ANTIOXIDANTS, POLYMERS

1. Introduction

Antioxidants are used to retard the reaction of organic materials, such as synthetic polymers, with atmospheric oxygen. Such reaction can cause degradation of the mechanical, aesthetic, and electrical properties of polymers; loss of flavor and development of rancidity in foods; and an increase in the viscosity, acidity, and formation of insolubles in lubricants. The need for antioxidants depends upon the chemical composition of the substrate and the conditions of exposure. Relatively high concentrations of antioxidants are used to stabilize polymers such as natural rubber and polyunsaturated oils. Saturated polymers have greater oxidative stability and require relatively low concentrations of stabilizers. Specialized antioxidants that have been commercialized meet the needs of the industry by extending the useful lives of the many substrates produced under anticipated conditions of exposure. In 2000, ~500 million pounds of antioxidants were sold in polymer applications with a value of $1.3 billion (1). On average, the growth rate of antioxidants is ~4%, roughly tracking the growth of the global polymers markets (2).

2. Mechanism of Uninhibited Autoxidation

The mechanism by which an organic material (RH) undergoes autoxidation involves a free-radical chain reaction is shown below (3–5):

Initiation

$$\mathrm{RH} \longrightarrow \text{free radicals, eg, } \mathrm{R\cdot, ROO\cdot, RO\cdot, HO\cdot} \tag{1}$$

$$\mathrm{ROOH} \longrightarrow \mathrm{RO\cdot} + \mathrm{OH\cdot} \tag{2}$$

$$2\,\mathrm{ROOH} \longrightarrow \mathrm{RO\cdot} + \mathrm{ROO\cdot} + \mathrm{H_2O} \tag{3}$$

$$\mathrm{ROOR} \longrightarrow 2\,\mathrm{RO\cdot} \tag{4}$$

Propagation

$$\mathrm{R\cdot} + \mathrm{O_2} \longrightarrow \mathrm{ROO\cdot} \tag{5}$$

$$\mathrm{ROO\cdot} + \mathrm{RH} \longrightarrow \mathrm{ROOH} + \mathrm{R\cdot} \tag{6}$$

Termination

$$2\,\mathrm{R\cdot} \longrightarrow \mathrm{R{-}R} \tag{7}$$

$$\mathrm{ROO\cdot} + \mathrm{R\cdot} \longrightarrow \mathrm{ROOR} \tag{8}$$

$$2\,\mathrm{ROO\cdot} \longrightarrow \text{nonradical products} \tag{9}$$

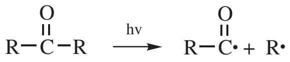
2.1. Initiation.

Free-radical initiators are produced by several processes. The high temperatures and shearing stresses required for compounding, extrusion, and molding of polymeric materials can produce alkyl radicals by homolytic chain cleavage. Oxidatively sensitive substrates can react directly with oxygen, particularly at elevated temperatures, to yield radicals.

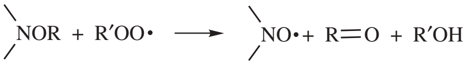
It is virtually impossible to manufacture commercial polymers that do not contain traces of hydroperoxides. The peroxide bond is relatively weak and cleaves homolytically to yield radicals (eqs. 2 and 3). Once oxidation has started, the concentration of hydroperoxides becomes appreciable. The decomposition of hydroperoxides becomes the main source of radical initiators.

The absorption of ultraviolet (uv) light produces radicals by cleavage of hydroperoxides and carbonyl compounds (eqs. 10–12).

$$\mathrm{ROOH} \xrightarrow{h\nu} \mathrm{RO}\cdot + \mathrm{OH}\cdot \tag{10}$$



$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R} \xrightarrow{\mathrm{hv}} \mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}\bullet} + \mathrm{R}\bullet \tag{11}$$



$$\rangle\mathrm{NOR} + \mathrm{R'OO}\bullet \longrightarrow \rangle\mathrm{NO}\bullet + \mathrm{R{=}O} + \mathrm{R'OH} \tag{12}$$

Most polymer degradation caused by the absorption of uv light results from radical-initiated autoxidation.

Direct reaction of oxygen with most organic materials to produce radicals (eq. 13) is very slow at moderate temperatures. Hydrogen-donating antioxidants (AH), particularly those with low oxidation–reduction potentials, can react with oxygen (eq. 14), especially at elevated temperatures (6).

$$\mathrm{RH} + \mathrm{O_2} \longrightarrow \mathrm{R}\cdot + \mathrm{HO_2}\cdot \tag{13}$$

$$\mathrm{AH} + \mathrm{O_2} \longrightarrow \mathrm{A}\cdot + \mathrm{HO_2}\cdot \tag{14}$$

2.2. Propagation.

Propagation reactions (eqs. 5 and 6) can be repeated many times before termination by conversion of an alkyl or peroxy radical to a nonradical species (7). Homolytic decomposition of hydroperoxides produced by propagation reactions increases the rate of initiation by the production of radicals.

The reaction rate of molecular oxygen with alkyl radicals to form peroxy radicals (eq. 5) is much higher than the reaction rate of peroxy radicals with a hydrogen atom of the substrate (eq. 6). The rate of the latter depends on the dissociation energies (Table 1) and the steric accessibility of the various carbon–hydrogen bonds; it is an important factor in determining oxidative stability (8).

Polybutadiene and polyunsaturated fats, that contain allylic hydrogen atoms oxidize more readily than polypropylene, which contains tertiary hydrogen atoms. A linear hydrocarbon such as polyethylene, that has secondary hydrogens is the most stable of these substrates.

Autocatalysis. The oxidation rate at the start of aging is usually low and increases with time. Radicals, produced by the homolytic decomposition of

Table 1. **Dissociation Energies of Carbon–Hydrogen Bonds**[a]

R–H	$D_{\mathrm{R-H}}$ kJ/mol[b]	Bond type
$CH_2{=}CHCH_2{-}H$	356	allylic
$(CH_3)_3C{-}H$	381	tertiary
$(CH_3)_2CH{-}H$	395	secondary

[a] Ref. (8).

[b] To convert kJ to kcal, divide by 4.184.

hydroperoxides and peroxides (eqs. 2–4) accumulated during the propagation and termination steps, initiate new oxidative chain reactions, thereby increasing the oxidation rate.

Metal-Catalyzed Oxidation. Trace quantities of transition metal ions catalyze the decomposition of hydroperoxides to radical species and greatly accelerate the rate of oxidation. Most effective are those metal ions that undergo one-electron transfer reactions, eg, copper, iron, cobalt, and manganese ions (9). The metal catalyst is an active hydroperoxide decomposer in both its higher and its lower oxidation states. In the overall reaction, two molecules of hydroperoxide decompose to peroxy and alkoxy radicals (eq. 5).

$$\mathrm{ROOH} + \mathrm{M}^{n} \longrightarrow \mathrm{ROO}\cdot + \mathrm{M}^{(n-1)+} + \mathrm{H}^{+} \tag{15}$$

$$\mathrm{ROOH} + \mathrm{M}^{(n-1)+} \longrightarrow \mathrm{RO}\cdot + \mathrm{M}^{n+} + \mathrm{OH}^{-} \tag{16}$$

$$2\,\mathrm{ROOH} \longrightarrow \mathrm{ROO}\cdot + \mathrm{RO}\cdot + \mathrm{H_2O} \tag{3}$$

Termination. The conversion of peroxy and alkyl radicals to nonradical species terminates the propagation reactions, thus decreasing the kinetic chain length. Termination reactions (eqs. 7 and 8) are significant when the oxygen concentration is very low, as in polymers with thick cross-sections where the oxidation rate is controlled by the diffusion of oxygen, or in a closed extruder. The combination of alkyl radicals (eq. 7) leads to cross-linking, which causes an undesirable increase in melt viscosity and molecular weight.

3. Radical Scavengers

Hydrogen-donating antioxidants (AH), such as hindered phenols and secondary aromatic amines, inhibit oxidation by competing with the organic substrate (RH) for peroxy radicals. This shortens the kinetic chain length of the propagation reactions.

$$\mathrm{ROO}\cdot + \mathrm{AH} \xrightarrow{k_{17}} \mathrm{ROOH} + \mathrm{A}\cdot \tag{17}$$

$$\mathrm{ROO}\cdot + \mathrm{RH} \xrightarrow{k_{6}} \mathrm{ROOH} + \mathrm{R}\cdot \tag{6}$$

Because k_{17} is $\gg k_6$, hydrogen-donating antioxidants generally can be used at low concentrations. The usual concentrations in saturated thermoplastic polymers range from 0.01 to 0.05%, based on the weight of the polymer. Higher concentrations, ie, ~0.5–2%, are required in substrates that are highly sensitive to oxidation, such as unsaturated elastomers and acrylonitrile–butadiene–styrene (ABS).

3.1. Hindered Phenols. Even a simple monophenolic antioxidant, such as 2,6-di-*tert*-butyl-*p*-cresol [128-37-0] **(1)**, has a complex chemistry in an autooxidizing substrate as seen in Figure 1 (10).

Stilbenequinones such as (**5**) absorb visible light and cause some discoloration. However, upon oxidation phenolic antioxidants impart much less color than aromatic amine antioxidants and are considered to be nondiscoloring and nonstaining.

