

POLYETHYLENE (Stabilization and Compounding)

Introduction:

Plastics are used in many fields because they can be processed easily, are relatively light, and possess excellent chemical and physical properties. However, they also have undesirable properties from a combination of the material itself and processing. Therefore, it is important to hide or reduce the defects of plastics while sustaining or enhancing the merits as much as possible. To attain that aim, many kinds of polymer additives have been developed.

Additives are agents that sustain material's properties or functions, provide desirable properties for the bulk of a material, or provide its surface properties. This article focuses on the most widely used additives in the PE industry.

Compounding is the general term for the operation converting the polyethylene (PE) produced in a polymerization reactor into a pelletized form suitable for use by a downstream processor. In the compounding process, the polymer is physically and chemically modified by incorporating various additives. The selection of additives and of compounding conditions depends on the end application of the compounded product.

Compounding is the overall process of incorporating and homogenizing additives into PE. The equipment needed for the compounding process includes additive feeders, mixers, extruders, blenders, and pelletizers. Auxiliary equipment is used to control the process.

In any compounding operation, the first step is stabilizing and incorporating other additives. Stabilizing the polymer is important to prevent thermal oxidation and discoloration during melt processing and to impart long-term heat and light stability.

Stabilizers are the most widely used additives in the PE industry. Other additives commonly added to polyethylene are stearates (e.g., calcium and zinc stearates to neutralize acidic catalyst residues and to impart lubricity), pigments (e.g., carbon black, cadmium yellow, and titanium dioxide), metal deactivators (e.g., oxalyl bishydrazide for PE cable insulation), processing aids (e.g., Dynamar, Ucarsil, Viton-A, to improve flow of the molten polymer), and optical brighteners (e.g., Uvitex OB to enhance appearance). Additives commonly added to polyethylene include antioxidants (hindered phenolics and phosphites for process stabilization), antiblock compounds (e.g., silica, talc, and kaolin to reduce sticking of adjacent film layers), and slip agents (e.g., erucamide and oleamide to reduce friction).

Properties of Polymeric Materials:

It is important to understand the properties of polymers in order to stabilize them. The processing of polymers also is a key factor for producing desirable properties for polymers. In processing, temperature, atmosphere, elongation, cooling velocity, as well as other factors affect the distribution of additives and fillers, the size and distribution of crystals, and the presence of spheric crystals, which determine whether the polymer's properties are drawn completely.

The degradation of polymeric materials, therefore, is complicated but generally is induced by heat, light, mechanical shear, and ozone, which essentially initiates autoxidation. Autoxidation follows

certain fundamental steps after an initiation reaction. However, reactions that induce crosslinking or gelatin of polymer molecules, resulting in the material hardening.

The degradation of polymer materials by autoxidation depends on the polymer and starts wherever bonds have low dissociation energy. A C-H bond, for example, cleaves more easily in the order of primary, secondary, tertiary, and additionally at the alpha carbon, adjacent to an olefinic double bond or a carbonyl group. Polymers with photosensitive functional groups such as carbonyls are likely to degrade when exposed to light.

Polymers degrade mainly through use, although some degradation occurs in preparing and processing stages. The primary route for degradation is autoxidation.

Part I: Additives

ADDITIVES (Types and Applications):

Plastics have the widest range of mechanical, physical, and other useful properties combined with easy fabricability and economical costs. However, plastics are seldom used alone and, to suit end-use requirements such as colorability and fire resistance, certain additives are almost always mixed with them.

ADDITIVES CLASSIFICATION:

Although additives may be solid, rubbery, liquid, or gaseous, the following nine classes of materials, the most frequently used, will be discussed here:

stabilizers,

fillers,

plasticizers and softeners,

lubricants and flow promoters,

colorants,

flame retardants,

blowing agents,

crosslinking agents, and

ultra violet degradable additives.

Some of the additive types are used for almost all applications; others are used only for specific applications.

SYNERGISTIC AND ANTAGONISTIC:

The PE compounder should be aware of the many synergistic and antagonistic interactions that can arise between additives in PE. In particular, antagonistic interactions should be avoided as they

generally reduce the effectiveness of both additives. Figure 1 summarizes some of these interactions.

Synergistic	Antagonistic
phenolic AO + phosphites	HALS + thioesters
phenolic AO + dialkyldithiocarbamates	HALS + acidic carbon black
UV absorbers + phenolic AO	HALS + some phenolic AO
phenolic AO + Kemamine™ AS990	silica + erucamide
sulphur containing AO + carbon black	talc/silica + processing aids
UVA + HALS	Irganox™ 1010 + DHT-4A
UVA + nickel dithiocarbamates	zinc stearate + erucamide
phenolic AO + zinc thiolate	calcium stearate + UVA

FIGURE 1: Synergistic and antagonistic interactions that can arise between additives in polyethylene. AO, antioxidant; UVA, UV absorber; and HALS, hindered-amine light stabilizer.

Synergistic additive interactions result from a cooperative action between the additives to produce an effect greater than that resulting from the sum of their contributions. The most common synergism is that occurring between chain-breaking antioxidants (such as hindered phenols) and hydroperoxide decomposers (such as aromatic phosphites). For instance, in PE compounded at 220 °C, approximately 55% of the Irganox 1076 remains after one extrusion pass when no Irgafos 168 is present. In contrast, in the presence of Irgafos 168, a much higher content (between 78 and 84%) of the hindered phenolic remains after the first extrusion pass.

Although the mechanism is not fully elucidated, one important role of phosphite stabilizers is to preserve the hindered phenol. This preservation occurs as the phosphite reduces the number of radicals formed. The chain-breaking antioxidant, however, reduces the amount of hydroperoxides produced in the propagation stage, thus increasing the efficacy of the hydroperoxide composer present.

A new class of antioxidants known as autosynergists consist of a hindered phenolic antioxidant and a hydroperoxide decomposer in a single molecule. Irganox 1035 is an example of such an autosynergist. It is bifunctional, with two hindered phenolic substituents attached to a central sulfur atom, and is used for special high-temperature applications in PE pipes and cables.

An additive combination that should be avoided is HALS (such as Chimassorb 944) and sulfur-containing antioxidants (i.e., thioesters) as they are antagonistic. The acidity of sulfur antioxidants neutralizes HALS effectiveness. For the same reason, HALS and acidic carbon black should not be used together. In contrast, alkylated thiobisphenols, such as Santonox R, exhibit a strong synergism with carbon black, whereas their methylenebis analogs and many phenolic antioxidants react antagonistically.

Antagonism has been reported between UV absorbers (i.e., hydroxyoctyloxybenzophenone) and calcium stearate. An antagonism between erucamide and zinc stearate has also been observed. Researchers at Witco Corp. found that considerable erucamide degradation can occur when the amide is compounded with zinc stearate to form a masterbatch. For instance, when compounding this combination at 200 °C, ~20% of the total amide degrades, and of this, 7% converts to nitriles.

Recently an antagonistic interaction between silica (diatomaceous earth) and erucamide (e.g., Crodamide ER) was found to degrade the fatty acid amide into various aldehydic groups (especially nonanal) with low thresholds of odor detection and consequently an undesirable odor in the polymer. This antagonism is believed to result from the acid-catalyzed degradation of erucamide by the acidic groups on the silica surface. In addition, the presence of relatively high levels of iron (i.e., 3000 ppm) in the silica may also contribute to metal-catalyzed redox reactions of erucamide.

Mineral additives such as silica and talc can reduce antioxidant effectiveness by adsorbing them on their surface. Compounders sometimes add an epoxy compound that coats the talc, minimizing the antioxidant's adsorption. Similarly, in fluoropolymer processing aids, a polyethylene glycol can prevent excessive adsorption of the fluoropolymer onto the talc. Silica antiblock agents can also reduce the lubricating performance of erucamide slip agents because the erucamide becomes adsorbed and immobilized on the high-surface-area silica.

STABILIZERS:

The properties of polymers deteriorate under the combined effects of high and ambient temperatures, atmospheric radiation, oxygen, ozone, water, microorganisms, and other atmospheric agents. The deterioration is attributed to the degradation or chain scission and crosslinking and to the formation of chromophoric and polar groups in the polymer. The overall effects on the polymer are loss of strength, hardening and embrittlement, color formation and/or reduction of optical clarity, changes in chemical activity, and a decrease in electrical insulation properties. Thus, for any meaningful use, the polymer needs to be protected from such detrimental influences.

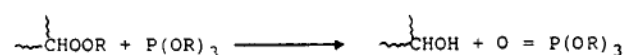
ANTIOXIDANTS AND UV STABILIZERS:

The degradation of polymers by heat, oxygen, ozone, mechanical shearing, UV exposure, metal ions, and other agents normally occurs by a free-radical mechanism. A host of radical species are produced by initiation and propagation mechanisms in which the hydroperoxide radical is by far the most reactive, decomposing to give rise to chain scission. Radical species recombine to form extended-chain or crosslinked polymers in the termination step.

Decomposition and/or crosslinking reactions depend on polymer type and environmental conditions. Effective antioxidants interrupt the sequence of chain reactions and are of two types depending on their mode of action: preventive antioxidants that prevent the formation of radicals

R \dot{u} and ROO \dot{u} and chain-breaking antioxidants that directly intervene in the propagation cycle reaction with R \dot{u} and ROO \dot{u} radicals and introduce new termination reactions.

