

On Increasing the Inhibiting Property of Amine Antioxidant in Contact With Copper and Its Compounds

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ABSTRACT: The mechanism of increasing efficiency of amine-type antioxidant (AO)-*N*-phenyl-2-naphthylamine (Neozon D)—used to inhibit oxidation of polyethylene (PE) under conditions of contact between the polymer and metallic copper has been investigated. It has been learned experimentally, that the hypothesis of formation of complex compounds by reaction of AO and copper-containing products—resulted from contact oxidation of PE melt on copper—is invalid. A different mechanism of raising the inhibiting efficiency of amine AO is suggested, according to which copper catalyzes transformation of Neozon D to nitroxyl radicals. The latter are

excellent inhibitors for oxidative transformations and appreciably enhance polymer resistance to oxidation. An amine-type AO can be converted to nitroxyl radicals in two ways: (i) before AO is added to the polymer; (ii) during direct contact between the AO and metallic copper (i.e., copper as metal) which is a component of the metalopolymeric material (e.g., polymer-coated substrate; filler particles introduced into a polymer) that is subjected to oxidation. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1430–1435, 2010

Key words: polyethylene; oxidation; antioxidant; copper

INTRODUCTION

It is well-known that metals, as well as their compounds, when they are in contact with inhibited polymers usually change the effectiveness of antioxidants (AO). For instance, oxidation of polyethylene (PE), containing phenol-type AO, in contact with copper or its compounds was found to reduce several times the induction period of oxidation (IPO) of the polymer.^{1,2} However, if amine-type AO in PE was used instead of the phenol AO, the IPO did not drop, but on the contrary, it rose under the same conditions of PE oxidation on copper.³

Enhancements in the inhibiting property of aromatic amines in their combination with copper compounds were reported quite long ago.^{4,5} It was found that joint use of *N*-phenyl-2-naphthylamine and copper-II-stearate accelerated decomposition of *n*-decyl-hydroperoxide.⁴ This result led to an idea that new and more effective AO could be produced by blending salts of transition metals (i.e., metals of unstable valency) with inhibitors of free-radical reactions. It was learned, that during oxidation of decane containing Neozon D and copper-II-stearate, AO was consumed quickly, but the IPO of hydrocarbon lasted for quite a long time.⁵ The authors believed

that the initial AO interacted with copper-II-stearate and gave a copper (I) complex with a radical of AO: $Cu(I) \cdot Am^{\bullet}$.⁵ The complex compound of copper formed was an effective inhibitor, which continued to suppress oxidation after the amine-type AO as the inhibitor had been fully consumed. If we assume that in an oxidizable system an AO is consumed only on interaction with copper-II-stearate and stearic acid formed, then an optimal content of AO and copper-II-stearate corresponds to a mole ratio of 2 : 1. Deviations from this ratio will result in a system with residual unreacted AO or copper-II-stearate and stearic acid. The latter two are known to be catalysts for oxidation,^{4,5} and their presence in polymer will decrease the IPO.

This work is aiming at estimating a possibility of applying the above method to enhance effectiveness of amine-type AO during oxidation of PE melt in contact with copper and its compounds.

MATERIALS AND METHODS

Materials

An unstabilized high-density polyethylene (HDPE powder), GOST 16338-85, Specification 20308-005, supplied by Polimir, Belarus, was used in the experiments. The following ingredients were used to prepare polymer (PE)-based compositions.

- Amine-type AO—Neozon D (*N*-phenyl-2-naphthylamine, GOST 39-79, Russia);

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TABLE I
Additives for PE and Compositions for Samples^a