The effect substitution on the phenolic ring has on activity has been the subject of several studies (11–13). Hindering the phenolic hydroxyl group with at least one bulky alkyl group in the ortho position appears necessary for high

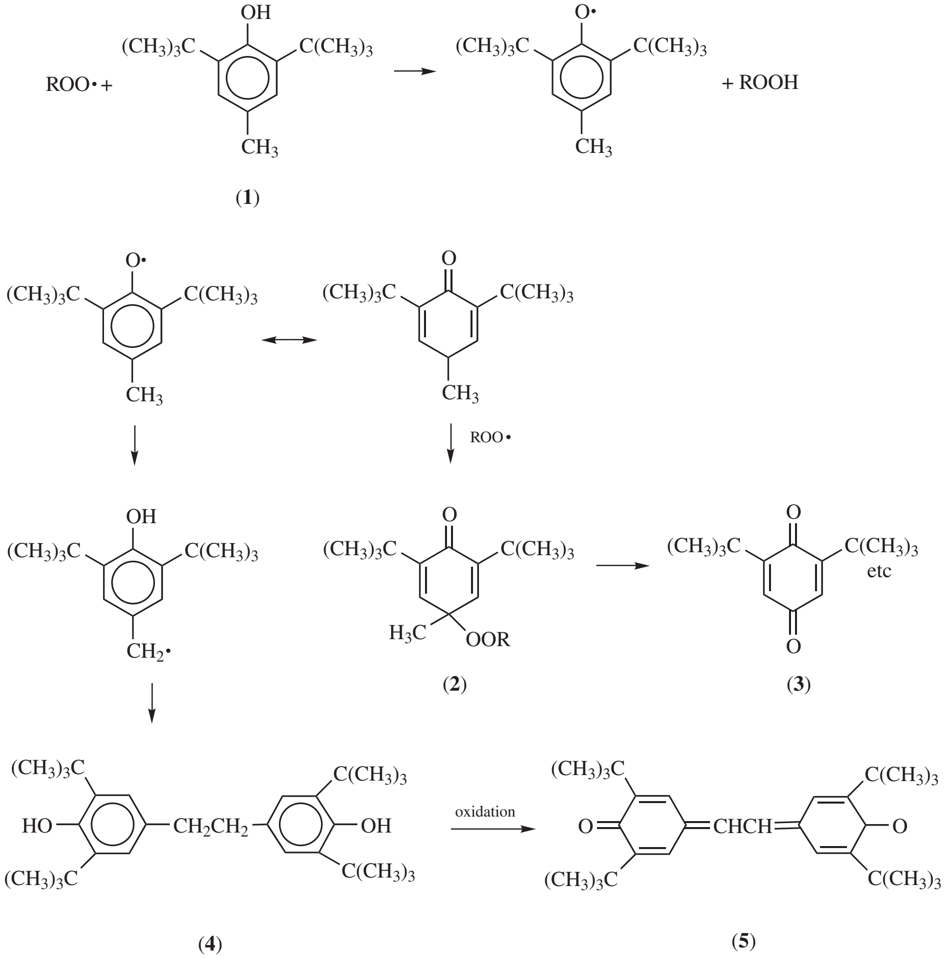


Fig. 1. Chemical transformations of 2,6-di-*tert*-butyl-*p*-cresol in an oxidizing medium (10).

antioxidant activity. Nearly all commercial antioxidants are hindered in this manner. Steric hindrance decreases the ability of a phenoxyl radical to abstract a hydrogen atom from the substrate and thus produces an alkyl radical (14) capable of initiating oxidation (eq. 18).

$$A\cdot + RH \longrightarrow AH + R\cdot \tag{18}$$

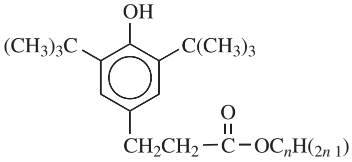
Replacing a methyl with a tertiary alkyl group in the para position usually decreases antioxidant effectiveness. The formation of antioxidants such as (**4**) by dimerization is precluded because all benzylic hydrogen atoms are replaced by methyl groups. A strong electron-withdrawing group on the aromatic ring, like cyano or carboxy, decreases the ability of the phenol to donate its hydrogen atom to a peroxy radical of the substrate and reduces antioxidant effectiveness.

The usefulness of a hindered phenol for a specific application depends on its radical-trapping ability, its solubility in the substrate, and its volatility under test conditions. Table 2 shows the importance of volatility to stabilizer performance. Equimolar quantities of alkyl esters (**6**) of 3,5,di-*tert*-butyl-4-hydroxyhydrocinnamic acid were evaluated in polypropylene (pp) at 140°C using two different procedures (15). When tested in an air stream, only the octadecyl ester (**6**), where $n = 18$, was effective in stabilizing the polymer. Under these conditions, the lower homologues were lost by volatilization. The oxygen-uptake test, carried out in a closed system that minimizes evaporative loss, showed that homologues were effective to varying degrees. The differences in effectiveness can probably be attributed to differences in the solubility of various homologues in the amorphous phase of the pp. When dodecane, a liquid in which all the compounds are soluble, was used as a substrate instead of pp, the antioxidant activities were relatively close.

Table 2. **Influence of Antioxidant (6) Volatility on Effectiveness at 140°C**

		Time to failure in PP, h		
n^a	$t_{1/2}$, h^b	O_2 Uptake	Air stream	Time to failure in dodecane, h
1	0.28	95	2	25
6	3.60	312	2	23
12	83.0	420	2	20
18	660.0	200	165	20

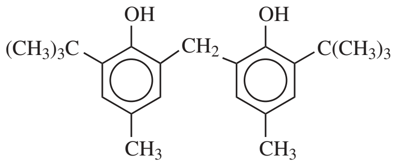
[a] n The letter the number of carbon atom in the ester chain of (**6**).



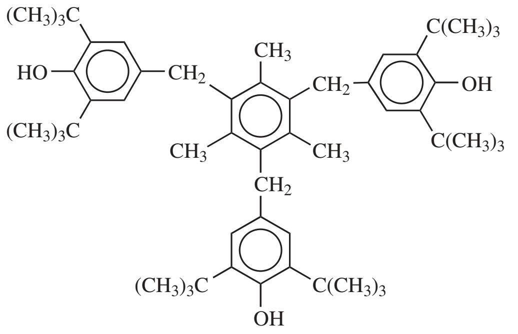
(**6**)

[b] Antioxidant half-life in pp exposed to a nitrogen stream at 140°C.

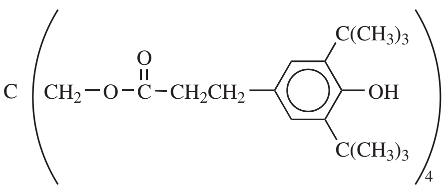
Introducing long aliphatic chains into a stabilizer molecule decreases volatility and increases solubility in hydrocarbon polymers, which improves performance. However, it also increases the equivalent weight of the active moiety. Di-, tri-, and polyphenolic antioxidants combine relatively low equivalent weights with low volatility. Commercially important di-, tri-, and polyphenolic stabilizers include 2,2′-methylenebis(6-*tert*-butyl-*p*-cresol) [85-60-9] (**7**), 1,3,5-trimethyl-2,4,6-tris(3′5′-di-*tert*-butyl-4-hydroxybenzyl)benzene [1709-70-2] (**8**), and tetrakis[methylene(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)]methane [6683-19-8] (**9**).



(**7**)



(**8**)

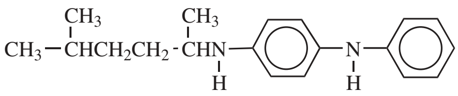


(**9**)

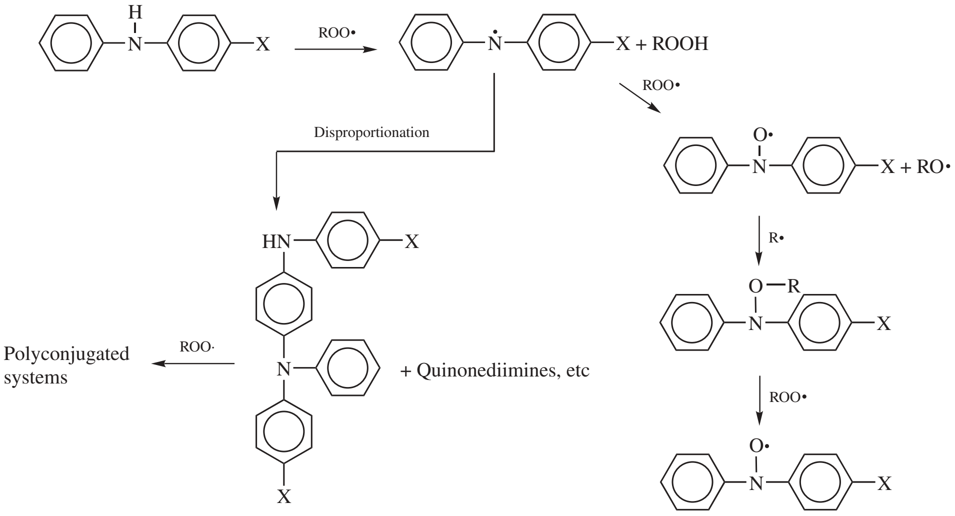
3.2. Aromatic Amines.

Antioxidants derived from *p*-phenylenediamine and diphenylamine are highly effective peroxy radical scavengers. They are more effective than phenolic antioxidants for the stabilization of easily oxidized organic materials, such as unsaturated elastomers. Because of their intense staining effect, derivatives of *p*-phenylenediamine are used primarily for elastomers containing carbon black (qv).

N,N′-Disubstituted-*p*-phenylenediamines, such as *N*-phenyl-*N*′-(1,3-dimethylbutyl)-*p*-phenylenediamine [793-24-8] (**10**), are used in greater quantities than other classes of antioxidants. These products protect unsaturated elastomers against oxidation as well as ozone degradation (see Rubber Chemicals).



(**10**)



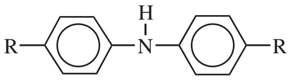
where X = H, NHR′

Fig. 2. Oxidation of aromatic amine antioxidants (**10**).

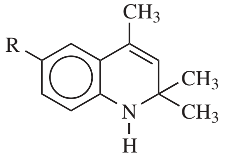
Low concentrations of alkylated paraphenylenediamines such as *N,N′*-di-*sec*-butyl-*p*-phenylenediamine [69796-47-0] *N,N′*-Di-*sec*-butyl-*p*-phenylenediamine [69796-47-0] are added to gasoline to inhibit oxidation.

Figure 2 shows some of the reactions of aromatic amines that contribute to their activity as antioxidants and to their tendency to form highly colored polyconjugated systems.

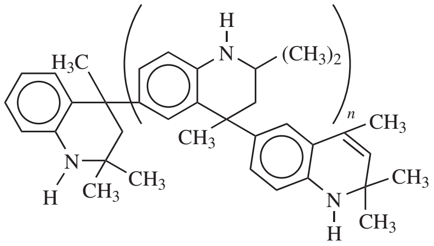
Alkylated diphenylamines (**11**) and derivatives of both dihydroquinoline (**12**) and polymerized 2,2,4-trimethyl-1,2-dihydroquinoline [26780-96-1] (**13**) develop less color than the *p*-phenylenediamines and are classified as semistaining antioxidants. Derivatives of dihydroquinoline are used for the stabilization of animal feed and spices.