Preventive antioxidants prevent the formation of free radicals and are classed as: peroxide decomposers, metal deactivators, and UV light protectors. Peroxide decomposers remove peroxide radicals and decompose hydroperoxides, forming stable products. They include many sulfur and phosphorus compounds such as sulfides, thioethers, mercaptans, sulfonic acids, tertiary phosphites and phosphates, zinc dialkyl dithiophosphates, and zinc dimethyldithiocarbamate. 2,3,6 Peroxides are deactivated and reduced to alcohols (Equation 1):



Variable-valency metal ions (e.g., Mn, Cu, Fe, Co, and Ni) contaminated in the polymer initiate oxidation by accelerating the rate of decomposition of hydroperoxides to active radicals. Metal ions can be deactivated by complexing with chelating agents based on organic phosphites and phosphines and on higher nitrogenated organic compounds (e.g., melamine, bis-salicylidene diamines, and oxam-ides).

UV protectors reduce the harmful energy level of radiation (wavelength 290-400 nm) by absorbing it in preference to the polymer without undergoing decomposition. Three classes of UV protector are screening agents (or light screens), UV absorbers, and excited-state quenchers. UV screens absorb the radiation before it reaches the polymer and are pigments that do not scatter and reflect light. The most effective is carbon black (particle size 15-25 nm, phr 2-3), which absorbs over the entire UV and visible range and transforms the radiation into less harmful IR radiation. Carbon black is a thermal antioxidant and a radical trap. UV absorbers are also light screens that should not absorb in the visible range. The absorbed energy is disposed of by radiation, conversion into heat, or chemical changes to harmless stable products. Examples are 2-hydroxy benzophenones, O-hydroxyphenyl benzotriazoles, resorcinol monobenzoate, phenyl salicylate and derivatives, and phenol/resorcinol esters of tere- or isophthalic acids. Excited-state quenchers react with photoexcited polymer molecules and dissipate the excess energy as irradiation (e.g., nickel(II) chelates and the newer hindered amines).

Chain-breaking antioxidants are nonstaining hindered phenols and aromatic amines (phr 0.02-1). Used in excess oxidation may be facilitated by these antioxidants.

Stabilizer Synergism, Autosynergism, and Antagonism:

Some stabilizer combinations are more powerful than the sum of the individual members; in some the effect of each component is doubled. This phenomenon is known as synergism. In polyolefins a chain-breaking antioxidant (e.g., 4-methyl-2,6-di-t-butyl phenol) and a peroxide decomposer (e.g., dilauryl thiodipropionate) give synergistic stabilization. Cd/Ba and Cd/Ba/Zn stearates and laurates make synergistic combinations in PVC. The most powerful combinations for polyolefins can be achieved using a chain-breaking antioxidant, a regenerating agent, a peroxide decomposer, a metal deactivator, and a UV stabilizer.

Some antioxidants functioning via more than one mechanism are autosynergistic. An antioxidant that is synergistic with one member may be antagonistic to another antioxidant. Carbon black is synergistic with some phenolic sulfides but is antagonistic to many phenols and amines, for example.

Antioxidants and Processing Stabilizers:

Oxidation of polymers i.e. plastics is invariably manifested by loss of physical properties and ultimate failure of polymer artifacts. Polymer stabilization deals primarily with the inhibition of oxidative processes throughout the lifetime of the polymeric material. The underlying mechanisms of polymer oxidation (and degradation) are well known, and the selection and design of stabilizers (and antioxidants) for polymers are made in the light of current understanding of their mode of action.

Environmental and physical factors, for example, high temperatures, stress, UV light, ozone, and high-energy radiation, exert detrimental effects on polymer performance. These effects, however, can be mitigated by the incorporation of low levels of stabilizers during the fabrication process; the more demanding the application, the greater the need for more efficient stabilizers to achieve economic optimum properties of polymer products. Antioxidants and stabilizers, therefore, occupy a key position in the market of compounding ingredients for polymers, in particular, commodity polymers, such as polypropylene, polyethylene, and polyvinyl chloride.

The terms “stabilizers” and “antioxidants” are generally used in the plastics industry to describe chemical agents that inhibit degradative effects of oxygen, light, heat, and high temperatures. The terms “antidegradants,” “antifatigue agents,” and “antiozonants,” are widely employed by rubber technologists to refer to similar chemical agents, as well as to inhibitors, that combat the effects of stress and ozone.

“Antioxidant” is used herein to comprehensively describe all chemical agents that act to inhibit oxidation of a polymer matrix arising from the adverse effects of mechanical, thermal, photochemical, and environmental factors during the manufacture of the polymeric material and throughout the service life of the end-use product.

EFFECTS OF PROCESSING AND ENVIRONMENTAL FACTORS ON OXIDATIVE DETERIORATION OF POLYMERS:

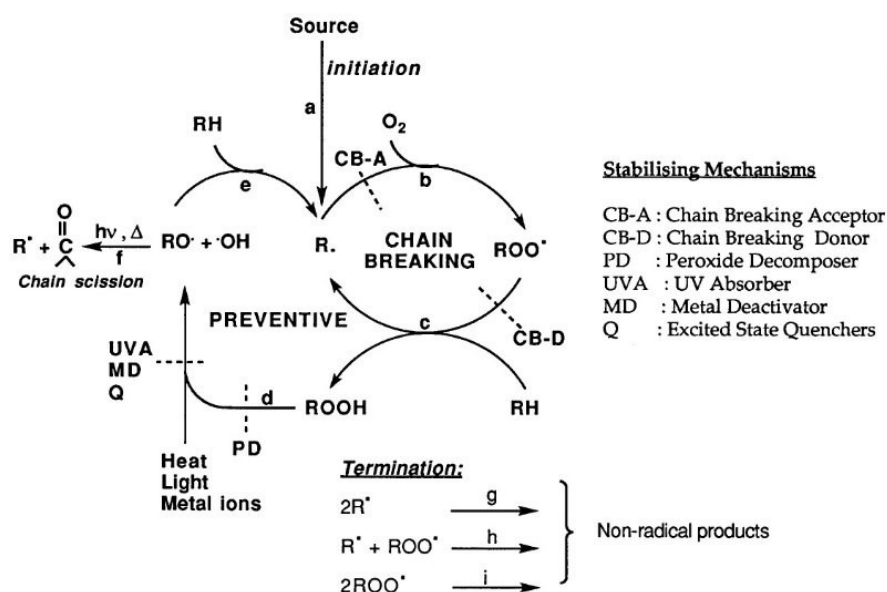
Thermooxidative degradation of polymers can occur at all stages of their life cycle (polymerization, storage, fabrication, weathering), but its effect is most pronounced during conversion processes of the polymer to finished products. Polymer fabrication and conversions are normally achieved through the use of high shear mixing machinery (e.g., in extrusion, injection moulding, internal mixing, milling, and calendaring). Oxidative degradation of polymer articles in the outdoor environment is often exacerbated by combined factors in the environment, such as sunlight, rain, ozone, temperature, humidity, atmospheric pollutants, and microorganisms.

Polymer oxidation is best described by a cyclical free-radical chain reaction (Scheme I). Free radicals are initially generated (reaction Ia) and are involved in propagation reactions that lead to the

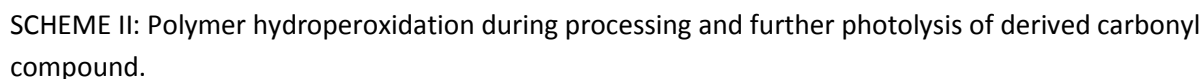
formation of hydroperoxides (reactions Ib and Ic), followed by termination reactions in which free radicals are eliminated from the oxidizing system (reactions Ig, Ih, Ii). Hydroperoxides are inherently unstable to heat, light, and metal ions and would therefore give rise to further radicals (reaction Id) that continue to initiate the chain reaction. This autooxidation process normally starts slowly but autoaccelerates, leading in most cases to catastrophic failure of the polymer product. It is generally accepted that this radical chain reaction, which involves both alkyl and alkylperoxyl radicals as propagating species, is similarly involved in both thermal- and photooxidation of polymers, albeit at faster rates of initiation for the latter.

Hydroperoxides are the main initiators in both thermal- and photooxidation. The prior thermal-oxidative history of polymers determines, to a large extent, their photooxidative behavior in service. Hydroperoxides formed during processing (and to a lesser extent during manufacturing and storage) are the primary initiators during the early stages of photooxidation, whereas the derived carbonyl-containing products (e.g., those formed via chain scission through hydrogen abstraction (reaction If), or via Norrish type I and II reactions), (Scheme II), exert deleterious effects during later stages of photooxidation. The initiating species, hydroperoxides and their decomposition products, for example, are responsible for the changes in molecular structure and overall molar mass of the polymer that are manifested in practice by the loss of mechanical properties (e.g., impact, flexural, tensile strengths, and elongation) and by changes in the physical properties of the polymer surface (e.g., loss of gloss, reduced transparency, cracking, chalking, and yellowing).

