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Novel Macromolecular Antioxidants for Industrial Applications in Multiple Sectors

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Antioxidants are used to protect organic materials from degradation during exposure to heat and/or light in the presence of oxygen. Novel macromolecular antioxidants have been developed which provide superior resistance to oxidative degradation to plastics, lubricants, and cooking oils vs. state-of-the-art commercial antioxidants.

Introduction

Auto-oxidation is a well known radical chain process which is the cause of the degradation of a wide range of organic materials, including plastics, elastomers, synthetic fibers, lubricants, and foods (1, 2). Carbon-centered free radicals are produced in the initiation step by the action of heat, light, or mechanical shear on the organic substance:

$$\text{Initiation:} \quad R-H \xrightarrow{heat,light,shear} R\bullet \tag{1}$$

Carbon centered radicals react rapidly with atmospheric oxygen to give a peroxy radical:

$$R\bullet + O_2 \longrightarrow R-O-O\bullet \tag{2}$$

Peroxy radicals readily abstract hydrogen from the substrate, producing a hydroperoxide and a new carbon-centered radical which serves to propagate the process:

$$\text{Propagation:} \quad R-O-O\bullet + R-H \longrightarrow R-O-OH + R\bullet \tag{3}$$

In the chain branching steps, decomposition of the hydroperoxide by the action of heat or light, gives two radicals, each of which can reinitiate the process by abstraction of hydrogen from the substrate:

$$\text{Branching:} \quad R-O-OH \xrightarrow{heat,light} RO\bullet + HO\bullet \tag{4}$$

$$R-O\bullet + R-H \longrightarrow R-OH + R\bullet \tag{5}$$

$$HO\bullet + R-H \longrightarrow H_2O + R\bullet \tag{6}$$

Alternatively, two peroxy radicals may undergo a termination reaction to give nonradical products:

$$\text{Termination:} \quad 2R-O-O\bullet \longrightarrow R-O-O-R + O_2 \tag{7}$$

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Primary antioxidants inhibit the oxidation process by preventing the propagation reaction (Equation (3)) (3). The abstraction of hydrogen from the primary antioxidant (AH) by the peroxy radical (Equation (8)) is more rapid than the abstraction of hydrogen from the substrate. The antioxidant is also designed so that the radical formed from it is relatively inert and unable to reinitiate the oxidation process.

$$\text{Inhibition:} \quad R-O-O\bullet + AH \longrightarrow R-O-OH + A\bullet \tag{8}$$

Common types of primary antioxidants include hindered phenols (e.g. BHT) and alkylated diphenylamines (e.g. 4,4'-di-*tert*-octyldiphenylamine).

Primary antioxidants are often used in combination with a secondary antioxidant which acts as a peroxide scavenger (Equation (9)) (3). In this way, the chain branching reactions associated with the decomposition of the hydroperoxide can be avoided and superior resistance to oxidation can be achieved. Typical secondary antioxidants include phosphites and thioethers.

$$R-O-OH + P(OR')_3 \longrightarrow R-OH + O = P(OR')_3 \tag{9}$$

This paper reports on the development of novel, macromolecular antioxidants which provide significant improvements in resistance to oxidation in plastics, lubricants, and foods.

Experimental

Control Antioxidants

AO-1: Pentaerythritol tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoate] obtained from Ciba Specialty Chemicals Corporation (Irganox® 1010).

BHT: 2,6-di-*tert*-butyl-4-methylphenol

DODP: 4,4'-di-*tert*-octyldiphenylamine

TBHQ: *tert*-Butyl hydroquinone

Tris(2,4-di-*tert*-butylphenyl)phosphite (secondary antioxidant) was obtained from Aldrich.

Concept and Design of New Antioxidants

The macromolecular antioxidants were prepared, for example, as described in U.S. Patent Application Numbers 2006/0041094 A1, 2006/0041087 A1, 2006/0029706 A1, 2005/0238789 A1, 2004/0214935 A1, and 2003/0230743 A1. The exact chemical identities of the macromolecular antioxidants are trade secrets of Polnox Corporation.

The platforms for design of these molecules are influenced by their structure-activity relationship and application. The design of some of Polnox® antioxidants involves the following concepts. These novel antioxidants have differing molecular weights depending on the suitability of the application.

Consider a multifunctional antioxidant containing two different kinds of active moieties or "warheads" (W1H and W2H), each of which is capable of acting as a hydrogen atom donor to a peroxy radical. With this multifunctional antioxidant there are two possible inhibition reactions (10a) and (10b):

$$\text{Polymer-OO}^{\cdot} + \text{W1H} \longrightarrow \text{Polymer-OOH} + \text{W1}^{\cdot} \tag{10a}$$

$$\text{Polymer-OO}^{\cdot} + \text{W2H} \longrightarrow \text{Polymer-OOH} + \text{W2}^{\cdot} \tag{10b}$$

The antioxidant is designed in such a way that the W1H warhead is much more reactive than the W2H warhead, i.e., $k_{10a} > k_{10b}$. In model oxidation studies conducted with antioxidants having similar warheads, the ratio k_{10a}/k_{10b} is ~ 20.