(**11**)



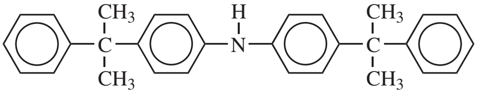
(**12**)



(**13**)

where $n = 0–6$

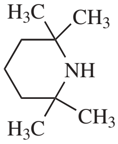
4,4′-Bis(α,α-dimethylbenzyl)diphenylamine [1008-67-1] (**14**) has only a slight tendency to stain and has been recommended for use in plastics as well as elastomers.



(**14**)

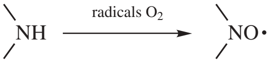
3.3. Hindered Amines. Hindered amines are extremely effective in protecting polyolefins and other polymeric materials against photodegradation. They usually are classified as light stabilizers rather than antioxidants.

Most of the commercial hindered-amine light stabilizers (HALS) are derivatives of 2,2,6,6-tetramethylpiperidine (15) [768-66-1] (16).

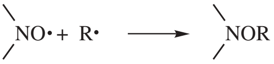


(**15**)

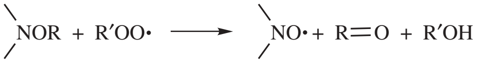
These stabilizers function as light-stable antioxidants to protect polymers. Their antioxidant activity is explained by the following sequence (17):



$$\mathrm{NH} \xrightarrow{\text{radicals } O_2} \mathrm{NO}\cdot$$ (19)



$$\mathrm{NO}\cdot + \mathrm{R}\cdot \longrightarrow \mathrm{NOR}$$ (20)

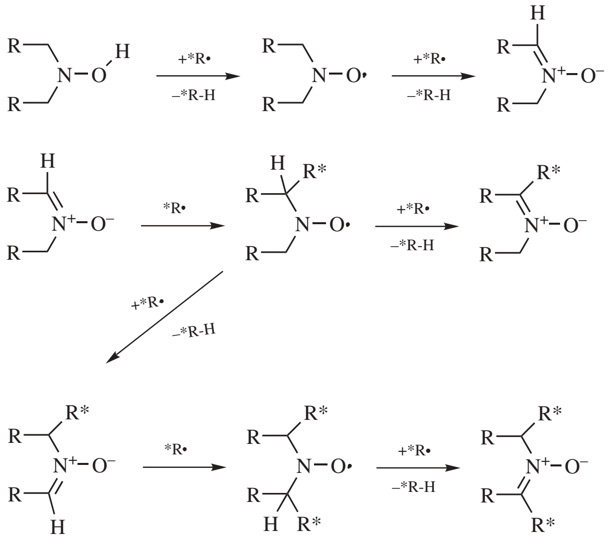


$$\mathrm{NOR} + \mathrm{R'OO}\cdot \longrightarrow \mathrm{NO}\cdot + \mathrm{R{=}O} + \mathrm{R'OH}$$ (21)

According to this mechanism, hindered-amine derivatives terminate propagating reactions (eqs. 5 and 6) by trapping both the alkyl and peroxy radicals. In effect, NO competes with O_2, and NOR competes with RH. Since the nitroxyl radicals are not consumed in the overall reactions, they are effective at low concentrations.

3.4. Hydroxylamines. A relatively new stabilizer chemistry, commercially introduced in 1996 (18), based on the hydroxylamine functionality, can serve as a very powerful hydrogen atom donor and free-radical scavenger (19), as illustrated in Figure 3.

This hydroxylamine chemistry is extremely powerful on an equivalent weight basis in comparison to conventional phenolic antioxidants and phosphite melt-processing stabilizers. However, in terms of it's free-radical scavenger capability, however, it is more effective during melt processing of the polymer, and not during long term thermal stability (ie, below the melting point of the polymer). This finding is quite interesting based on the similarity between the



*R• = alkyl (R•), alkoxy (RO•), or peroxy (ROO•) type radicals

Fig. 3. Free-radical decomposition mechanism for hydroxylamines.

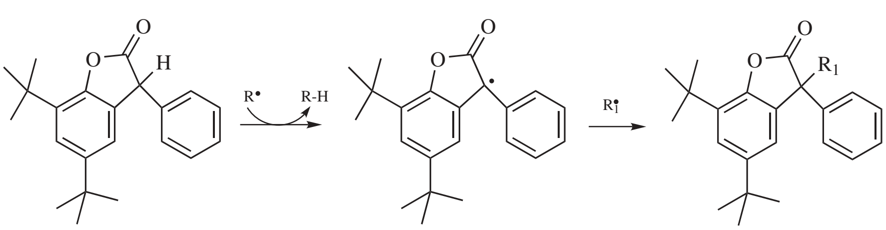
type of free-radical scavenging chemistry that hydroxylamines and phenols are both capable of providing. However, the temperature range is different, which is discussed further below.

The only commercial hydroxylamine product used in polyolefins and other selected polymers is a product by process based on the oxidation of bis tallow amine [14325-92-2].

There is a similar commercially available product based on similar chemistry. It is a product by process based on the oxidation of methyl-bis-tallow amine [204933-93-7]. The oxidation product of the methyl-bis-tallow amine is a trialkylamineoxide, a precursor to hydroxylamine stabilization chemistry. The trialkylamineoxide is converted to a hydroxylamine during the initial melt compounding of the polymer via a Cope elimination reaction, as shown below in equation 22.

$$R_2(CH_3)N^+ - O^- + \text{heat} \longrightarrow R(CH_3)N{-}OH + R{-}CH{=}CH_2 \tag{22}$$

R• = carbon *or* oxygen centered radical



Highly stabilized radical

Fig. 4. Proposed stabilization mechanism of arylbenzofuranones.

3.5. Benzofuranones. In 1997, a fundamentally new chemistry was introduced, that not only inhibits the autoxidation cycle, but attempts to shut it down as soon as it starts (20). The exceptional stabilizer activity of the class of benzofuranones is due to the ready formation of a stable benzofuranyl radical by donation of the weakly bonded benzylic hydrogen atom; see Figure 4.

The resonance stabilized benzofuranyl (lactone) radicals can either reversibly dimerize or react with other free radicals. Model experiments have demonstrated that this class of chemistry behaves as a powerful hydrogen atom donor and are also effective scavengers of carbon centered and oxygen centered free radicals (21); (see Figure 5).

While the sterically hindered phenols react preferentially with oxygen-centered radicals like peroxy and alkoxy rather than with carbon-centered radicals, benzofuranones can scavenge both types of radicals. Accordingly, a benzofuranone, can be repeatedly positioned at key locations around autoxidation cycle to inhibit the proliferation of free radicals. In addition, the scavenging of carbon-centered radicals is representative of a mode of stabilization that is more like “preventive maintenance”, in comparison to more traditional stabilizers such as phenols and phosphites, which operate in something more like a “damage control” mode.

Benzofuranones are similar to hydroxylamines in that on an equivalent weight basis, they are more powerful than conventional phenolic antioxidants or phosphite-based melt-processing stabilizers. Once again, note that even though benzofuranones are capable of providing free-radical scavenging chemistry similar to phenolic antioxidants, the effective temperature domain is typically above the melting point of the polymer; eg, during melt processing (similar to hydroxylamines). This will be discussed further below.

4. Peroxide Decomposers

Thermally induced homolytic decomposition of peroxides and hydroperoxides to free radicals (eqs. 2–4) increases the rate of oxidation. Decomposition to nonradical species removes hydroperoxides as potential sources of oxidation initiators. Most peroxide decomposers are derived from divalent sulfur and trivalent phosphorus.

4.1. Divalent Sulfur Derivatives. A dialkyl ester of thiodipropionic acid (**16**) is capable of decomposing at least 20 mol of hydroperoxide (22). Some of the reactions contributing to the antioxidant activity of these compounds are shown in Figure 6 (23).

According to Figure 6, hydroperoxides are reduced to alcohols, and the sulfide group is oxidized to protonic and Lewis acids by a series of stoichiometric reactions. The sulfinic acid (**21**), sulfonic acid (**23**), sulfur trioxide, and sulfuric acid are capable of catalyzing the decomposition of hydroperoxides to nonradical species.

When used alone at low temperatures, dialkyl thiodipropionates are rather weak antioxidants. However, synergistic mixtures with hindered phenols are highly effective at elevated temperatures and are used extensively to stabilize polyolefins, ABS, impact polystyrene (IPS), and other plastics.

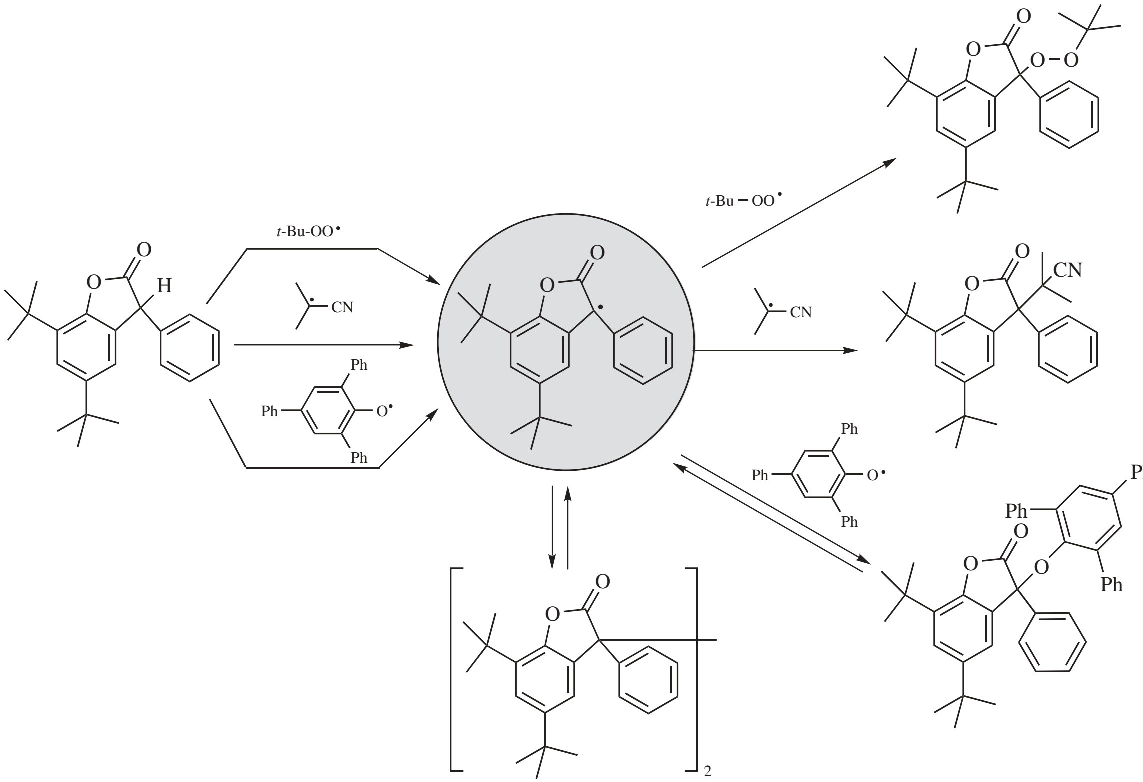


Fig. 5. Carbon-centered free-radical trapping reactions with benzofuranones.