The extent of oxidative degradation of the macromolecular chain during melt processing and in service depends ultimately on the nature and structure of the base polymer. Polyolefins exhibit widely different oxidative stabilities as a result of both chemical and physical effects. Morphological differences, for example, are implicated in the greater susceptibility of polypropylene (PP) and high-density polyethylene (HDPE) toward photodegradation than of low-density polyethylene (LDPE). See scheme III



SCHEME I: Oxidative degradation processes and antioxidant mechanisms.



Everyone is familiar with the oxidation of iron; the oxidation reaction product is the reddish, dusty material called rust. With polymers, the oxidation reaction product is not as easily identified or recognized. Polymers have more subtle changes such as indirect changes in color, loss of initial gloss or clarity, crazing, chalking, or brittleness. With iron, rust spreads and penetrates deeper into the body of the material. Eventually, the iron becomes brittle, small pieces and flakes start to break off, and the article begins to lose its original strength and physical properties. A less obvious process occurs with polymers; nevertheless, the end result is still an overall loss of

physical properties.

Slowing down this process of oxidation is what many scientists strive to do. Trace amounts of transition metals and carbon are used to turn iron into stainless steel. For polymers, trace amounts of antioxidants are used. These antioxidants do not transform polymers into “stainless” polymers; however, they do significantly inhibit the oxidation process, thereby increasing the useful lifetime of the polymer. Antioxidants have been well reviewed.

Since the invention of plastics, there has been a need for antioxidants. At first, these antioxidants were only somewhat effective. The colloquialism “cheap plastic” is often used to describe plastic articles that fail at their intended use. Important strides have been made in the improvement and utility of plastic articles, primarily because of better chemistries for preventing oxidation. This does not mean that cheap plastic has completely disappeared. It only means that producers of cheap plastic have thriftily chosen to avoid the proper stabilization for their products. Often, plastics have become high quality materials, primarily through polymer structure but also through the use of antioxidants to preserve that structure.

Polymer Autoxidation:

Often, free radicals are generated at the onset of high temperatures and high shear associated with melt compounding the polymer. Still, the melt compounding of the polymer is virtually unavoidable if the polymer powder, granules, or beads are to be transformed into a useful article. Lower temperatures could be used, but melt viscosity will increase, thereby further straining the processing equipment so that throughput rates would diminish. Similarly, lower shear extrusion equipment could be used, but insufficient melting or mixing might occur. Consequently, there are trade-offs to consider.

Because it is generally accepted that oxidation is the key process by which a polymer loses its original properties, it is important to discuss the chemistry of oxidation. Actually, the most appropriate term is autoxidation as the process is automatic once polymers are exposed to oxygen. Autoxidation then feeds upon itself because of the by-products of the process, giving it a catalytic aspect. In addition, impurities in the polymer also tend to accelerate the process. There are four general steps as shown in Scheme I (Equations 1-13), where R is a macromolecule.

Reactions 1-13, via free-radical chemistry, eventually lead to polymer chain scission, polymer crosslinking, and sometimes a combination of both. Changes in molecular weight and molecular weight distribution occur. This alteration of the polymer is the mechanism by which the original properties of the polymer are significantly transformed. These types of changes in molecular weight and molecular weight distribution not only affect polymer processing characteristics but also significantly affect physical properties. Ultimately, without interrupting the free-radical chemistry, the polymer is oxidized to the point where discoloration, brittleness, crazing, cracking, and chalking are eventually observed.

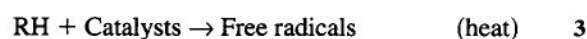
Polymer Stabilization:

To prevent this undesirable chain of events, various chemistries can be used to interrupt the free-radical process of oxidation. One class of chemistries is based on chain breaking or primary antioxidants. Another class is based on preventive or secondary antioxidants, which decompose hydroperoxides before they are transformed into free radicals.

Chain-Breaking or Primary Antioxidants:

This general class of antioxidants is capable of interrupting free-radical processes by donating labile hydrogen atoms that neutralize or quench the free radical. These hydrogen-donating antioxidants, AH, slow down oxidation by effectively competing with the polymer for free radicals, thereby abbreviating the chain length of the propagation reactions (Equations 17 and 18).

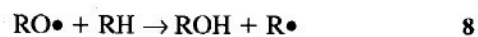
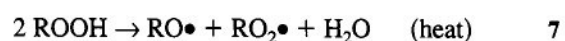
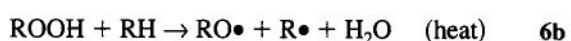
Chain initiation



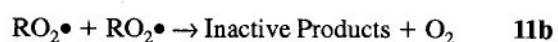
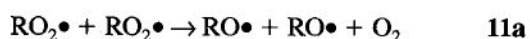
Chain propagation

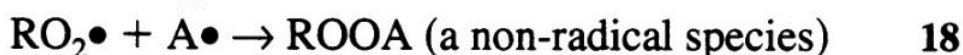


Catalysis



Chain Termination





The formation of ROOA is not necessarily the only product nor the end result. Heat, shear, and light can affect this type of molecule so that it initiates free-radical chemistry. However, certain antioxidants are less likely to undergo damaging transformation chemistries because of the nature of their molecular structure. They will be discussed below.

Phenolics:

The chemistry of phenolic antioxidants will not be discussed in detail here other than to describe how they can be used in practice. The point of incorporating them into the polymer is to stop the chemistry associated with free radicals by first donating hydrogen atoms, not a proton or a hydride, to interrupt the autoxidation process. Phenolics typically react with oxygen-centered free radicals, and consequently, can interrupt the autoxidation cycle depicted in Scheme 1 in the equations with oxygen-centered free radicals at either side. In general, phenolic antioxidants quench free radicals by donating hydrogen atoms. Thermodynamically, this occurs because the resulting phenoxyl radical is more stable than the oxygen-centered free radical it quenches, primarily through resonance structures in the phenyl ring, Figure 2 .

Depending on the structure of the phenolic, several different reaction schemes resulting in the rearrangement or deactivation of the phenoxyl radical are possible (Figures 2 and 3). The main point is that the phenolic, on the basis of its molecular structure, is capable of donating hydrogen atoms, undergoing rearrangement reactions, and further reacting with free radicals until it is fully consumed. This total consumption of the phenolic is typically undesirable because it generates color bodies. Because discoloration should be avoided, many practical techniques that prevent the total consumption of the antioxidant have been developed. These techniques typically involve using co-additives with the phenolic, such as trivalent phosphorous compounds and scavengers for acidic catalyst residues.

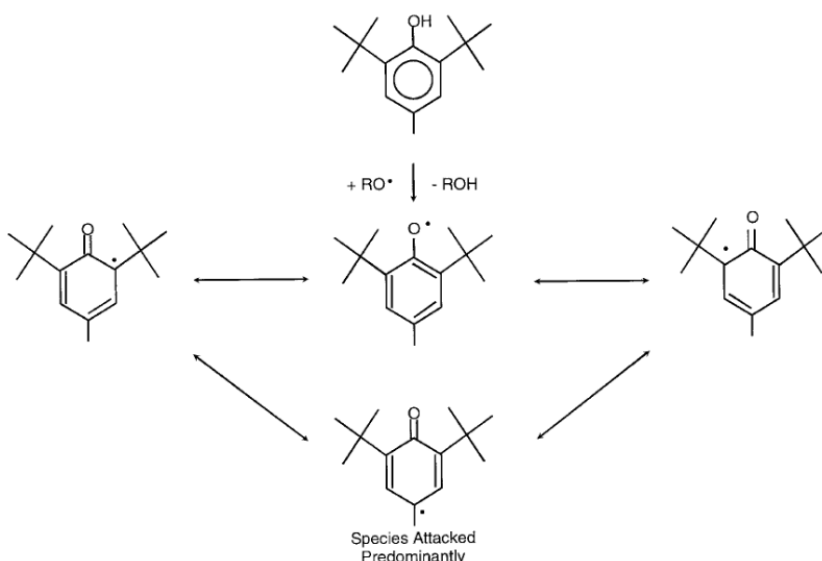


Fig. (2): Oxidation chemistry of a representative hindered phenol, butylated hydroxytoluene (BHT), followed by resonance stabilization of the phenoxyl free radical.

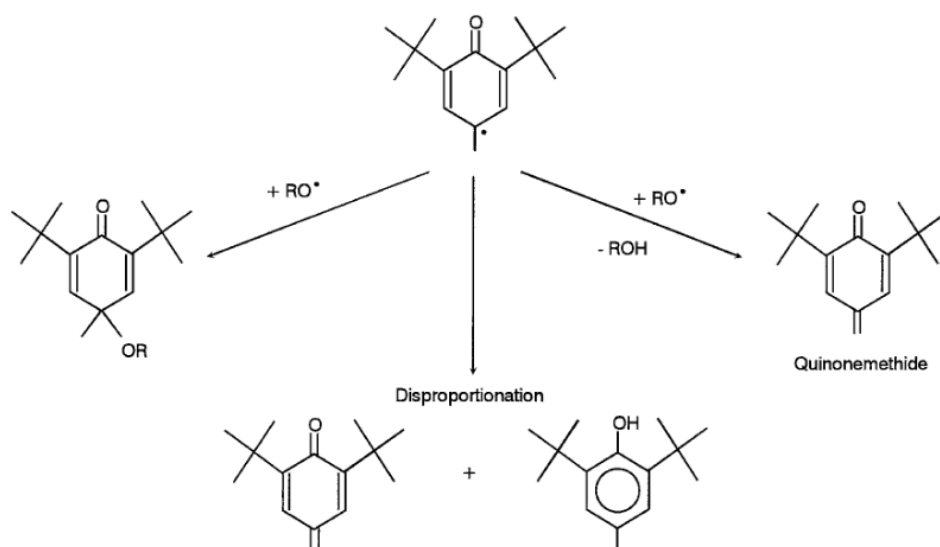


Fig. (3): Oxidation chemistry of the phenoxyl radical producing different end products.

