. F. *Tekhnica Laboratory Rabot; Khimia: Leningrad*, 1982 (in Russian).
13. Sviridenko, V. G.; Lin, D. G.; Eliseeva, I. M. *Russian J of Analytical Chemistry (Zhurnal analiticheskoi khimii)* 1987, 42, 1525 (in Russian).
14. *Bolshoi Entsiklopedichesky Slovar, (Chemistry: Great Encyclopaedic Dictionary), Bolshaya Rossiyskaya Entsiklopedia; Khimia: Moscow*, 1998 (in Russian).
15. Denisov, E. T.; Sarcisov, O. M.; Likhtenshtein, G. I. *Khimicheskaya kinetika (Chem Kinetics); Khimia: Moscow*, 2000 (in Russian).