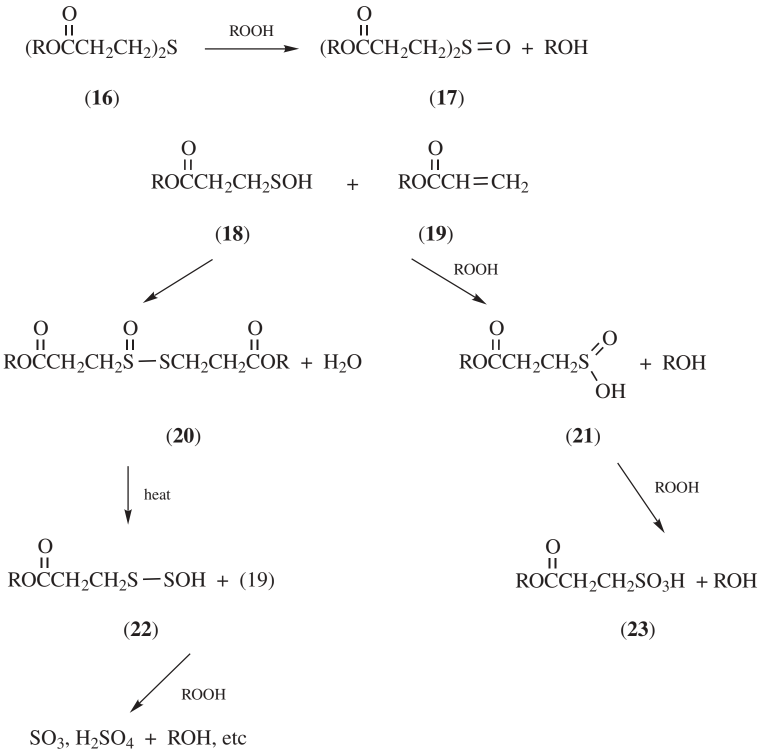


Fig. 6. Decomposition of hydroperoxides by esters of thiodipropionic acid.

Esters of thiopropionic acid tend to decompose at high processing temperatures, and their odor makes them unsuitable for some food-packaging applications.

4.2. Trivalent Phosphorus Compounds.

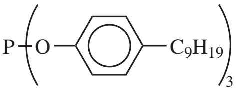
Trivalent phosphorus compounds reduce hydroperoxide to alcohols:

$$\mathrm{ROOH} + \mathrm{PR}'_3 \longrightarrow \mathrm{ROH} + \mathrm{O{=}PR}'_3 \qquad (23)$$

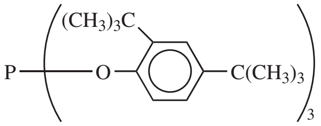
These compounds are used most frequently in combination with hindered phenols for a broad range of applications in rubber and plastics. They are also able to suppress color development caused by oxidation of the substrate and the phenolic antioxidant. Unlike phenols and secondary aromatic amines, phosphorus-based stabilizers generally do not develop colored oxidation products.

Esters of phosphorous acid derived from aliphatic alcohols and unhindered phenols, eg, tris(nonylphenyl)phosphate (**24**), hydrolyze readily and special care must be taken to minimize decomposition by exposure to water or high humidity. The phosphorous acid formed by hydrolysis is corrosive to processing equipment, particularly at high temperatures.

The hydrolysis of phosphites is retarded by the addition of a small amount of a base such as triethanolamine. A more effective approach is the use of hindered phenols for esterification. Relatively good resistance to hydrolysis is shown by two esters derived from hindered phenols: tris(2,4-di-*tert*-butylphenyl)-phosphite [31570-04-4] (**25**) and tetrakis(2,4-di-*tert*-butylphenyl) 4,4′-biphenylenediphosphonite [38613-77-3] (26). A substantial research effort over the last decade to develop hydrolytically stable phosphites while retaining the excellent hydroperoxide decomposing activity has resulted in the introduction of a number of new commercial products such as the dicumyl phosphite [154862-43-8] (**27**).



(**24**)



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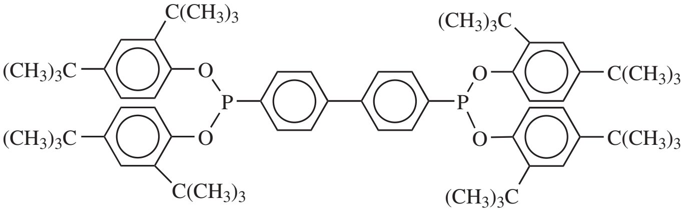

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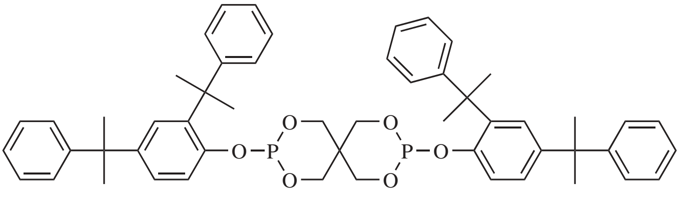


(**27**)

4.3. Hydroxylamines. As mentioned above, hydroxylamines are very effective as free radical scavengers. They are also noted for their ability to decompose hydroperoxides (24); shown in equation 24 and illustrated in Figure 7.

$$R_2N - OH + R^*OOH \rightarrow RR{-}CH - N^+{-}O^- + R^*OH + H_2O \qquad (24)$$

Hydroxylamines serve as a sequential source of hydrogen atoms, reducing hydroperoxide to their corresponding alcohol. In the course of this reaction, the hydroxylamine is converted to a nitrone.

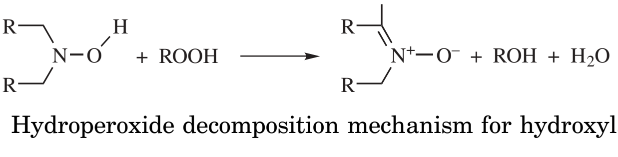


Fig. 7. Hydroperoxide decomposition mechanism for hydroxylamines.

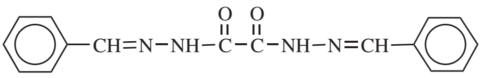
5. Metal Deactivators

The ability of metal ions to catalyze oxidation can be inhibited by metal deactivators (25). These additives chelate metal ions and increase the potential difference between their oxidized and reduced states, which decreases the ability of the metal to produce radicals from hydroperoxides by oxidation and reduction (eqs. 15 and 16). Complexation of the metal by the metal deactivator also blocks its ability to associate with a hydroperoxide, a requirement for catalysis (26).

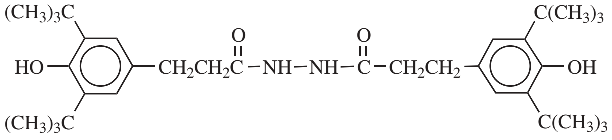
Examples of commercial metal deactivators used in polymers areoxalyl bis (benzylidene)hydrazide [6629-10-3] (**28**), *N,N′*-bis(3,5-di-*tert*-butyl-4-hydroxy hydrocinnamoylhydrazine [32687-78-8] (**29**), 2,2′-oxamidobis-ethyl(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate) [70331-94-1] (**30**), *N,N′*-(disalicylidene)-1,2-propanediamine [94-91-7] (**31**), and ethylenediaminetetra-acetic acid [60-00-4] (**32**) and its salts and critic acid (**33**) (Fig. 8).

6. Effect of Temperature

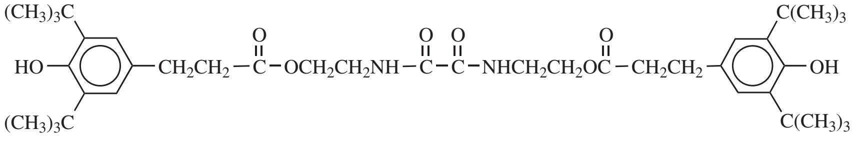
As mentioned above, certain types of antioxidants provide free-radical scavenging capability; albeit over different temperature ranges. Figure 9, illustrates this in a general fashion for representative classes of stabilizers, over the temperature range of 0–300°C.



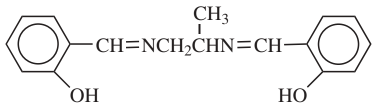
(**28**)



(**29**)

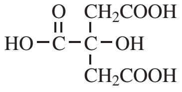


(**30**)



(**31**)

(**32**)



(**33**)

Fig. 8. Commercial metal deactivators.