For many phenolic antioxidants, the complete exhaustion of the molecule results in a conjugated system that typically appears yellow. As an example, the overoxidation of butylated hydroxytoluene (BHT) is shown in Figure 4 .

The structure of the original phenolic and the resulting conjugated system will dictate the nature of the discoloration, λ_{max} , and the strength of the discoloration through the absorption coefficient, ϵ . Many commercial antioxidants are designed to avoid a rapid transformation into highly colored species. A review of this phenomenon, including transformation products and their associated color and intensity, has been discussed

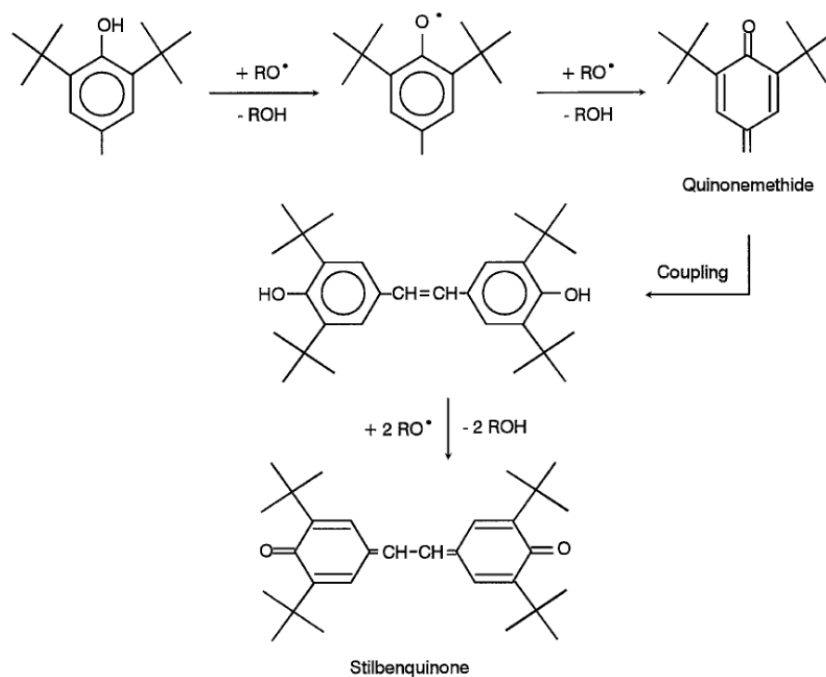
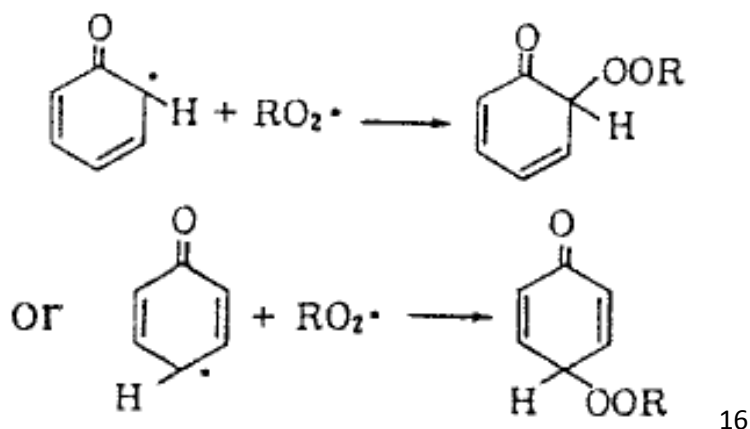
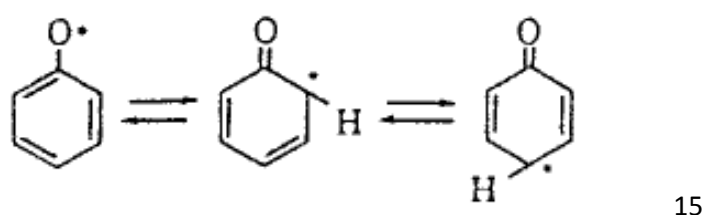
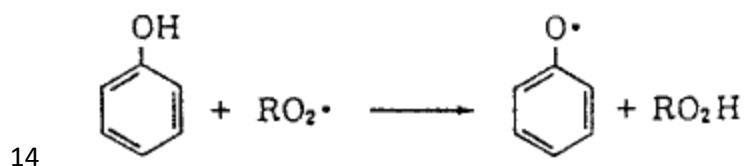


Fig. (4): Stepwise oxidation chemistry of a representative hindered phenol, butylated hydroxytoluene (BHT), producing a discolored transformation product.

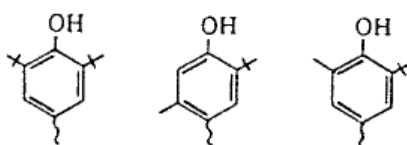
Phenolic antioxidants are radical scavengers combined with aromatic amine antioxidants. The latter antioxidant is used almost entirely in rubber because it colors the materials during use. A phenolic antioxidant, however, is used in many fields and is an indispensable component for stabilizing plastics. A phenolic antioxidant is effective for scavenging oxygen-containing radicals such as RO_2^\bullet and RO_2H . The steps can be illustrated, using phenol as an example, as follows:



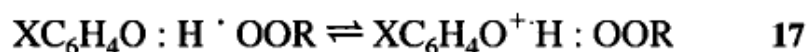
The step of Equation 14 proceeds 10³ to 10⁴ times faster than the steps shown in Equations 4 and 5 because of the stabilization from the resonance of an intermediate phenoxy radical (see Equation 15). Accordingly, adding 1% of a phenolic antioxidant to polymers can stop the competing steps in Equations 4 and 5 effectively, breaking the cycle of autoxidation (Equation 16).

Structure and Action:

Phenolic antioxidants used today contain the following moieties: (Structure 1) as fundamental skeleton. The effect of substituents of phenolic moieties has been studied by Howard and Ingold and is explained by the mechanism that substituents influence an electrophilic reaction of peroxy radical as shown in Equation 17



Structure 1



In addition, the role of substituents are also explained from the standpoint of steric hindrance. As shown in Table 3, less hindered phenols (e and f) exhibit higher rate constants than hindered phenols (a through d). The latter phenols, however, have higher values of n , which the number of many phenoxy radicals trapped by an equivalent of a phenol. Although a phenol can generally trap twice as many moles of peroxy radicals per mole of a phenolic moiety, a less hindered phenol or a phenol having small substituent at para-position, such as 2,6-di-*tert*-butyl-4-methyl-phenol (BHT), can enter into the coupling reaction between phenoxy radicals, resulting in a lower n value (Equations 18-20):

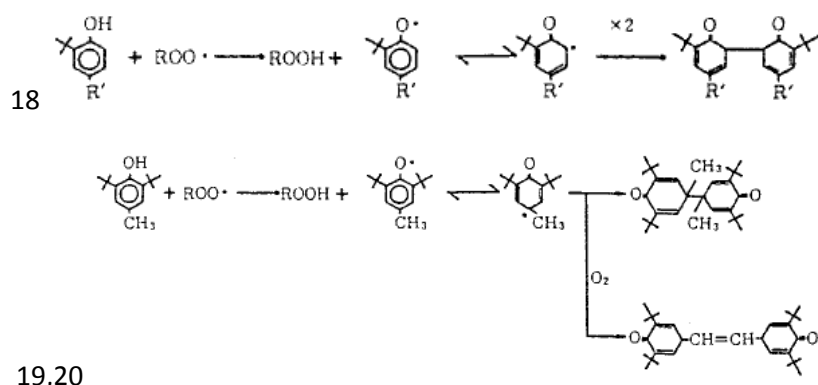
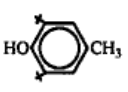
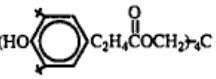
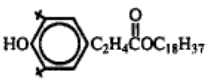
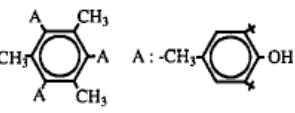

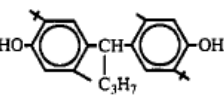
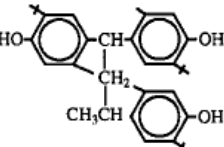