The radicals derived from warheads W1H and W2H present different levels of reactivity in propagation reaction (11). Once again, there are two possible propagation reactions (11a) and (11b):

$$\text{Polymer-H} + \text{W1} \longrightarrow \text{Polymer}^{\cdot} + \text{W1H} \quad (11a)$$

$$\text{Polymer-H} + \text{W2} \longrightarrow \text{Polymer}^{\cdot} + \text{W2H} \quad (11b)$$

In this multi-functional antioxidant, $W1^{\cdot}$ is much more reactive than W2, i.e., $k_{11a} \gg k_{11b}$. In model studies conducted using antioxidants with similar warheads, only reaction (11a) could be observed.

The undesired propagation reaction (11a) is effectively prevented by a transfer equilibrium reaction (12), which regenerates the highly active antioxidant warhead W1H and gives the stable radical $W2^{\cdot}$ as a by-product:

$$W1^{\cdot} + W2H \rightleftarrows W1H + W2^{\cdot} \quad (12)$$

The commercial antioxidants are normally sacrificial. It means that these molecules become inactive after they participated in the oxidation inhibiting event. On the contrary, the design of new antioxidants suggests (Equation (12)) that some of these antioxidant activities are rejuvenated through W1H while others are sacrificed (W2H) at the same time. The net result is that novel antioxidants provide extended protection.

PNX-1: Macromolecular antioxidant for plastics
PNX-2: Macromolecular antioxidant for plastics
PNX-3: Macromolecular antioxidant for lubricants
PNX-4: Macromolecular antioxidant for cooking oils

Testing in Plastics

Testing of antioxidants was conducted in a commercial-grade polypropylene homopolymer (Pro-fax® PH 350 supplied by Basell USA). The primary antioxidants and other additives (secondary antioxidant and calcium stearate) were incorporated into the polymer by a melt compounding method using a twin-screw extruder at a maximum temperature of 270°C. The resulting formulations were reprocessed four additional times (five times total) to give samples with different thermal histories. The performance of the antioxidants was assessed by measuring the oxidative induction time (OIT) at 200°C per ASTM D 3895.

Testing in Lubricants

Testing of antioxidants was conducted in low-viscosity Group II hydrocarbon (Chevron 220R), Group III hydrocarbon (Chevron 600R), and Group V ester-based (AIR BP 5cSt) lubricant base oils. The antioxidants were dissolved in the lubricant base oils at 200 ppm concentration and the performance assessed by measuring the oxidative induction time (OIT) at 180°C (hydrocarbon oils) or 200°C (ester-based oil) per ASTM D 3895.

Testing in Cooking Oil

Testing of antioxidants was conducted in commercial soybean and canola oils. The antioxidants were dissolved in the oils at 200 ppm concentration and performance was assessed using either the Oxidation Stability Index (OSI) method (AOCS Cd-12b-92 method of American Oil Chemists Association) after heating at 190°C for 36 h or by measuring the free fatty acid (FFA) content of the oil (per ASTM D 5555) as a function of heating time at 190°C.

Results and Discussion

Plastics

Antioxidants are used in plastics to inhibit oxidative degradation during storage, high temperature melt processing operations, and end-use (3). The use of oxidative induction time to assess the oxidative stability of a plastic material is well established in the industry. In the first set of experiments, the oxidative stability of polypropylene samples containing a primary antioxidant and an acid neutralizer after multiple processing histories was determined. The results are summarized in Table 1. The macromolecular antioxidants PNX-1 and PNX-2 provided superior oxidative stability vs. the commercial Control AO-1 as evidenced by the longer oxidative induction times.

A second series of experiments was used in which the secondary antioxidant tris(2,4-di-tert-butylphenyl)phosphite was used in combination with the primary antioxidants and acid neutralizer. The results are summarized in Table 2. Once again, the macromolecular antioxidants PNX-1 and PNX-2 provided superior oxidative stability vs. the commercial Control AO-1 as evidenced by the longer oxidative induction times.

The strong beneficial effect of the secondary antioxidant on the oxidative stability is also apparent from the much longer oxidative induction times observed vs. the first series (Table 1) in which no secondary antioxidant was included. At 200°C, the decomposition of polymer hydroperoxides (Equation (4)) is expected to be rapid and would result in the formation of radicals which would reinitiate the oxidation process (Equations (5)) and (6). Combinations of primary and secondary antioxidants are very effective due to scavenging of both the peroxy radicals (Equation (8)) and the hydroperoxides (Equation (9)).