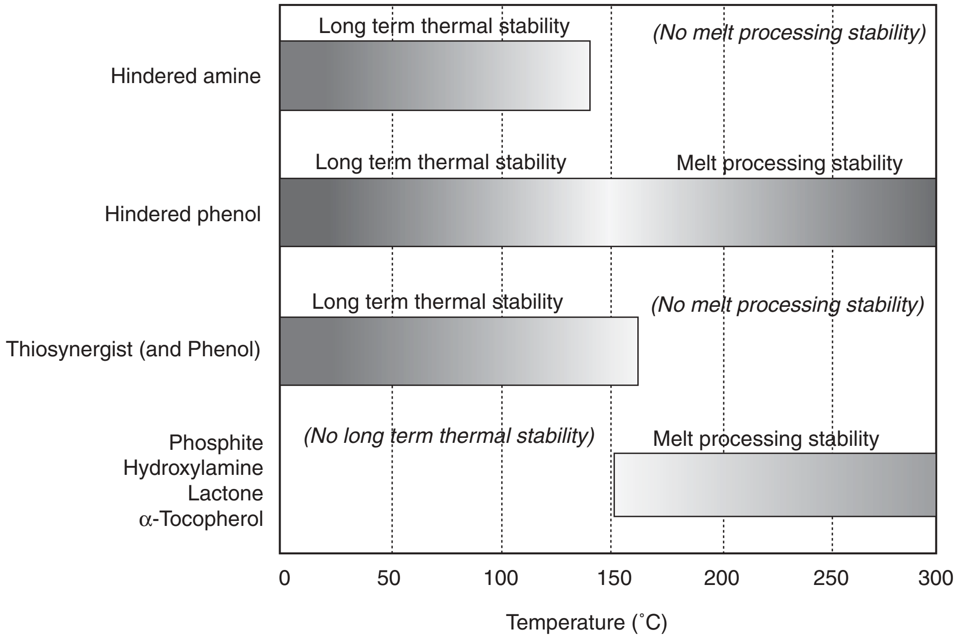


Fig. 9. General representation of effective temperature ranges for selected types of antioxidants.

As a representative example, hindered phenols are capable of providing long term thermal stability below the melting point of the polymer, as well as melt-processing stability above the melting point of the polymer. As such most (if not all) hindered phenols are useful across the entire temperature range.

Thiosynergists, in combination with a hindered phenol, contribute to long term thermal stability, primarily below the melting point of the polymer. In extreme cases, where peroxides have built up in the polymer, thiosynergist can be shown to have a positive impact during melt processing. This finding, however, is not the norm, and this type of melt processing efficacy has been left out of the figure.

Hindered amines, commonly thought of as being useful for uv stabilization, are also useful for long term thermal stability below the melting point of the polymer. This effectiveness is due the fact that hindered amines work by a free-radical scavenging mechanism, but they are virtually ineffective at temperatures $>150°C$. Therefore, hindered amines, when used as a reagent for providing long term thermal stability, should always be used in combination with an effective melt-processing stabilizer.

Phosphites, hydroxylamines, and lactones, are most effective during melt processing; either through free-radical scavenging or hydroperoxide decomposition. They are not effective as long term thermal stabilizers. These type of stabilizers also help with long term thermal stability. By sacrificing themselves during melt processing, they lessen the workload on the phenolic antioxidant, allowing more to remain intact to help with long term thermal stability.

One anomaly that should be pointed out are the hindered phenols based on tocopherols. Even though tocopherols, such as Vitamin E [10191-41-01], fall into the general class of hindered phenols, they behave more as melt processing stabilizers, and less as reagents for providing long term thermal stability, at least with regard to polymer stabilization.

7. Antioxidant Blends

In practical application, it is reasonable to use more than one type of antioxidant in order to meet the requirements of the application, such as melt-processing stability as well as long term thermal stability. The most common combination of stabilizers used, particularly in polyolefins, are blends of a phenolic antioxidant and a phosphite melt-processing stabilizer. Another common combination is a blend of a phenolic antioxidant and a thioester; especially for applications that require long term thermal stability. These common phenol-based blends have been used successfully in many different types of end-use applications. The combination of phenolic, phosphite, and lactone moieties represents an extremely efficient stabilization system since all three components provide a specific function.

For color critical applications requiring “phenol free” stabilization, synergistic mixtures of hindered amines (for both uv stability as well as long term thermal stability) with a hydroxylamine or benzofuranone (for melt processing), with or without a phosphite, can be used to avoid discoloration typically associated with the overoxidation of the phenolic antioxidant(27). The use of “phenol free” stabilization systems is very effective in color critical products such as polyolefin films and fibers as well as selcted thermoplastic polyolefin (TPO) applications.

7.1. Synergism Mixtures of Antioxidants. A mixture of antioxidants that function by different mechanisms might be synergistic and provide a higher degree of protection than the sum of the stabilizing activities of each component. The most frequently used synergistic mixtures are combinations of radical scavengers and hydroperoxide decomposers.

Typically, blend titration experiments are performed at a set loading of additives, starting with 100% of component A and 0% of component B. A series of formulations are designed to shift to the other extreme with 0% component A and 100% component B. By measuring a series of performance parameters, the optimum ratio of A to B can be determined. This type of work is time consuming, but in the end, the optimum ratio can be identified with real data. If three or more components are being assessed at the same time, statistically designed experiments are often useful in terms of sorting out the data.

7.2. Antagonistic Mixtures of Antioxidants. Mixtures of antioxidants can also work against each other. Chemistries that interfere with each other may not necessarily be obvious until the evidence is presented. For example, to ensure long term thermal stability and good light stability, one might use a combination of a phenolic antioxidant and a divalent sulfur compound for thermal stability and a hindered amine for light stability.

Unfortunately, the oxidation products of the sulfur compound can be quite acidic and can complex the hindered amine as a salt, preventing the hindered amine from entering into its free-radical scavenging cycle. This antagonism has been generally known for quite a while (28) and has recently been discussed (29).

Other types of antagonistic chemistry often involve relatively strong acids or bases (either Brønstead or Lewis) that can interact with the antioxidants in such a way as to divert them into transformation chemistries that have nothing to do with polymer stabilization.

8. Application of Antioxidants in Polymers

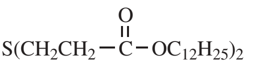
Nearly all polymeric materials require the addition of antioxidants to retain physical properties and to ensure an adequate service life. The selection of an antioxidant system is dependent upon the polymer and the anticipated end use.

8.1. Polyolefins. Low concentrations of stabilizers ($< 0.01\%$) are often added to polyethylene and polypropylene after synthesis and prior to isolation to retard oxidation of the polymer before they are exposed to sources of oxygen or air. Higher concentrations are added downstream during the conversion of the reactor product to a pelletized form. The antioxidant components and concentrations are selected by the manufacturer to yield general purpose grades, or can be optimized to meet a specific end-use application.

In downstream applications, these polymers can be subjected to temperatures as high as 300°C, during cast film extrusion and thin wall injection molding. In these type of demanding applications, processing stabilizers are used to decrease both the change in viscosity (molecular weight) of the polymer melt and the development of color. A phosphite, such as tris(2,4-di-*tert*-butylphenyl)phosphite (**25**) or bis(2,4-di-*tert*-butylphenyl)pentaerythritol diphosphite [26741-53-7], in combination with a phenolic antioxidant such as octadecyl 3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate (**6**), may be used. Concentrations usually range from 0.01 to 0.5% depending on the polymer and the severity of the processing conditions. For long term exposure, a persistent antioxidant like tetrakis[methylene(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)]methane (**9**), at a concentration of 0.1–0.5%, may be added to the base stabilization package.

A sulfur-containing synergistic mixture can be used to obtain an extended service life at a decreased cost.

The synergistic effect of a hydroperoxide decomposer, eg, dilauryl thiodipropionate [123-28-4] (**34**), and a radical scavenger, eg, tetrakis[methylene(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)]methane (**9**), in protecting polypropylene during an oxygen-uptake test at 140°C is shown in Table 3.



$$S(CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OC_{12}H_{25})_2$$

(**34**)

The sum of the individual activities of these antioxidants was 20 days, whereas a mixture of the two stabilizers protected the polymer for 45 days (30).

Table 3. **Synergism between a Hindered Phenol and a Thiosynergist**[a]

Additive, %		Induction period, days
Radical scavenger[b]	Hydroperoxide decomposer[c]	
0.0	0.3	4
0.1	0.0	16
0.1[d]	0.3[d]	45

[a] Ref. 21.

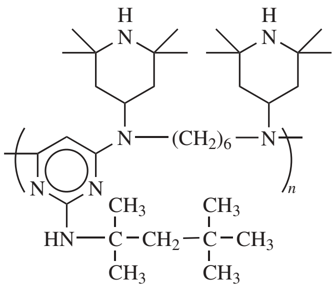
[b] Tetrakis[methylene(3,5-di-*tert*-butyl-4-hydroxyhydro-cinnamate)]methane.

[c] Dilauryl thiodipropionate.

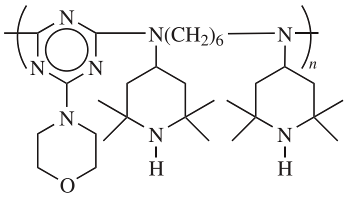
[d] Mixture.

Oligomeric hindered amine light stabilizers are effective thermal antioxidants for polypropylene. Thus 0.1% of *N,N′*-bis(2,2,6,6-tetramethyl-4-piperadinyl)-1,6-hexanediamine polymer, with 2,4,6-trichloro-1,3,5-triazine and 2,4,4-trimethyl-2-pentaneamine [70624-18-9] (**35**) (Fig. 10), protects polypropylene multifilaments against oxidation when exposed at 120°C in a forced-air oven for 47 days (31). The simple hindered phenol 3,5-di-*tert*-butyl-4-hydroxytoluene [128-37-0] (0.1%) affords protection for only 14 days. Other examples of hindered amine light stabilizers are [82451-48-7] (**36**) and [106990-43-6] (**37**).

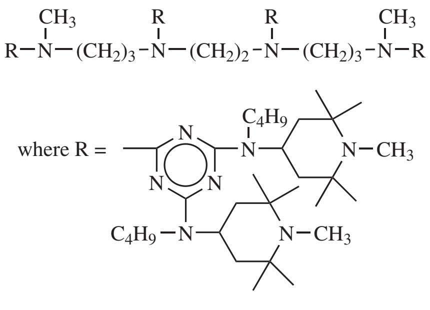
The stabilization of polyolefins used to insulate copper conductors requires the use of a long term antioxidant plus a copper deactivator. Both *N,N′*-bis(3,5-di-



(**35**)



(**44**)



(**45**)

Fig. 10. Hindered 1,6-hexanediamine antioxidants.

tert-butyl-4-hydroxycinnamoyl)hydrazine (**29**) and 2,2′-oxamidobisethyl(3,5-di-*tert*-butyl-4-hydroxycinnamate) (**30**) are bifunctional antioxidants that have built-in metal deactivators. Oxalyl bis(benzylidenehydrazide) (**28**) is an effective copper deactivator as part of an additive package that includes an antioxidant.