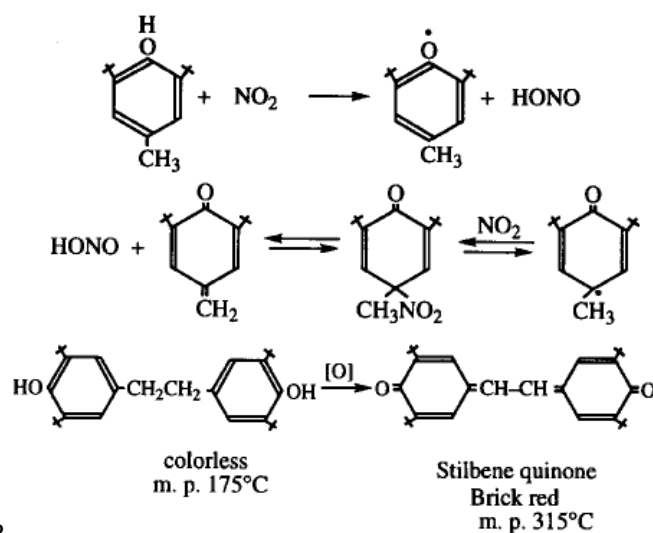
TABLE 3. Evaluation of Phenolic Oxidants

		Oxidation of styrene ^a		PP oven test	
		$k_{\text{inh}} \times 10^3$ (50 °C) (l/mol.sec)	n	IP (min)	150 °C (h)
(a)	 BHT	15.8	1.71	108	48
(b)		8.8	1.97	125	960
(c)		10.4	2.00	129	264
(d)	 A: -CH ₃ -  -OH	13.0	1.92	121	240
(e)		48.6	1.13	70	48
(f)		45.4	1.26	80	120

^aStyrene = 3.48M, phenolics = 1×10^{-3} M, solvent: chlorobenzene.

Characteristics:

A phenolic antioxidant shows synergistic effects when it is used with one or more additives. A phenol, for example, can contribute to heat stabilization with a sulfur- or phosphorus-containing compound. However, phenols color polymer materials such as fabrics, which have frequent contact with NO_x gases. The mechanism is shown in Equations 21-23.



Fabrics and carpets are inclined to lose antioxidants by extracting during dry cleaning, followed by much easier degradation. Extracting an antioxidant from plastics depends on the molecular weight of a phenol. A phenol having a molecular weight greater than 2000 can resist extraction remarkably well. However, a phenol with a molecular weight of 2500 decreases the effect because of a bad affinity with plastics and difficult mobility. A phenol with a molecular weight of about 100,000 exhibits little effect, if any. Thus, the preferred molecular weight for a phenol used for extraction resistance will range from a few hundred to 3000, depending on use.

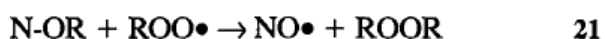
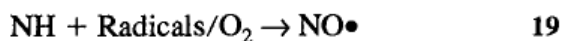
Aromatic Amines:

Certain classes of antioxidants, such as aromatic amines, are effective at scavenging free radicals as are the phenolic antioxidants. Aromatic amines are even more powerful in easily oxidized polymers like unsaturated elastomers. The chemistry, however, is not as well understood because of the nature of the products and their reactions. Although potent, aromatic amines tend to stain or discolor. This discoloration is not necessarily caused by the original antioxidant structure, but rather, by the chemical transformations that occur when aromatic amines interact with free radicals. Aromatic amines are typically used in elastomeric systems that are pigmented or loaded with carbon black to mask staining.

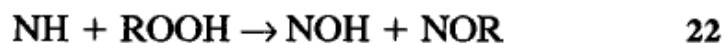
Hindered Amines:

This class of chemistry is typically associated with light stabilizers because they are extremely effective at protecting certain classes of polymers from the damaging effects of ultraviolet radiation.

However, hindered amines also belong to the family of chain-breaking antioxidants because they are also capable of scavenging free radicals. The most common hindered amine is based on 2,2,6,6-tetramethylpiperidine. The four methyl groups create steric hindrance and block elimination reactions at the carbon atoms adjacent to the amine group. The N-H group also exists as N-R and N-OR, where R is a hydrocarbon. Their antioxidant behavior based on the N-H group is shown below (Equations 19-20).



Some researchers suggest that hindered amines are capable of decomposing hydroperoxides (Equation 22).



These are only representative mechanisms, and they have been the subject of much discussion. Nevertheless, the point is that hindered amines in one way or another efficiently interrupt the autoxidation chain reaction. The mechanism may involve reacting with carbon and oxygen-centered radicals, as well as decomposing peracids or hydroperoxides. Although in practice, hindered amines are eventually exhausted, the processes described above clearly show that hindered amines are capable of regenerating. This multiple turnover performance may include either free-radical scavenging, hydroperoxide, or peracid decomposition. Regardless, hindered amines perform well as long-term thermal stabilizers at lower temperatures, in addition to their recognized capability as light stabilizers.

The antioxidant capability of hindered amines proceeds most efficiently at temperatures below 135 °C and preferably below 120 °C. Consequently, hindered amines should not be considered as melt-processing stabilizers. In practice, after melt compounding, most polymers are not typically exposed to such high temperatures.

Metal Deactivators:

Polymers that come into contact with metals that have low oxidation potentials, such as copper, are susceptible to oxidation from the metal catalyzed decomposition of hydroperoxides, as shown in reactions in Scheme I. One way to avoid these types of free radical activators is by using metal deactivators. Metal deactivators are designed to contain hydrazide or amine functional groups, which can complex to the metal. Most commercial materials also include a phenolic antioxidant as part of the molecular structure. Metal deactivators are usually melt compounded into the polymer, which then interacts with the metal by migrating to the polymer/metal interface. This chemistry is particularly important for wire and cable applications.

Preventive or Secondary Antioxidants:

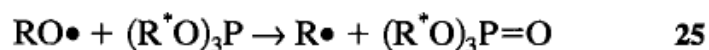
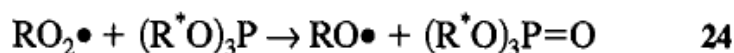
One of the most damaging species in the autoxidation process is the hydroperoxide, ROOH. Under elevated temperatures, hydroperoxides decompose via a homolytic cleavage to yield two free radicals. This step demonstrates the catalytic nature of autoxidation. The destruction of the hydroperoxides, which continually build up in the polymer, is essential in protecting the polymer. Most commercially available peroxide decomposers are based on trivalent phosphorus compounds and divalent sulfur compounds.

Trivalent Phosphorus Compounds:

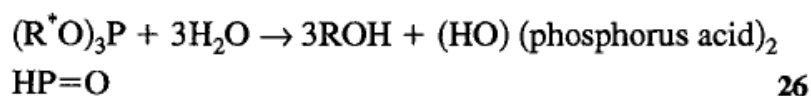
The chemistry of phosphites and phosphonites has been studied. In essence, a P(III) compound reacts with a hydroperoxide converting it to alcohol, ROH, with the subsequent oxidation of P(III) to P(V), as shown in Reaction 23. This chemistry takes place during melt compounding of the polymer in processing equipment. At ambient temperatures, the reaction is very slow. This slower reaction rate increases the importance of the hindered amines mentioned above, which are capable of decomposing hydroperoxides at temperatures below 120 °C to 135 °C (Equation 23).



Phosphorus III compounds are also capable of reacting with free radicals; however, the contribution of this chemistry is secondary in comparison to hydroperoxide decomposition (Equations 24 and 25).
28



The groups attached to phosphorus play a key role in the reactivity and the hydrolytic stability of the compound. In a very general sense, with less steric hindrance, the reactivity with hydroperoxides increases and the hydrolytic stability decreases. Sometimes co-additives are used to increase the hydrolytic stability, such as tri-isopropanol amine, alkaline acid scavengers, or both. In addition, material with small particle size can be compacted so that there are larger particles with less surface area. These techniques will improve handling of the material in the open atmosphere. Nevertheless, when the additives are melt compounded into the polymer, the hydrolysis inhibitors are diluted into the polymer in the same way that the phosphorus compound is dispersed. This process leaves hydrolytically unstable phosphites at the mercy of residual water in the polymer whenever it has contact with water for prolonged periods. Hydrolysis of phosphites, which is a stepwise reaction for each of the RO- groups attached to the phosphorus atom, is summarized as follows (Equation 26).

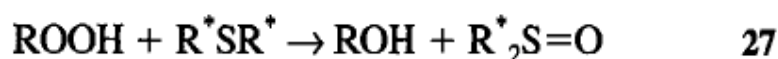


The phosphorous acid corrodes processing and compounding equipment, leading to a phenomenon known as black specks. In addition, the liberated alcohols, or phenols, usually have low molecular weight and can be oxidized.

However, increasing the steric hindrance can improve the compound's hydrolytic stability which allows for easier handling in the open atmosphere; yet, the reactivity with hydroperoxides decreases. Typically, one must decide which is more important: fast reactivity or safe handling of the material and stability in the postproduction polymer. Some commercial phosphites offer a balance between these two extremes. Recent efforts have focused on designing phosphorus-based compounds with improved hydrolytic stability to provide excellent performance as a melt processing stabilizer.