Composition No	Additive and its preparation	Polymer composition
1	None	PE = 100%
2 and 3 ^b	Initial Neozon D	PE = 99.9% Neozon D = 0.1%
4	Mix of Neozon D and powdery copper; copper content = 10 wt %	PE = 89.9% Powdery copper = 10% Neozon D = 0.1%
5	Mix of Neozon D and copper-II-stearate in mole ratio 2 : 1; mix is added to PE with a solvent	PE = 99.755% Copper-II-stearate = 0.145% Neozon D = 0.1%
6	Neozon D heat-treated on copper in air for 10 h at 150°C	PE = 99.9% Modified Neozon D = 0.1%
7	Mix of Neozon D and copper-II-stearate with copper = 1 wt % The mix obtained from acetone solution of the ingredients was heat-treated in air for 10 h at 150°C	PE = 99.89% Additive = 0.11% (including modified Neozon D = 0.1%)
8	Mix of Neozon D and copper-II-stearate with copper = 0.1 wt % Preparation like for Composition 7	PE = 99.899% Additive = 0.101% (including modified Neozon D = 0.1%)
9	Mix of Neozon D and powdery copper (copper content = 1 wt %) Neozon D + acetone is added to the mix; the solvent is removed; the mix is heat-treated in air for 10 h at 150°C	PE = 99.899% Additive = 0.101% (including modified Neozon D = 0.1%)
10	Like with Composition 9; only the copper was removed from the mix before the additive was added to PE	PE = 99.9% Modified Neozon D = 0.1%
11	Neozon D, heat-treated on copper in air at 150°C for different periods of time between 1 h and 20 h	PE = 99.9% Modified Neozon D = 0.1%
12	Like with Composition 10; only thermal treatment at 145° for time periods between 2 h and 20 h	PE = 99.9% Modified Neozon D = 0.1%
13	Like with Composition 10; only thermal treatment at 135° for time periods between 2 h and 12 h	PE = 99.9% Modified Neozon D = 0.1%
14	Like with Composition 10; only thermal treatment at 160° for time periods between 2 h and 6 h	PE = 99.9% Modified Neozon D = 0.1%

^a Film-on-substrate samples were heat formed.

^b Copper substrate was used for Samples 3–14.
KBr was for Sample 2.

- Copper-II-stearate (TU 609-12-15275, Russia);
- Copper powder (GOST 4960-75, Grade M1, particle size of 5 to 10 μm, Russia).
- A solvent—dimethylketone (acetone, GOST 2603-79)—was used to uniformly distribute the components in polymer compositions. Substrates, on which polymer composition samples were oxidized, were KBr crystals and copper foil (Grade M1, GOST 5638-75, Russia).

Experimental techniques

Preparation of samples

Various PE-based compositions tested are listed in Table I. The compositions and samples made from them are numbered. The same numbers of compositions and samples are used through the text. Table I also shows formulations of additives along with

technological regimes of their preparation from initial ingredients.

To make PE-based compositions, some of the additives required special pretreatment. For Compositions 6–14, Neozon D (Compositions 6, 11–14) or its mix with copper powder (Compositions 9 and 10) or with copper-II-stearate (Compositions 7 and 8) were heat-treated in air at 135–165°C.

Some additives in the form of a 1mm-thick-layer were placed either onto an inactive glass substrate (Compositions 7–10) or active copper (Compositions 6, 11–14) and subjected to heat treatment.

The ingredients for Compositions 4 and 5 were mixed by mechanical means. For Compositions 7–10, the mixes of mechanically treated ingredients were put into the solvent and stirred with a magnetic agitator for 3 min. Then the solvent was evaporated at the room temperature (20°C) during 24 h. The dry mixes were treated in air at regimes in Table I.

All of the additives (mixes, modified or initial Neozon D) were introduced into PE powder with a solvent. The suspensions were stirred on a magnetic agitator for 3 min. The solvent was evaporated at the room temperature (20°C) during 24 h.

The dry polymer mixes were hot-pressed (temperature = 150°C; time = 30–90 s) into films of 100 μm thickness. The films were then welded onto substrates (KBr or copper) and the samples obtained were tested for oxidation stability. The tests were run in thermal chambers at 150°C.

Methods

The degree of oxidation of PE films was estimated from IR-spectra. The IR-spectra were recorded on IR-spectrophotometer Specord-75 (Germany) and Fourier spectrometer Vertex -70 (Germany).

The extinction coefficient of absorption band at 1720 cm^{-1} belonging to carbonyl groups was employed as a characteristic of the oxidation degree of PE. The extinction coefficient was found from the ratio of optical density of absorption at 1720 cm^{-1} to the film thickness in cm. The optical density was determined by the datum line method; the absorption band at 1460 cm^{-1} served as a working standard.

The additive effectiveness was characterized by IPO duration of the polymer. The IPO duration was determined from kinetic curves of carbonyl groups accumulated in the PE; it is assumed that the extinction coefficient of 3–4 cm^{-1} corresponds to the moment of IPO completion.

RESULTS AND DISCUSSION

Figure 1 shows oxidation data for PE films inhibited by Neozon D. The films were oxidized on inert (KBr) and active (copper) substrates: Compositions 2 and 3, curves 1 and 2, respectively. It is shown that contact of the polymer with copper increases the IPO. A similar pattern for variation of IPO has been obtained for oxidation of inhibited PE films containing copper powder, Figure 1, curve 3, Composition 4. It can be concluded, therefore, that irrespective of sample type—PE film on copper substrate or PE containing copper powder—contact between copper and PE inhibited by Neozon D causes an enhancement in AO effectiveness.