8.2. Polyamides. Due to their excellent mechanical properties at high temperatures, polyamides, particularly mineral and glass-filled grades, are finding increased usage in demanding applications such as automotive under-the-hood application. Only a few publications dealing with stabilization of polyamides are found in the literature (32). The aliphatic polyamides differ in their structure, PA 6,6, PA 6, PA 4,6, PA 11, and PA 12 being the most common types. The oxidative stability of the various types is dependent on the density of the amorphous phase and the degree of crystallinity because these two factors control oxygen migration into the polymer matrix (33). Aromatic polyamides are rather insensitive to oxidative degradation.

The traditional stabilization system for aliphatic polyamides are copper salts. Typical systems are based on low levels of copper (< 50 ppm) and iodide or bromide salts (34). The mechanism of stabilization is not well understood but may be due to hydroperoxide decomposition initiated by metal ions (35). These systems are effective in polyamides whereas in other polymers, such as polylefins, small amounts of oxidized copper can often as prodegradants. Good dispersion of the copper is critical to good performance. Since copper salts are water soluble, they can be leached from the polymer in certain applications (eg, aqueous dye baths) leading to reduced efficacy and environmental issues. Aromatic amines are effective long term stabilizers but due to their discoloring nature, their use is limited to carbon black filled systems. Phenolic antioxidants, when added during the polycondensation reaction, contribute to improved initial color and long term thermal stability, particularly at lower end use temperatures. The relative merits of the various stabilization systems are shown in Table 4.

8.3. Styrenics. Unmodified styrenics such as crystal polystyrene are relatively stable and under most end-use conditions it is not necessary to add antioxidants. Low levels (0.1%) of a hindered phenolic antioxidant are added to protect the polymer during repeated processing of scrap. Styrene–acrylonitrile copolymers (SAN) discolor during processing >220°C. While this is primarily a

Table 4. **Stabilization Systems**

Antioxidant system	Advantages	Disadvantages
Cu/halogen salts	best performance at elevated temperatures (>150°C) very low levels required	discoloration leaching in aqueous environment must be well dispersed
aromatic amines	good long term thermal stabilizer performance	discoloration needs high concentration
phenolics	best performance at lower temperatures when copper salts cannot be used good initial and long term color performance	less effective at high temperature conditions such as under-the-hood

nonoxidative process related to the acrylonitrile comonomer, the color can be suppressed to some extent through the addition of a combination of a phenolic antioxidant and a phosphite (36). High impact polystyrene (HIPS) is more susceptible to oxidative degradation due to the presence of an unsaturated butadiene rubber phase. Antioxidants can be added either during the manufacturing process to protect the rubber phase during polymerization and monomer stripping or post-polymerization. Color and impact properties are typically better if the antioxidant is added during polymerization but care must be taken to avoid adverse effects on the kinetics through interaction with the peroxide catalysts. This is particularly problematic if phosphites are added. The polymer ABS is a graft copolymer produced primarily in an emulsion process followed by a compounding step in which the high rubber content polymer is blended with SAN in various ratios to achieve the desired end-use properties. Antioxidants are required during the coagulation and drying steps to protect the high rubber content particles. The best performance is achieved through the use of a combination of hindered phenol (0.25%) and thioester synergist (0.5%) (37). The stability of the finished ABS is directly related to the butadiene content (38).

8.4. Polyesters. Poly(ethylene terephthalate) (PET) requires little to no antioxidant during thermal processing. In some cases, phosphites are added to improve the color of regrind. During polycondensation, pentavalent phosphorus compounds such as triphenylphosphate or trimethylphosphate may be added. These additives form complexes with the transesterification catalyst residues (manganese, tin, zinc), yielding a polymer with reduced hydroxyl end groups. This affords better hydrolytic stability during end use and reduced discoloration prior to the condensation reaction (39). Poly(butylene terephthalate) (PBT), because of its higher hydrocarbon content, is more susceptible to oxidative degradation than PET. The combination of a phenolic antioxidant (0.05–0.10%) and a phosphite (0.1%) is typically used to stabilize PBT.

8.5. Polycarbonate. Polycarbonate (PC) is susceptible to photooxidation, and antioxidants are necessary to maintain the low color and high transparency critical to its end-use applications. Phosphites (0.1%) are used to minimiz color development during processing. It has been shown that the inherent stability of PC is related to the level of phenolic end groups (40). These levels can increase as a result of humidity induced hydrolysis catalyzed by acid. The phosphite chosen must be very stable to avoid the generation of catalytic amounts of phosphorus acids.

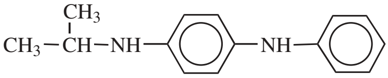
8.6. Polyacetal. Polyacetals thermal decompose by an acid-catalyzed depolymerization process starting at the chain ends. The polymer structure is stabilized by end capping of the polymer and introducing comonomers to interrupt the unzipping. The process is autocatalytic since the liberated formaldehyde is easily oxidized to formic acid, which is a prodegradant. Formaldehyde scavengers and phenolic antioxidants are typically used in polyacetal formulations (41).

8.7. Polyurethanes. The oxidative stability of polyurethanes (PURs) is highly dependent on the chemical nature of both the polyol component and the isocyanate. Thus, PUR derived from a polyester polyol is typically more stable than one derived from a polyether polyol. The methylene group adjacent to the ether linkage in polyether polyols is easily oxidized to hydroperoxides during storage. If not inhibited, decomposition of these built-up hydroperoxides can occur catastrophically during the highly exothermic reaction of the polyol and the isocyanate. Blends of a hindered phenol (0.2%) and an aromatic amine (0.1%) are typically used as storage stabilizers in polyether systems providing PUR foams with excellent color. Similar systems are used in polyester polyols, but at lower use levels (42).

8.8. Elastomers.

Polyunsaturated elastomers are sensitive to oxidation. Stabilizers are added to the elastomers prior to vulcanization to protect the rubber during drying and storage. Nonstaining antioxidants such as butylated hydroxytoluene (**1**), 2,4-bis(octylthiomethyl)-6-methylphenol [110553-27-0], 4,4′-bis(α,α-dimethylbenzyl)diphenylamine (**14**), or a phosphite such as tris(nonylphenyl)phosphite (**24**) may be used in concentrations ranging from 0.01 to 0.5%.

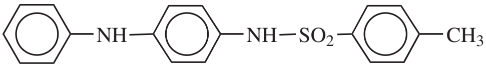
Staining antioxidants such as *N*-isopropyl-*N*′-phenyl-*p*-phenylenediamine [101-72-4] (**38**) are preferred for the manufacture of tires. These potent antioxidants also have antiozonant activity and retard stress cracking of the vulcanized rubber. Carbon black (qv), used in tires for reinforcement, hides the color developed by the antioxidant. According to use requirements, up to 3% of an amine antioxidant having antiozonant activity is added prior to vulcanization.



(**38**)

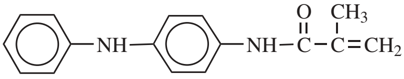
When staining tendencies of the substituted paraphenylene diamines cannot be tolerated, semistaining amine antioxidants are used to provide some protection to the elastomers. The semistaining antioxidants include polymerized 2,2,4-trimethyl-1,2-dihydroquinolines (**13**) and substituted diphenylamines such as 4,4′(-bisα,α-dimethylbenzyl)diphenylamine (**14**). These compounds, however, provide no protection against ozone.

Antioxidants resistant to extraction by lubricants and gasoline are preferred for the stabilization of elastomers used in automotive applications such as gaskets and tubing. Aromatic amine antioxidants, such as *N*-phenyl-*N*′-(*p*-toluenesulfonyl)-*p*-phenylenediamine [100-93-6] (**39**), with low solubility in hydrocarbons, are extracted slowly from elastomers and are used for these applications.



(**39**)

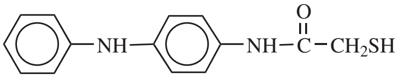
Binding the antioxidant chemically to the elastomer chain by copolymerization or grafting is a better solution to this problem. The addition of *N*-(4-anilino-phenyl)methacrylamide [22325-96-8] (**40**) to a polymerization recipe for NBR rubber produces a polymer with a built-in antioxidant resistant to extraction (43).



(**40**)

Raw NBR containing 1.5% of the built-in antioxidant retained 92% of its original resistance to oxidation after exhaustive extraction with methanol. NBR containing a conventional aromatic amine antioxidant (octylated diphenylamine) retained only 4% of its original oxidative stability after similar extraction.

It is also possible to graft an aromatic amine antioxidant bearing a sulfhydryl group on to the backbone of an elastomer.



(**41**)

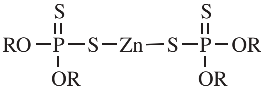
When 4-(mercaptoacetamido)diphenylamine [60766-26-9] (**41**) is added to EPDM rubber and mixed in a torque rheometer for 15 min at 150°C, 87% of it chemically binds to the elastomer (44). The mechanical and thermal stress placed on the polymer during mixing ruptures the polymer chain, producing free radicals that initiate the grafting process.

8.9. Poly(vinyl chloride). While reasonably stable with respect to oxidative degradation, poly(vinyl chloride) (PVC) is very susceptible to thermal degradation. Protection of PVC from thermal degradation leading primarily to dehydrohalogenation reactions is out of the scope of this article. Some additives, used primarlily as HCl scavengers, also have antioxidant properties. Aralkylphosphites in particular are used as components of thermal stabilizing mixtures that also exhibit antioxidant properties, leading to improved resin color.

8.10. Fuels and Lubricants. Gasoline and jet engine fuels contain unsaturated compounds that oxidize on storage, darken, and form gums and deposits. Radical scavengers such as 2,4-dimethyl-6-*tert*-butylphenol [1879-09-0], 2,6-di-*tert*-butyl-*p*-cresol (1), 2,6-di-*tert*-butylphenol [128-39-2], and alkylated paraphenylene diamines are used in concentrations of ~5–10 ppm as stabilizers.

The catalytic activity of copper as an oxidant in fuels and lubricants can be inhibited by the use of a metal deactivator such as *N,N′*-disalicylidene-1,2-diaminopropane (**31**) at a concentration of 5–10 ppm.