Divalent Sulfur Compounds:

The chemistry of S(II) compounds has been discussed and reviewed. They react similarly to phosphorus compounds in that hydroperoxides are transformed into alcohols with concomitant oxidation of S(II) to S(IV) as shown below (Equations 27 and 28).



The chemistry does not stop with the sulfone or sulfoxide. Elimination reactions result in the formation of sulfenic and sulfonic acids, which can further decompose to sulfur dioxide and sulfur trioxide. The good news is that these sulfur transformation products are also very effective at decomposing hydroperoxides. On a per-weight basis, the sulfur compounds, after the first two oxidation steps, provide multiple equivalents of stabilization via the sulfur transformation chemistry. The concern is that organoleptics can form, which becomes an issue when polymers are used in products that have contact with food.

Peroxide Decomposers:

Sulfur-Containing Antioxidants:

A sulfur-containing antioxidant is known as an effective hydroperoxide decomposer and is added to various polymers with a phenol because it is ineffective when used alone. A sulfur-containing antioxidant decomposes hydroperoxides ionically to inhibit initiation reactions, which would otherwise be induced by homolytic cleavage. Of all such antioxidants only a thiopropionic acid derivative is very effective, and this may be because of the action mechanism of a sulfur compound. One action mechanism that has been proposed is shown in Equation 24

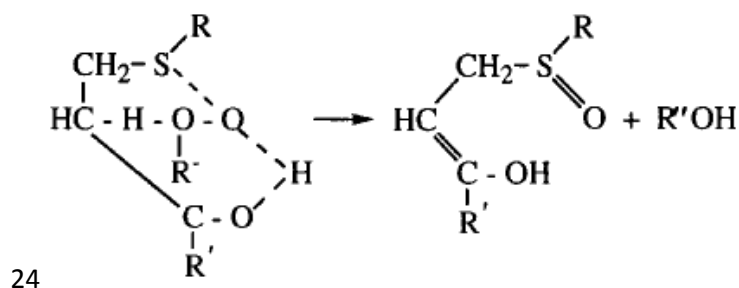


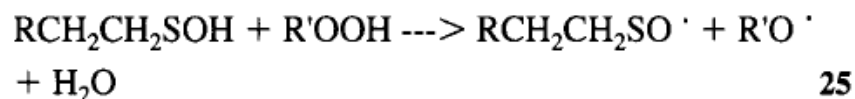
Table 4 shows the heat resistance of polypropylene when various sulfur-containing antioxidants are mixed with phenolic antioxidants.

TABLE 4. Structures and Effect of Sulfur-Containing Antioxidants in the Presence of 4,4'-Thiopsis (3-Methyl-4-tert-Butyl-Phenol)

	Time to failure (days) ^a
$ \begin{array}{c} \text{O} \\ \\ (\text{H}_{25}\text{C}_{12}\text{OCCH}_2\text{CH}_2)_2\text{S} \end{array} $	43
$ \begin{array}{c} \text{O} \\ \\ (\text{H}_{25}\text{C}_{12}\text{OCCH}_2\text{CH}_2)_2\text{O} \end{array} $	5
$ \begin{array}{c} \text{O} \\ \\ (\text{H}_{25}\text{C}_{12}\text{OCCH}_2\text{CH}_2)_2\text{NH} \end{array} $	4
$ \begin{array}{c} \text{O} \\ \\ (\text{H}_{27}\text{C}_{13}\text{OCCH}_2\text{CH}_2)_2\text{S} \end{array} $	51
$ \begin{array}{c} \text{O} \\ \\ (\text{H}_{29}\text{C}_{14}\text{OCCH}_2)_2\text{S} \end{array} $	15
$ \begin{array}{c} \text{O} \\ \\ (\text{H}_{27}\text{C}_{13}\text{COCH}_2\text{CH}_2)_2\text{S} \end{array} $	10
$ (\text{CH}_{16}\text{H}_{33})_2\text{S} $	19

^aTested in ovens at 150 °C for polypropylene.

A sulfur compound does not provide good stabilization at a higher temperature because of the formation of an intermediate, which forms during decomposition of hydroperoxides and works as a pro-oxidant as shown in Equation 25



A sulfur compound acts on hindered amine light stabilizers with antagonism, resulting in the decreased weather resistance of plastics.

However, it exhibits remarkable synergism with a phenolic antioxidant.

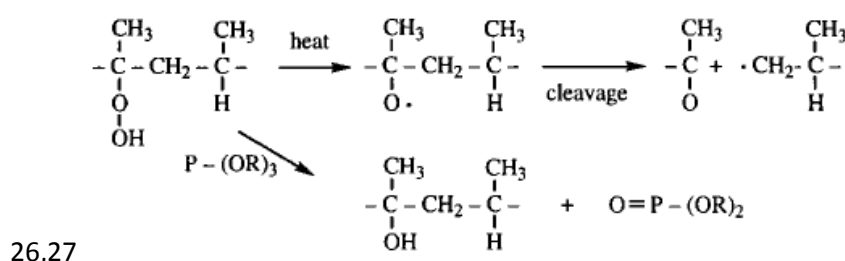
Phosphorus-Containing Antioxidants:

A phosphorus-containing antioxidant functions similarly to one containing sulfur. Thus, it also is used advantageously as a processing stabilizer.

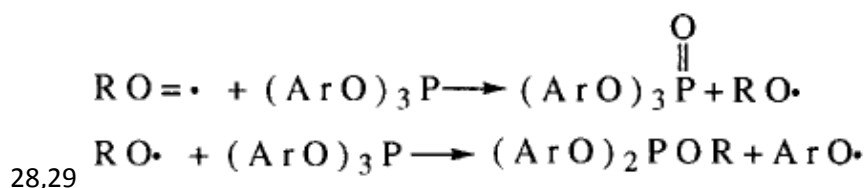
A phosphorus compound can decompose hydroperoxides ionically by the overlapping of the d-orbital of a trivalent phosphorus over a hydroperoxide formed in oxidative

Ahmed M. Eltayef, POLYETHYLENE (Stabilization and Compounding), 2001

degradation of polymers. Thus, it controls the cleavage of polymer chains during processing (see Equations 26 and 27)

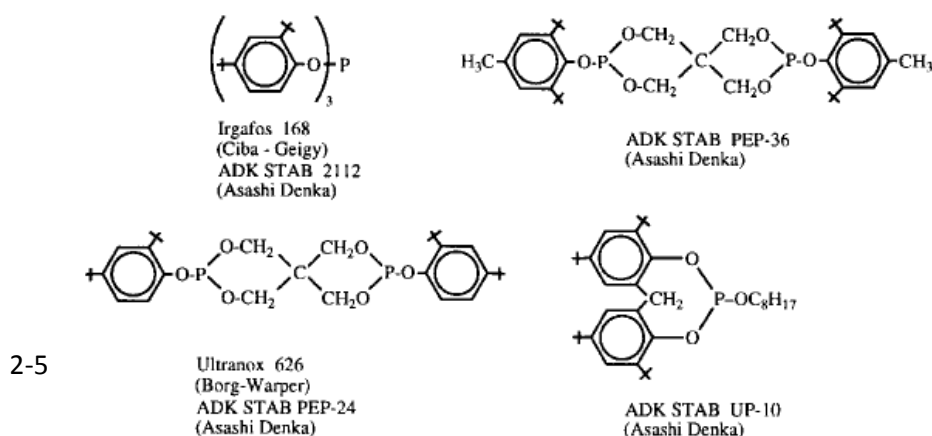


A phosphorus compound also acts as a radical scavenger as shown in Equations 28 and 29



In the oxidation of cumene, however, phosphorus compound does not show any eminent inhibition. Its radical-scavenging ability is inferior to that of BHT. The inhibitive action radical-trapping, therefore, may be neglected in a practical use.

Phosphorus compounds are used to stabilize plastics by ionic decomposition of hydroperoxides, the rate of which depends on the molecular structure of a phosphorus compound. An alkyl phosphite, in general, decomposes hydroperoxides faster than an aryl phosphite. The former, however, is sensitive to hydrolysis and heat degradation during processing and on the shelf and consequently does not show firm effect. The stabilization of phosphorus compounds against hydrolyses is considerably important and is achieved in the compounds shown in Structures 2-5



A phosphorus compound behaves like a sulfur compound in terms of the hydroperoxide decomposition, but the former compound shows remarkably higher effects, especially in processing at a temperature above 200 °C. A phosphorus compound is also characterized by no formation of any pro-oxidant like a sulfur compound after the hydroperoxide decomposition.

Although the synergism with a phenol is not so remarkable as that of a sulfur compound, a phosphorus compound often can inhibit coloration in plastics stabilized by a phenol.

Synergist Mixtures of Antioxidants:

When used alone, neither trivalent phosphorus compounds nor divalent sulfur compounds are capable of providing complete melt processing and thermal stability of the polymer. However, combined with a phenolic antioxidant, the results are better than the sum of the performance levels of each additive type. This is known as synergism. What represents a synergistic mixture of additives in one polymer does not necessarily translate into an optimum mixture in another polymer system.