Lubricants

Antioxidants are used to maintain the properties of lubricants during exposure to high temperatures (4). For example, automotive engine oils contain antioxidants to prevent

Table 1
Oxidative induction time (200°C) of polypropylene after melt processing all formulations contain 0.1% calcium stearate

Formulation	OIT (min) First pass	OIT (min) Third pass	OIT (min) Fifth pass
0.1% PNX-1	37.9	32.6	29.5
0.1% PNX-2	32.9	25.2	23.2
0.1% AO-1 (Control)	12.2	11.6	9.6

Table 2

Oxidative induction time (200°C) of polypropylene after melt processing all formulations contain 0.1% tris(2,4-di-*tert*-butylphenyl)phosphite + 0.1% calcium stearate

Formulation	OIT (min) First pass	OIT (min) Third pass	OIT (min) Fifth pass
0.1% PNX-1	73.3	58.5	44.5
0.1% PNX-2	93.1	68.8	44.3
0.1% AO-1 (Control)	41.9	34.7	24.6

oxidative breakdown under the high temperatures encountered in an internal combustion engine.

The oxidative stabilities of lubricant base oils containing different antioxidants were assessed by measuring the Oxidative Induction Time at 180°C (hydrocarbon oils) or 200°C (ester-based oil). The results are summarized in Table 3. The macromolecular antioxidant PNX-3 provided superior oxidative stability vs. the commercial control phenolic and aminic antioxidants BHT and DODP as demonstrated by the longer oxidative induction times.

Cooking Oils

Antioxidants help to preserve the quality of cooking oil by retarding oxidative degradation at high temperatures, for example during frying operations. The oxidative stability of

Table 3

Oxidative induction time of lubricant base oils

Oil type	Antioxidant	OIT (min)
Group II hydrocarbon (measured at 180°C)	200 ppm BHT	3
	200 ppm DODP	40
	200 ppm PNX-3	117
Group III hydrocarbon (measured at 180°C)	200 ppm BHT	3
	200 ppm DODP	11
	200 ppm PNX-3	45
Group V ester (measured at 200°C)	200 ppm DODP	18
	200 ppm PNX-3	40

Table 4

Oxidation stability index of soybean oil after heating (190°C, 36 h)

Antioxidant	OSI (h)
None	7.8
200 ppm TBHQ	10.8
200 ppm PNX-4	19.2

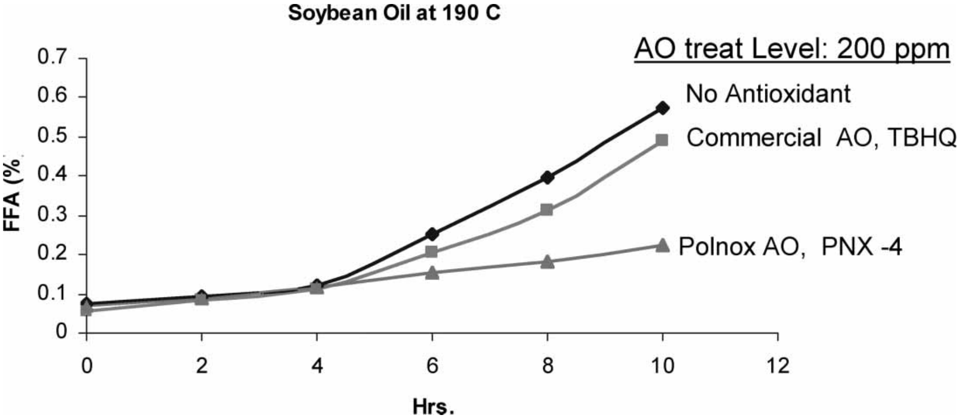

Figure 1. Formation of free fatty acids (FFA) in soybean oil during heating (190°C) as a function of heating time.

soybean oil with and without antioxidants was assessed by measuring the Oxidation Stability Index after heating at 190°C for 36 h to simulate a commercial frying operation. The results are summarized in Table 4. The macromolecular antioxidant PNX-5 provided superior oxidative stability vs. the currently used antioxidant TBHQ.

Oxidative degradation of cooking oils results in the formation of free fatty acids (FFA) which have been linked to health problems (5, 6). In a second experiment, the formation of FFA in soybean oil containing different antioxidants (200 ppm concentration) was measured as a function of heating time at 190°C. As shown in Figure 1, oil stabilized with the macromolecular antioxidant PNX-4 showed superior stability as measured by inhibiting the increase in FFA content.

Conclusions

Novel macromolecular antioxidants have been developed which provide superior resistance to oxidation in plastics, lubricants, and cooking oils as measured by commercially accepted test methods.

References

1. Bolland, J.L. and Gee, G. (1946) *Trans. Faraday Soc.*, 42: 236.
2. Bolland, J.L. (1949) *Q. Rev.* (London); Vol. 3, 1.
3. Schwarzenbach, K., Schmitter, A., Zingg, J., and Kramer, E. (2001) *Antioxidants*. In *Plastic Additives Handbook,* 5th Ed.; Zweifel, H. (ed.); Hanser Gardner Publications: Cincinnati, Ch. 1.
4. Migdal, C.A. (2003) In *Lubricant Additives*, and Rudnick, L.R. (ed.); Marcel Dekker: New York, pp. 1–28.
5. http://www.webmd.com/content/article/62/71539.htm?pagenumber=1(accessed December 2004).
6. http://www.webmd.com/content/article/34/1728_86581.htm (accessed December 2004).