Lubricants for gasoline engines are required to withstand harsh conditions. The thin films of lubricants coating piston walls are exposed to heat, oxygen, oxides of nitrogen, and shearing stress. Relatively high concentrations of primary antioxidants and synergists are used to stabilize lubricating oils. Up to 1% of a mixture of hindered phenols, of the type used for gasoline, and secondary aromatic amines, such as alkylated diphenylamine and alkylated phenyl-α-napththylamine, are used as the primary antioxidants. About 1% of a synergist, zinc dialkyldithiophosphonate, is added as a peroxide decomposer. Zinc dialkyldithiophosphates (**42**) are cost effective multifunctional additives. They interrupt oxidative chains by trapping radicals by electron donation, decompose peroxides, and serve as a corrosion and wear inhibitors.



$$RO-\overset{\overset{S}{\|}}{\underset{\underset{OR}{|}}{P}}-S-Zn-S-\overset{\overset{S}{\|}}{\underset{\underset{OR}{|}}{P}}-OR$$

(**42**)

$R = C_3H_7, C_8H_{17}$

Both zinc and phosphorus deactivate the catalysts used to control emissions and governmental regulations limit their concentrations to $< 0.1\%$.

9. Test Methods

9.1. Polymers.

There are a variety of test methods available for monitoring the oxidative stability in the polymer as it is exposed to different types of stresses. These changes can be physical or aesthetic. Physical transformations of the polymer might involve changes in molecular weight, molecular weight distribution, or crystallinity. Aesthetic transformations of the polymer might involve changes such as discoloration or changes in the surface appearance due to microscopic cracks that affect gloss.

These changes can be measured using simple testing equipment and procedures described in ASTM methods (eg, tensile strength, impact resistance, color development; oxidative induction time, oven aging, etc).

Estimation of oxidative stability under conditions of use is more difficult to measure. To decrease the time required for oxidative failure, specimens are exposed at temperatures higher than those anticipated in use. Oven aging the polymer at temperatures below the melting point of the polymer is a method for assessing the long term thermal stability of a given substrate. A range of test temperatures can be used to create an Arrhenius plot as test temperature (°C or kelvin) versus time to failure (eg, embrittlement, or 50% retention of tensile strength or elongation). If the apparent activation energy remains constant, a plot of the logarithm of failure time against the reciprocal of the absolute temperature results in a straight line. Extrapolation to temperature of use provides an estimate of failure time.

Due to different reactions and the raw materials used, the apparent activation energy of the overall process can deviate considerably from linearity and an extrapolation can lead to serious errors in estimating failure time (45).

Representative measures of aesthetic properties would include color development, loss of gloss, increase in haze, chalking, loss of surface smoothness, exudation and/or blooming of additives or low molecular weight polymer, staining, and the like.

To assess the retention of physical or aesthetic properties, it is important to understand that increasing surface/volume ratio increases susceptibility to oxidation as does the rate of loss of the antioxidant by volatilization (46).

In the past, oxygen-uptake measurements at elevated temperatures were used to determine oxidation resistance. Today, other types of testing, such as oxidative induction time, OIT (by differential scanning calorimetry, DSC) or chemiluminescence are used.

For oxygen uptake experiments, the time required to absorb a specified volume of oxygen is an indication of failure when the change in the rate of oxygen absorption is not sufficient to permit an accurate measurement of the induction period. However, the amount of oxygen absorbed and the loss of desired properties must be correlated. This type of test is not reliable for estimating service life under conditions in which the polymer is exposed to air movement.

Oxidative induction time or oxidative induction temperature experiments are used to assess the relative oxidative stability of the polymer. The experiments are typically conducted under severe testing conditions, typically at elevated temperatures (significantly above the melting point of the polymer) using oxygen as the oxidant. Note that this method is not useful for predicting long term thermal stability; however, these methods can be useful for quickly assessing the relative potency of different types of stabilizer systems (47).

For chemiluminescence experiments, the procedure is similar to the aforementioned oxidative induction time experiments, in that the time to catastrophic oxidative of the polymer is measured; in this case, below the melting point of the polymer. During this catastrophic oxidation, there are certain chemistries taking place that result in chemiluminescence. The amount of light that is given off during this process is measured by a charge coupled device. This method has been developing over the last decade, can provide useful information about the oxidative stability of the polymer in a much shorter time period than conventional oven aging, but under more realistic oxidative environment in comparison to oxidative induction time (48).

9.2. Lubricants.

A sequence of tests has been devised to evaluate antioxidants for use in automotive crankcase lubricants. The Indiana Stirring Oxidation Test (ISOT) JISK2514 is an example of a laboratory screening test. The oil is stirred at 165.5°C in the presence of air. Copper and iron strips are used as metal catalysts. The development of sludge, viscosity, and acidity are determined periodically. Failure time is determined when the development of acidity requires 0.4-mg KOH/g for neutralization. Formulated lubricants are then evaluated for performance in engines (see Oldsmobile Sequence III D) (49). Candidate lubricants containing the antioxidants are tested in fleets of automobiles for thousands of miles. As described above for polymers, modified oxygen uptake tests can also be used with lubricants to measure oxidative stability (50).

The effectiveness of antioxidants as preservatives for fats and oils is evaluated by determining the rate of peroxide development using the active oxygen method (AOM) (51). The development of a rancid odor is used to evaluate the stability of food items (Schaal oven stability test) (52).

10. Ancillary Properties

In reality, there is more to antioxidants than providing stability to the polymer by quenching free radicals and decomposing hydroperoxides. Other key issues besides rates of reactivity and efficiency include performance parameters such as volatility, compatibility, color stability, physical form, taste or odor, regulatory issues associated with food contact applications, and polymer performance versus cost (53).

10.1. Volatility. Most additives are melt compounded into the polymer after the polymerzation stage. The melt compounding and downstream conversion (into shaped articles) processing steps represent significant heat histories. Storage of the product can also be quite warm in certain climates. It is important that the antioxidant, as well as its transformation products that may also provide stability, not volatilize from the polymer. Many commercial antioxidants have been designed with higher molecular weights to address this issue.

10.2. Compatibility. Antioxidants should be soluble in the polymeric matrix. If they are not soluble, they should at least migrate or diffuse slowly. If the solubility limit of the antioxidant in the polymer is exceeded, exudation will occur. Exudation or blooming involves the migration of the additive out of the polymer matrix onto the surface as a very thin film. Blooming of the antioxidant can also diminish surface gloss, create stickiness, eliminate blocking (cling) of film surfaces to one another, negatively affect printability.

10.3. Color Stability. It is important that antioxidant do not provide unwanted color due to the transformation chemistries associated with preventing oxidation. Some antioxidants are prone to forming color by their very nature, while other antioxidants discolor only when they have been overoxidized. Pigments can be used to mask the subtle changes in the base color of the polymer.

10.4. Physical Form. Because of hazards associated with dusting, many antioxidants are now being offered commercially in dust free forms, such as granules or pellets. Liquid or molten antioxidants are another interesting alternative, as long as they are compatible in the polymer matrix. Still, some polymer manufactures need the additives as fine powders in order to achieve good premixing with their reactor product before melt compounding into the traditional pellet form.

10.5. Taste and Odor. For applications that involve food contact, home or personal use, taste, and odor are key issues. The human nose is very sensitive, more so than some analytical instruments, able to detect some compounds at the part per billion (ppb) level.

11. Health and Safety Factors

Safety is assessed by subjecting the antioxidant to a series of animal toxicity tests, eg, oral, inhalation, eye, and skin tests. Mutagenicity tests are also carried out to determine possible or potential carcinogenicity. Granulated and liquid forms of antioxidants are receiving greater acceptance to minimize the inhalation of dust and to improve flow characteristics.

A number of antioxidants have been regulated by the U.S. Food and Drug Administration as indirect additives for polymers used in food contact applications (primarily food packaging) under Title 21 of the U.S. Code of Federal Regulations (21CFR), Part 175 (Adhesives and Coatings) and/or Part 177 (Polymers). Acceptance is determined by subchronic or chronic toxicity in more than one

Table 5. **Commonly Used Antioxidants by Class**

Chemical Name	CAS No.	FDA Reg.[a]	Suggested substrates [b]	Suppliers
Monophenols				
alpha tocopherol	[10191-41-01]	x	PO, PUR	Ciba SC, BASF
2,6-di-*tert*-butyl-4-methylphenol	[128-37-0]	x	PA, PES, PO, POM, PUR, PVC, RU, PS	Great Lakes, Merisol, PMC, Crompton
octadecyl, 3,5-di-*tert*-butyl-4-hydroxycinnamate	[2082-79-3]	x	CE, PA, PO, PUR, PVC, PS	Ciba SC, Crompton, Great Lakes, GE Specialty
isooctyl, 3,5-di-*tert*-butyl-4-hydroxycinnamate	[126-43-61-0]	x	PUR	Ciba SC, Crompton
Bisphenols				
2,2′-methylenebis(4-methyl-6-*tert*-butylphenol)	[119-47-1]	x	CE, PA, POM, PUR, PVC, RU, PS	Cytec, RT Vanderbilt, Great Lakes, Ferro
2,2′-methylenebis(4-ethyl-6-*tert*-butylphenol)	[88-24-4]	x	PA, PO, PVC	Cytec
4,4′-butylidenebis(6-*tert*-butyl-3-methylphenol)	[85-60-9]	x	CE, EVA, PA, PES, PO, PVC, RU, PS	Flexsys
N,*N*′-hexamethylene bis(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamide)	[23128-74-7]	x	PA, PES, PA, RU	Ciba SC, Great Lakes
1,6-hexamethylenebis(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)	[35074-77-2]	x	CE, PES, PO, POM, PUR, PVC, PS	Ciba SC
benzenepropanoic acid, 3-(1,1-dimethylethyl)-4-hydroxy-5-methyl-, 2,4,8,10-tetraoxaspiro [5.5]undecane-3,9-diylbis(2,2-dimethyl-2,1- ethanediyl) ester	[90498-90-1]			Sumitomo
triethyleneglycol bis(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)	[36443-68-2]	x	PA, POM, PVC, PS	Ciba SC, Great Lakes
calcium bis[*O*-ethyl(3,5-di-*tert*-butyl-4-hydroxybenzyl)-phosphonate	[65140-91-2]	x	PO, RU	Ciba SC
Polyphenols				
1,3,5-trimethyl-2,4,6-tris(3′,5′-di-*tert*-butyl-4′-hydroxybenzyl)-benzene	[1709-7-2]	x	CE, PA, PES, PO, POM, PVC, RU, PS	Albemarle, Ciba SC, Great Lakes, Sigma 3V

Table 5 (*Continued*)