For example, blends of a phenolic antioxidant and a phosphite are very useful for melt compounding of polyolefins and for engineering polymers. Together, they work well to maintain the polymer's molecular weight while simultaneously affording low color. The phosphite shares the work load with the phenolic so that neither one becomes exhausted or overoxidized. Even if the phosphite is entirely consumed, it has done its share of work by preserving more of the phenolic antioxidant for long-term thermal stability. For example, blends of a phenolic antioxidant and a divalent sulfur compound provide an excellent combination for improving a polymer's long-term thermal stability. Although the sulfur compound produces no activity during melt processing, it does perform well as a hydroperoxide decomposer during long-term thermal aging. This contribution, along with the free radical scavenging capability of the phenolic, offers a good mix (provided that taste or odor are not key measurements of performance). 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.

The optimum ratio of A to B can be determined by measuring a series of performance parameters. Although time consuming, this procedure eventually can identify the optimum ratio with real data. If three or more components are assessed at the same time, statistically designed experiments often can sort out the data set.

Antagonistic Mixtures of Antioxidants:

Mixtures of antioxidants can work together synergistically, as described above; they can also work against each other. Chemistries that interfere with each other may not necessarily be obvious until the evidence is presented. For example, a phenolic antioxidant combined with a divalent sulfur

compound for thermal stability and a hindered amine for light stability ensures long-term thermal and good light stability.

Regrettably, the oxidation products of the sulfur compound can be quite acidic. These acidic species from the sulfur compound can complex the hindered amine as a salt, preventing the hindered amine from entering into its free-radical scavenging cycle. This antagonism has been known for quite a while and recently was discussed. Other types of antagonistic chemistry often involve relatively strong acids or bases, either Bronstead 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. These types of interactions are sometimes difficult to elucidate, typically time consuming, and always a waste of a perfectly good antioxidant.

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, propensity to form transformation products with taste or odor, regulatory issues associated with products used in food packaging, and in-polymer performance versus cost.

Volatility:

Most additives are melt compounded into the polymer after the polymer exits the polymerization reactor. The exiting polymer, as either a molten mass or a free-flowing powder, is converted to pellets that are stored in containers and then shipped to customers. The customer then transforms these pellets into shaped articles, which are stored and then shipped to the next customer. The two melt-compounding steps represent significant heat histories. In some climates, the product is stored in warm temperatures. It is important that the stabilizer and its transformation products, which may also provide stability, not volatilize from the polymer. Many commercial antioxidants have been designed with higher molecular weights with climatic conditions in mind. For those antioxidants with lower molecular weights, volatility may actually be desired.

Compatibility:

Antioxidants should be soluble in the polymeric matrix. If they are not, they should at least migrate or diffuse slowly. A slower diffusion rate is important because if the antioxidant exceeds its solubility limit in the polymer, there is a driving force for additives to be exuded. Exudation or blooming involves the migration of the additive out of the polymer matrix and onto the surface as a very thin film. At the surface, the additive becomes susceptible to extraction, oxidation, volatilization, or being washed away. Blooming of the antioxidant also can diminish surface gloss, create stickiness, or eliminate blocking (cling) of film surfaces to one another. Antioxidants can be modified to improve compatibility.

Color Stability:

Antioxidants need to perform well as stabilizers for the polymer, but they must also not produce unwanted color from the transformation chemistries associated with preventing oxidation. As mentioned earlier, some antioxidants produce color by their very nature, while other antioxidants discolor only when they have been overoxidized. If masks are used, color is not a key issue.

Physical Form:

Antioxidants often are free-flowing white powders; however, health and safety hazards associated with fine powders or dust are becoming more of a concern. Many antioxidants now are offered commercially in dust-free forms. Liquid or molten antioxidants are another interesting alternative, provided that they are compatible in the polymer matrix. Some manufacturers require fine powders to mix well with their reactor product.

Taste and Odor:

Taste and odor become key issues when applications are for home or personal use or involve contact with food. Interestingly enough, the human nose often detects these odors better than many powerful analytical instruments.

Regulatory Issues:

Antioxidants used in polymers that come into contact with food require clearance from various regulatory agencies. Chronic and subchronic toxicological testing is performed in different species. Extractability using different food simulants is also evaluated. Accordingly, concentrations of the material expected in the diet can be assessed. A product typically should have minimal health hazards associated with its use or handling. Safety is usually assessed by studying the toxic effects in tests where antioxidants are tasted, inhaled, or come into contact with eyes and skin. Mutagenicity tests are also carried out.

Performance Versus Cost:

Antioxidants are not free, but they are affordable. Essentially, the appropriate type and level of antioxidants must be selected in order to stabilize the polymer adequately for a particular use. Some articles are used once, such as bags and food wrap, and others are expected to last, such as geomembranes, an insulation for electric cables or for gas and water transmission pipes.

For example, if the material is a nondurable good, an article used only once or twice before disposal, then the type and concentration of antioxidant are chosen to minimize unnecessary costs associated with stabilizing the polymer. The antioxidants should provide stabilization for the initial melt compounding of polymerization reactor granules into pellets and from pellets into a finished article,

be it tape, film, fiber, sheet, cups, or eating utensils. Stabilizing the polymer to last 10 years when the product is going to be used only once or twice does not make sense. However, maintaining quality becomes important when scrap from the melt compounding is recycled. Minimizing costs by reducing antioxidants can sometimes result in inferior products. In addition, a cushion usually is built into the system to avoid unexpected shut-downs and start-ups or prolonged storage in hot places.

However, if the material is a durable good, a product with a long period of use, the type and concentration of the phenolic antioxidant is chosen to meet the performance criteria. The costs associated with this type of antioxidant is worth the additional value for such products as pipes, insulation bumpers, gears, rotors, covers, housings, membranes, hose, tubing, carpet, furniture, toys, and so on. The value-added feature of the product pays for the additional stabilizers needed to ensure high quality and durability.

Performance Testing:

Testing is needed to validate the use of a particular antioxidant system before a product is commercialized. Initial testing frequently involves melt compounding of the polymer with various formulations composed of different additive systems or mixtures. Color, appearance, and retention of molecular weight are common measures. Long-term thermal stability is carried out usually in ovens set at elevated temperatures to accelerate the aging process. Color development and retention of physical properties are measured as a function of time at that test temperature. Varying extrusion temperatures and changing shear rates afforded by the processing equipment are also useful measurements. Testing the ancillary properties mentioned above is also important.

INHIBITION OF OXIDATIVE DEGRADATION: CLASSIFICATION OF ANTIOXIDANTS AND THE BASIS OF THEIR MECHANISMS OF ACTION:

The terms “antioxidants” and “stabilizers” cover a number of chemical classes of compounds that can interfere with the oxidative cycles (see Scheme I) to inhibit or retard oxidative degradation of polymers. Two major classes have been identified according to the way they interrupt the overall oxidation process: chain-breaking and preventive antioxidants. Tables 1a and 1b show some typical examples of different classes of commercial thermal- and photo-antioxidants.

Chain-breaking (CB) antioxidants (sometimes referred to as primary antioxidants) interrupt the primary oxidation cycle by removing the propagating radicals, $\text{ROO}\cdot$ and $\text{R}\cdot$. Chain-breaking donor (CB-D) antioxidants are electron or hydrogen atom donors that are capable of reducing $\text{ROO}\cdot$ to ROOH , (Scheme IV , reaction IV b). To perform their function, CB-D antioxidants must compete effectively with the chain-propagating step (reaction IV f) and the antioxidant radical ($\text{A}\cdot$) produced from reaction IV b must lead to stable molecular products, that is, $\text{A}\cdot$ must not continue the kinetic chain either by hydrogen abstraction (reaction IV g) or reaction with oxygen (reaction IV h). Hindered phenols and aromatic amines (Table 1a , AO1-AO12) are significant examples of commercial CB-D antioxidants. Chain-breaking acceptor (CB-A) antioxidants act by oxidizing alkyl radicals (reaction IV

d) in a stoichiometric reaction ($R\dot{u}$ are removed from the autoxidizing system) in competition with the chain-propagating reaction (reaction IV a) and hence are effective only under conditions of low oxygen concentration. Quinones and stable free radicals that can act as alkyl radical trapping agents are good examples of CB-A antioxidants.

Preventive antioxidants (sometimes referred to as secondary antioxidants), however, interrupt the second oxidative cycle by preventing or inhibiting the generation of free radicals. The most important preventive mechanism is the nonradical hydroperoxide decomposition, PD. Phosphite esters and sulfur-containing compounds, for example, AO13-AO18 (Table 1), are the most important classes of peroxide decomposers. The simple trialkyl phosphites (e.g., Table 1 , AO13) decompose hydroperoxides stoichiometrically (PD-S) to yield phosphates and alcohols (Scheme V , reaction V a). Sterically hindered aryl phosphites have an additional chain-breaking activity: they react with peroxy and alkoxy radicals during their function as antioxidants (reactions V b, V c).

Sulfur compounds, e.g., thiopropionate esters and metal dithiolates (Table 1 , AO16-AO18), decompose hydroperoxides catalytically whereby one antioxidant molecule destroys several hydroperoxides through the intermediacy of sulfur acids. Metal deactivators (MDs) primarily act by retarding metal-catalyzed oxidation of polymers; they are, therefore, important under conditions in which polymers are in contact with metals, e.g., wires and power cables. Metal deactivators are normally polyfunctional metal-chelating compounds (e.g., Table 1 , AO19-AO22) that can chelate with metals and decrease their catalytic activity.