It is mentioned earlier that enhancement of the inhibiting property of Neozon D in the presence of copper-II-stearate was known earlier^{4,5}; this fact had been investigated for oxidation of systems based on low-molecular weight organic substances. In those works,^{4,5} the increased effectiveness of Neozon D was explained by deactivation of copper ions in the course of formation of complex compounds from

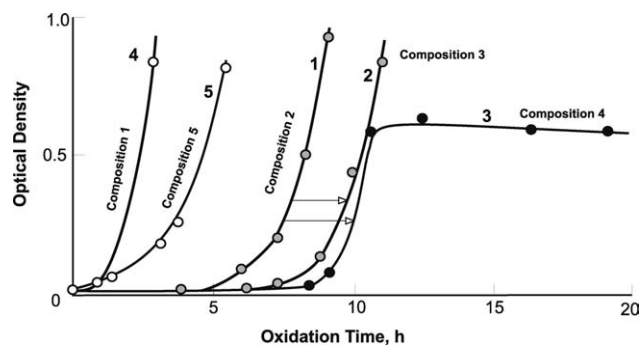


Figure 1 Optical density at 1720 cm^{-1} in IR-spectra of uninhibited polyethylene films (curve 4) and films containing Neozon D = 0.1 wt % (curves 1–3, 5) + copper = 10 wt % (curve 3) versus oxidation time at 150°C on KBr (curves 1, 3–5) and copper (curve 2). Curve 5 stands for PE containing a mix of Neozon D and copper-II-stearate in the ratio of 2 : 1. * Composition numbers are given on curves of Figures 1–3.

copper and AO. It is quite reasonable to hypothesize the same mechanism to act at oxidation of PE, containing Neozon D, in contact with copper: substrate or copper powder. The known fact favors this hypothesis⁶—copper ions get transferred from the substrate into the polymer as carboxylates. The latter, by interacting with AO, can form copper complex compounds that suppress oxidation in the polymer after the initial amine AO has been depleted.

To verify the hypothesis, a mix of Neozon D and copper-II-stearate was prepared with a mole ratio of 2 : 1. This ratio was found to be the best for producing a complex of copper (I) and amine AO. This mix was added to PE in the amount to make Neozon D content in the polymer = 0.1 wt %, Composition 5. The copper content in the film sample was 1.4×10^{-2} wt %. The samples were tested and the result appeared unexpected: the IPO of the polymer wasn't increased; on the contrary, it was reduced, Figure 1, curves 1 and 4. The unusual behavior of PE containing a mix of AO and copper-II-stearate can be explained, in our opinion, by the fact that actually no copper (I) complexes are formed in this case.

Unlike the situation with liquid-phase hydrocarbons,^{4,5} the migration power of modifiers is much lower in polymer melts. To form a complex compound and inhibit polymer oxidation, it is necessary that two molecules of AO be present simultaneously around one copper ion; this is almost impossible with viscous PE melt and low concentrations of AO and copper. That is, formation of copper complex compounds is hardly probable. Under such conditions, modifiers mostly act according to their direct designated purpose: copper-II-stearate catalyzes polymer oxidation; AO, on the contrary, suppresses oxidation. The catalytic effect of copper-II-stearate reduces IPO of the polymer.