Chemical Name	CAS No.	FDA Reg. [a]	Suggested substrates [b]	Suppliers
3:1 condensate of 3-methyl-6-*tert*-butylphenol with crotonaldehyde	[1843-03-4]	x	CE, PA, PES, PO, POM, PUR, PVC, RU, PS	ICI Americas
tetrakis[methylene(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)methane	[6683-19-8]	x	CE, PA, PES, PO, POM, PVC, PS	Ciba SC, Great Lakes, Crompton, GE Specialty Chem
1,3,5-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)isocyanurate	[27676-62-6]	x	CE, PA, PES, PO, POM, PVC, PS	Ciba SC, RT Vanderbilt, Great Lakes Chem, Sigma 3V
3,5-di-*tert*-butyl-4-hydroxy-hydrocinnamic triester with 1,3,5-tris (2-hydroxyethyl)-s-triazine-2,4,6,(1*H*,3*H*,5*H*)-trione	[34137-09-2]	x	CE, PA, PO, PUR, PVC, RU, PS	Ciba SC, RT Vanderbilt
1,3,5-tris(4-*tert*-butyl-3-hydroxy-2,6-dimethylbenzyl)-s-triazine-2,4,6-(1*H*,3*H*,5*H*)trione	[40601-76-1]	x	CE, PA, PES, PO, POM, PUR, PVC, RU, PS	Cytec, Ciba SC, Great Lakes Chem
bis[3,3-bis(4-hydroxy-*tert*-butylphenyl)butanoic acid] glycol ester	[32509-66-3]	x	CE, PA, PES, PO, POM, PVC, PS	Clariant
butylated reaction product of *p*-cresol and dicyclopentadiene	[31851-03-3]	x	CE, PA, PES, PO, POM, PVC, RU, PS	Goodyear
Phenolics with Dual Functionality				
4,4′-thiobis(6-*tert*-butyl-3-methylphenol)	[96-69-5]	x	PA, PES, PO, PVC, RU, PS	Flexsys, Sumitomo
4,4′-thiobis(2-methyl-6-butylphenol)	[96-66-2]		PO, RU	Albemarle
thiodiethylene bis(3,5-di-*tert*-butyl-4-hydroxycinnamate)	[41484-35-9]	x	CE, PA, PO, PUR, PVC, RU, PS	Ciba SC, Great Lakes
4,6-bis(octylthiomethyl)-*o*-cresol	[110553-27-0]	x	RU, PS	Ciba SC
Reaction product of nonylphenol, dodecanethiol and formaldehyde	[188793-84-2]	x	RU, PS	Goodyear
2,4-bis(*n*-octylthio-6-(4-hydroxy-3,5-di-*tert*-butylanilino)-1,3,5-triazine	[991-84-4]	x	RU, PS	Ciba SC
2-(1,1-dimethylethyl)-6-[3-(1,1-dimethylethyl)-2-hydroxy-5-methylphenyl]-methyl-4-methylphenylacrylate	[61167-58-6]	x	PS	Sumitomo, Ciba SC

Metal Deactivators				
N,*N*′-bis(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamoyl)hydrazine	[32687-78-8]	x	PA, PO, RU	Ciba SC, Great Lakes
2,2′-oxamidobisethyl(3,5-di-*tert*-butyl-4-hydrocinnamate)	[70331-94-1]	x	PA, PO, RU	Crompton
oxalic acid, bis(benzylidenehydrazide)	[6629-10-3]		PA, PO, RU	Eastman
Arylamines				
4,4′-bis(dimethylbenzyl)-diphenyl amine	[10081-67-1]	x	RU, PO, PS, PUR	Crompton
N-phenyl-alpha-naphthylamine	[90-30-2]	x	PA, PES, PO, RU	Bayer, Flexsys, RT Vanderbilt
N-phenyl-*N*′-isopropyl-*p*-phenylenediamine	[101-72-4]	x	RU	Bayer, Flexsys, RT Vanderbilt, Crompton
polymerized 2,2,4-trimethyl-1,2-dihydroquinoline	[26780-96-1]		RU	Flexsys, RT Vanderbilt, Crompton
octylated diphenylamine	[68411-46-1]	x	RU, PUR	Ciba SC, Crompton, Great Lakes, RT Vanderbilot
Thioethers				
didodecyl-3,3′-thiodipropionate	[123-28-4]	x	PA, PO, RU	Cytec, Crompton, Evans Chemetic
distearyl-3,3′-thiodipropionate	[693-36-7]	x	PA, PO, RU	Cytec, Crompton, Evans Chemetic
pentaerythritol tetrakis(3-dodecylthio)-propionate	[29598-76-3]	x	PA, PO	Crompton
S,*S*′distearyldisulfide	[2500-88-1]	x	PA, PO, RU	Clariant
Phosphites/Phosphonites				
tris nonylphenylphosphite	[26523-78-4]	x	CE, PES, PO, PUR, PVC, RU, PS	Crompton, GE Specialty, Dover
tris (2,4-di-*tert*-butylphenyl) phosphite	[31570-04-4]	x	CE, PES, PO, PUR, PS	Ciba SC, GE Specialty, Great Lakes, Crompton
distearyl pentaerythritoldis phosphite	[3806-34-6]	x	CE, PES, PO, PUR, PS, RU	GE Specialty
bis(2,4-di-*tert*-butylphenyl)-pentaerythritol diphosphite	[26741-53-7]	x	CE, PES, PO, PUR, PS, RU	GE Specialty, Ciba SC, Great Lakes
2,4,6-tri-*tert*-butylphenyl-2-butyl-2-ethyl-1,3-propanediol phosphite	[161717-32-4]	x	PO, PS	GE Specialty
bis(2,4-dicumylphenyl) pentaerythritol diphosphite	[154862-43-8]	x	CE, PES, PO, PUR, PS, RU	Dover
tetrakis(2,4-di-*tert*-butylphenyl)4,4′-biphenylenediphosphonite	[119345-01-6]	x	CE, PES, PO, PUR, PS, RU	Clariant, Ciba SC, Great Lakes

Table 5 (*Continued*)

Chemical Name	CAS No.	FDA Reg. [a]	Suggested substrates [b]	Suppliers
Hindered Amines				
poly[6-[(1,1,3,3-tetramethylbutyl) amino]-1,3,5-triazine-2,4-diyl][2,2,6,6-tetramethyl-4-piperidinyl)imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidinyl)imino]	[71878-19-8]	x	PO, EVA	Ciba SC
poly[6-[1-morpholino]-1,3,5-triazine-2,4-diyl][2,2,6,6-tetramethyl-4-piperidinyl) imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidinyl)imino]	[82451-48-7]	x	PO, EVA	Cytec
butanedioic acid, dimethylester, polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol	[65447-77-0]	x	PO, EVA	Ciba SC
7-oxa-3,20-diazadispiro[5.1.11.2] heneicosan-21-one, 2,2,4,4-tetramethyl-, hydrochloride, reaction products with epichlorohydrin, hydrolyzed, polymd	[202483-55-4]	x	PO, EVA	Clariant
1,3-propanediamine, *N*,*N*″-1,2-ethanediylbis-, polymer with 2,4,6-trichloro-1,3,5-triazine, reaction products with *N*-butyl-2,2,6,6-tetramethyl-4-piperidinamine	[136504-96-6]	x	PO, EVA	Sigma 3V
1,3,5-triazine-2,4,6-triamine,*N*,*N*[1,2-ethane-diyl-bis([(4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidinyl)amino]-3,1-propanediyl)]bis(*N*′,*N*′-dibutyl-*N*′,*N*′-bis(1,2,2,6,6-pentamethyl-4-piperidinyl)-	[106990-43-6]	x	PO, EVA	Ciba SC

siloxanes and silicones, methyl-hydrogen, reaction products with 2,2,6,6-tetramethyl-4-(2-propenyloxy)piperidine	[182635990]	x	PO, EVA	Great Lakes
Processing Stabilizers				
2(3*H*)-benzofuranone, 5,7-bis-(1,1-dimethylethyl)-3-hydroxy, reaction products with *o*-xylene	[181314-48-7]	x	PO, PUR	Ciba SC
1-octadecanamine, *N*-hydroxy-*N*-octadecyl-	[123250-74-8]	x	PO, RU	Ciba SC
di (rape oil)alkyl-*N*-methylamine oxide	[204933-93-7]	x	PO, RU	GE Specialty

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[a] Regulated by the US Food and Drug Administration as an indirect food additive under Title 21 of the *U.S. Code of Federal Regulations* (21 CFR), Part 175 (Adhesives and Coatings) and/or Part 177 (Polymers).

[b] CE = cellulosics, EVA = ethylene vinylacetate copolymers, PA = polyamides, PES = polyesters, PO = polyolefins, POM = polyoxymethylenes, PUR = polyurethanes, polyols, RU = rubber, PS = polystyrenes, PVC = poly(vinyl chloride).

animal species and by the concentration expected in the diet, based on the amount of the additive extracted from the polymer by solvents that simulate food in their extractive effects. Materials are regulated by the FDA for use in plastics contacted by food stuffs to ensure a minimum risk to the consumer. Broad FDA regulation is increasingly a requirement for the successful introduction of a new antioxidant.

12. Cost Effectiveness

The point in using an antioxidant is to chose the apropriate type and level to adequately stabilize the polymer for a particular end-use application.

For example, if the material is a nondurable good, such as bags and food wrap, the type and concentration of antioxidant is chosen to minimize unnecessary costs associated with stabilizing the polymer. The antioxidant should be able to provide stabilization for the initial melt compounding and processing into the finished article. It is important to consider that scrap from the melt compounding needs to be recycled and unexpected shut downs and start-ups may occur.

On the other hand, if the material is a durable good, such as geomembranes, insultation for wire and cable, or gas and water transmission pipes, the type and concentration of the phenolic antioxidant is chosen to meet the long service life criteria. The costs associated with this type or level of antioxidant is worth the additional value of the final product.

12.1. Commercial Antioxidants. Table 5 includes the main classes of antioxidants sold in the United States and the supplier's suggested applications. Some of these are mixtures rather than single components, which is especially true of alkylated amines and alkylated phenols. The extent of alkylation and the olefins used for alkylation can vary among manufacturers. Table 5 is not a complete listing of available antioxidants in the United States.

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Richard Thomas
Ciba Specialty Chemicals
Martin Dexter
Consultant
R. E. King III
Ciba Specialty Chemicals