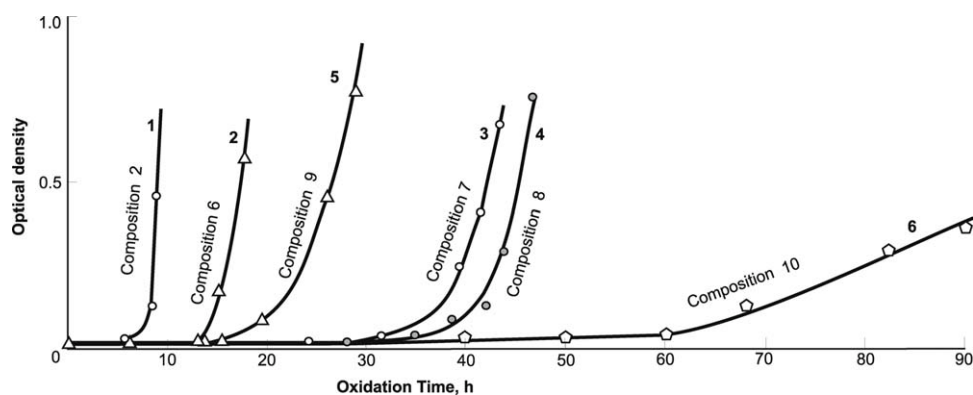


Figure 2 Optical density at 1720 cm^{-1} in IR-spectra of PE films containing Neozon D = 0.1 wt % versus oxidation time on KBr at 150°C . Curve 1 = film containing initial AO (Composition 2); Curve 2 = film contains AO heat pretreated on copper for 10 h at 150°C (Composition 6); Curve 3 = PE contains a mix of Neozon D and copper-II-stearate (copper content = 1.0 wt %) heat-treated at 150°C for 10 h (Composition 7); Curve 4 = PE contains a mix of Neozon D and copper-II-stearate (copper content = 0.1 wt %) heat-treated at 150°C for 10 h (Composition 8); Curve 5 = PE contains AO heat-pretreated in contact with powdery copper (copper content = 1.0 wt %, temperature = 150°C ; time = 10 h), Composition 9; Curve 6 = PE contains additive of Composition 9 from which copper was removed to obtain Composition 10.

A conclusion can be made that enhanced effectiveness of Neozon D—when an inhibited PE is found in contact with copper—is not a result of complex compounds formed by copper and AO; it is a result of some other transformations. We are of opinion that under conditions of PE oxidation on copper, AO does not participate in generation of new complex compounds; it is only transformed into another—more active—product. In this AO transformation, copper acts as a catalyst, not as a reagent.

To check this assumption, an experiment was run as follows. Neozon D was spread over a copper substrate (a layer of about 1 mm thick), subjected to heat treatment in air at 150°C for 10 h and cooled up to 20°C . Then 0.1 wt % of AO was added to PE powder (Table I, Sample 6); the inhibiting property of the modified AO was estimated in terms of IPO-value. It appeared that the thermal pretreatment of AO in air in contact with copper much increased its inhibiting efficiency: IPO of the samples became more than twice longer (Fig. 2, curves 1 and 2).

Similarly, an experiment was run for a mix of AO with copper powder under the same time-and-temperature regimes. After the thermal treatment, the mix of AO and copper was added to the polymer powder; the AO concentration in the polymer was 0.1 wt % (Table I, Composition 9). In this case the AO effectiveness also rose: IPO became longer (Fig. 2, curves 1 and 5). If after the heat treatment of AO+ copper mix, the particles of metal were removed from the mix (Table I, Composition 10), then the additive was introduced into the polymer powder—the enhancement of inhibiting property of AO was more distinct (Fig. 2, curves 5 and 6). The metal particles were removed as follows. The mix of Neozon D and copper powder was first subjected to heat treatment in the air, and then dissolved in ace-

tone. The solution containing suspended copper powder was run through a filter to catch the metal particles. The filtered solution was used to introduce into the polymer in a required concentration of AO. To do this, PE powder was impregnated with the AO+ acetone solution; the suspension was then dried to remove the solvent. The AO concentration in the polymer was 0.1 wt %, Composition 10. The effectiveness of AO, separated from the copper powder after thermal treatment, happened to be higher than AO in mix with copper (Fig. 2, curves 5 and 6). That was because copper added together with AO acted catalytically upon oxidation leading to a shorter IPO.

We have investigated a possibility of increasing the effectiveness of Neozon D by heat treatment in contact with copper-II-stearate. Two versions of mix of Neozon D and copper-II-stearate were prepared; the weight contents of copper were 1.0 wt % (Table I, Composition 7) and 0.1 wt % (Table I, Composition 8). In mole units, the ratios of Neozon D to copper-II-stearate are 24 : 1 (Table I, Composition 7) and 242 : 1 (Table I, Composition 8). The quantities of AO in the mixes were in a high excess in relation to the optimal quantity needed to form complex compounds with copper (2 : 1). A low content of copper-II-stearate was required to suppress at maximum the catalytic effect of the additive upon oxidation after the mix had been added to the polymer. The mixes of AO and copper-II-stearate were heat-treated in air at 150°C for 10 h. Then a solution of modified AO in acetone was prepared and added to the polymer powder. The heat pretreatment of the mixes appeared to appreciably enhance the inhibiting property of Neozon D. The IPO with Composition 7 increased about five times; that with Composition 8, six times (Fig. 2, curves 1, 3, and 4). The

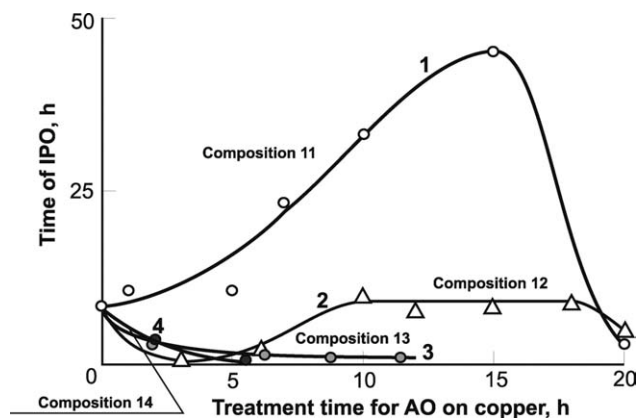
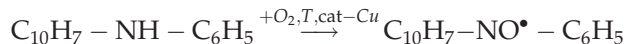


Figure 3 IPO for PE films versus time of heat pretreatment of Neozon D copper at 150°C (1); 145°C (2); 135°C (3) and 160°C (4).

enhancement of AO inhibiting power in this case is not related to copper-containing complexes because a reverse ratio would take place in IPO variation. With a higher copper-II-stearate content in the mix (Composition 7, copper content 1.0 wt %), the quantity of complexes⁵ formed would be greater. For this mix (Composition 7), the degree of increase in IPO would also be higher. In reality, an opposite situation was observed. Maybe Composition 8 (copper content is 0.1 wt %) was more effective owing to lower copper-II-stearate content; as a result, the effect of copper on polymer oxidation was weaker.

The results of the investigations led to an idea of a different mechanism that governs enhancement in the inhibiting property of amine-type AO in contact with copper and its compounds. At a high temperature, free access of oxygen and direct contact with a powerful catalyst of oxidative transformations (e.g., copper⁷), amine compounds (e.g., Neozon D) undergo oxidation and form stable nitroxyl radicals:



When in the polymer mass, nitroxyl radicals terminate many times the chain of oxidative transformations, and for this reason they are extremely good inhibitors of oxidation.^{8,9} The presence, in PE, of newly formed nitroxyl radicals (strong inhibitors of oxidation) in place of Neozon D (a weak inhibitor of oxidation) causes the thermooxidative stability of the polymer to increase and explains enhancement in the inhibiting property of amine-type AO in oxidizable PE, when in contact with copper or its compounds. In other works^{10,11} attempts have been made to transform amine compounds into nitroxyl ones.

In our pattern for AO transformations, copper is the catalyst; to make the catalytic reaction suc-

cessful, contact is a must between the reagents and catalyst. As mentioned above for Composition 5, the ingredients in low concentrations (AO = 0.1 wt %; copper-II-stearate = 0.145 wt %) can hardly touch each other in the viscous melt of PE, i.e., direct contact is unlikely between the amine compound and catalyst for its oxidation. At a direct contact of AO and copper-II-stearate (preparation of additives for Compositions 7 and 8), oxidative transformations of AO become a possibility; nitroxyl radicals are formed; as a result, longer IPO have been observed (Fig. 2, curves 1, 3, and 4). Compositions 3 and 4 have also showed some enhancement in the inhibiting power of amine AO (Fig. 1, curves 1, 2 and 3). In these Compositions, a contact between AO and copper is more likely than in Composition 5 (Fig. 1, curves 1 and 5).

During preparation of the additives for Compositions 6–14, there is a direct contact between AO and copper (powder or foil) or its compounds (e.g., copper-II-stearate), which raises the degree of transformation of AO into nitroxyl radicals.

Catalysis of AO-transformation on copper takes place within a narrow range of time-temperature conditions. Figure 3 shows the time effect of thermal pretreatment—of AO on copper at different temperatures—on AO effectiveness as characterized by IPO-value. The AO thermal treatment at 135°C (curve 3, Composition 13) and 160°C (curve 4, Composition 14) reduces its effectiveness still further. A best temperature for AO thermal treatment is within this interval. The thermal treatment of AO at 150°C can ten times enhance its effectiveness (Fig. 3, curve 1).

So, to transform AO successfully, it is necessary to ensure maximum contact of AO with copper (as a catalyst) and to control the temperature effect.

CONCLUSION

It has been revealed experimentally that effectiveness of amine-type AO at contact oxidation of molten PE with copper increases as a result of oxidative transformation of AO to a more active inhibitor for PE oxidation, namely, nitroxyl radicals. The process of AO transformation to nitroxyl radicals proceeds at a catalytic effect of copper on AO (*N*-phenyl-2-naphthylamine, Neozon D). This process can be carried out before the additive is incorporated into the polymer if AO is heat-treated in contact with metallic copper in air. The inhibiting property of the modified antioxidative additive, in this case, can be much increased if copper is separated from AO before the additive is incorporated into the polymer.

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