UV absorbers (UVAs) act by absorbing UV light, hence retarding the photolysis of hydroperoxides. Typical examples are based on 2-hydroxybenzophenones (AO 16) and 2-hydroxybenztriazoles (e.g., Table 1 , AO23-AO27); both are relatively stable to light between 300 and 360 nm and have high molar absorptions in this region. Their activity is also associated with hydrogen bonding between the 2-hydroxy group and the chromophore.

PROCESSING ANTIOXIDANTS:

Stabilization against mechano-oxidative degradation during high-temperature processing is essential in order to stabilize the polymer melt and to minimize the formation of adverse molecular impurities and defects that may contribute to early mechanical failure of finished articles during service. The choice of antioxidants for melt stabilization varies depending on the level of oxidizability of the base polymer, the extrusion temperature, and the performance target of the end-use application.

The effectiveness of melt-processing antioxidants is normally measured by their ability to minimize changes in the melt flow index (MFI) of the polymer that occur in their absence. Chain-breaking antioxidants are generally used to stabilize the melt in most hydrocarbon polymers. Hindered phenols (CB-D, e.g., Table 1 , AO1-AO4) are very effective processing antioxidants for polyolefins, (Table 2). Aromatic amines, however, have limited use because they give rise to highly colored conjugated quinonoid structures during their antioxidant function. Although hindered phenols do not suffer as much from the problem of discoloring polymers during melt processing, yellowing can occur as a result of intensely colored oxidation products, such as stilbene quinone (SQ) from BHT (Scheme VI). Transformation products of stabilizers formed during melt processing may exert anti-

and/or prooxidant effects. For example, in BHT, peroxydienones (PxDs) (reactions VI b, VI b_a) lead to prooxidant effects, because of the presence of the labile peroxide bonds, whereas quinonoid oxidation products BQ, SQ, and G_u (reactions VI, VI b, VI c, VI d) are antioxidants and are more effective than BHT as melt stabilizers for PP. The quinones are effective CB-A antioxidants, and those that are stable in their oxidized and reduced forms (e.g., galvinoxyl, G_u, and its reduced form, hydrogalvinoxyl, H G) may deactivate both alkyl (CB-A mechanism) and alkylperoxyl (CB-D mechanism) radicals in a redox reaction (reactions VI, VI e, VI f). Alkyl sulphides (e.g., Table 1 , AO-16, AO-17), which are catalytic peroxide decomposers (PD-Cs) acting through further oxidation to sulfur acids, are also used as antioxidants during processing of polyolefins. However, a major disadvantage of these simple sulfides is that their conversion to sulfur acids (Scheme VII) involves a parallel series of prooxidant reactions involving the formation of propagating radicals (e.g., reaction VII e). Therefore, such antioxidants (e.g., AO-17) are always used in combination with effective chain-breaking donor antioxidants. Similarly, in the case of phosphites (e.g., AO-14), free-radical-forming reactions (reactions V a, V a_a) are believed to occur simultaneously with the stoichiometric peroxide decomposition reaction, hence the normal practice of using phosphites in combination with CB-D antioxidants (e.g., Irganox 1010) for stabilizing polyolefin melts. Table 2 shows the improvement in melt stabilization of PP achieved when the sulfide (AO-17) and phosphite (AO-14) antioxidants are used in combination with Irganox 1010 (AO-4).

Aromatic amines (e.g., Table 1 , AO-6 and AO-7) are more effective than hindered phenols (e.g., Table 1 , AO-1 and AO-4) for melt stabilization of polyamides. Copper salts (e.g., copper acetate) in combination with small amounts of a halide (e.g., potassium iodide) are also used to stabilize polyamides, although this system gives rise to polymer discoloration and suffers from the ease of loss by water extraction.

Stabilizers with high molar masses (e.g., antioxidants 4 and 5 in Table 1) have lower volatility and are potentially more effective than those with lower molar masses containing the same antioxidant function, e.g., BHT (antioxidant 1 in Table 1) for thermooxidative stabilization in service. Furthermore, peroxide decomposers, such as sulfur-containing compounds enhance the performance of high-molar-mass phenols under high-temperature conditions in service. For example, in polyolefins, dialkyl sulfides such as antioxidants 16 and 17 (see Table 1) are often used as peroxide decomposer synergists.

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TABLE 1b. Some Commercial Photoantioxidants (Light Stabilizers)

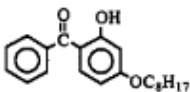
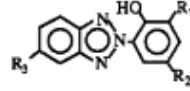

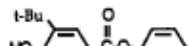
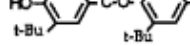
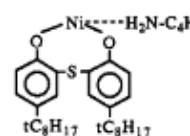
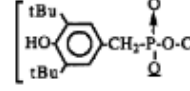
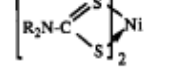
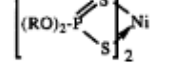
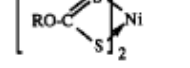
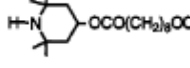
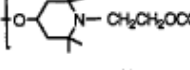
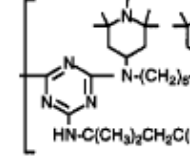
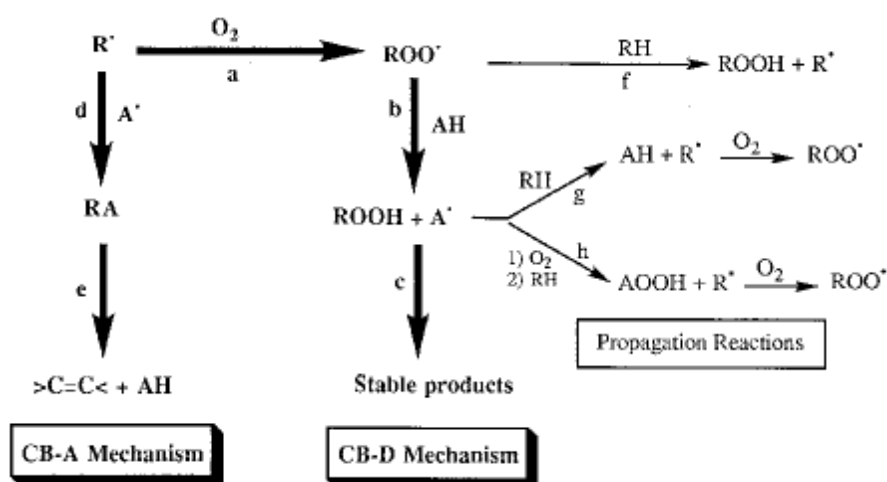
Antioxidant	Commercial or Common Name	AO Code
UV Absorbers		
	Cyasorb UV531 Chimasorb 81	23 24
 $R_1=R_2= \text{tBu}, R_3=\text{Cl}$	Tinuvin 327	25
 $R_1=\text{tBu}, R_2=\text{CH}_3, R_3=\text{Cl}$	Tinuvin 326	26
 $R_1=\text{H}, R_2=\text{CH}_3, R_3=\text{H}$	Tinuvin P	27
	Tinuvin 120	
Nickel Complexes		
	Cyasorb UV1084 Chimasorb N-705	28
	Irgastab 2002	29
	Nickel dialkyl- dithiocarbamate (NiDRC)	30
	Nickel dialkyl- dithiophosphate (NiDRP)	31
	Nickel dialkyl- xanthate (NiRX)	32
Hindered Amines		
	Tinuvin 770	33
	Tinuvin 622	34
	Chimasorb 944 35	

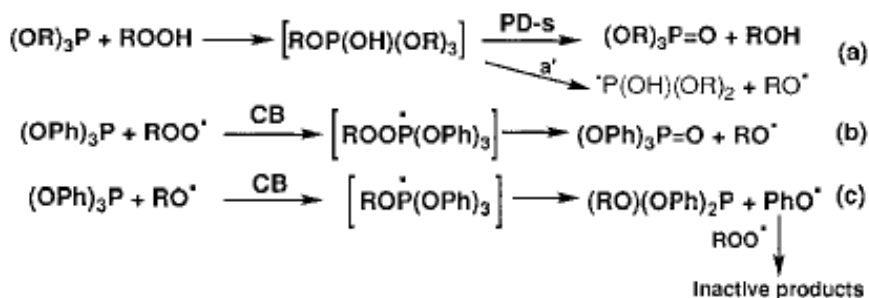
TABLE 2. Antioxidant Efficiency of Hindered Phenols, Alkyl Sulphides, Phosphites, and Their Combinations as Processing Antioxidants in PP

Antioxidant	% w/w	MFI, g/10 min
Control (no antioxidant)	0	11.7
Irganox 1010 (AO-4)	0.05	5.8
Irganox 1010 (AO-4)	0.10	4.1
Irgafos 168 (AO-14)	0.05	7.7
Irgafos 168 (AO-14)	0.10	7.2
Irganox PS 800 (AO-17)	0.10	8.4
Irganox 1010 + Irgafos 168	0.05 + 0.05	4.3
Irganox 1010 + Irganox PS 800	0.05 + 0.10	4.9

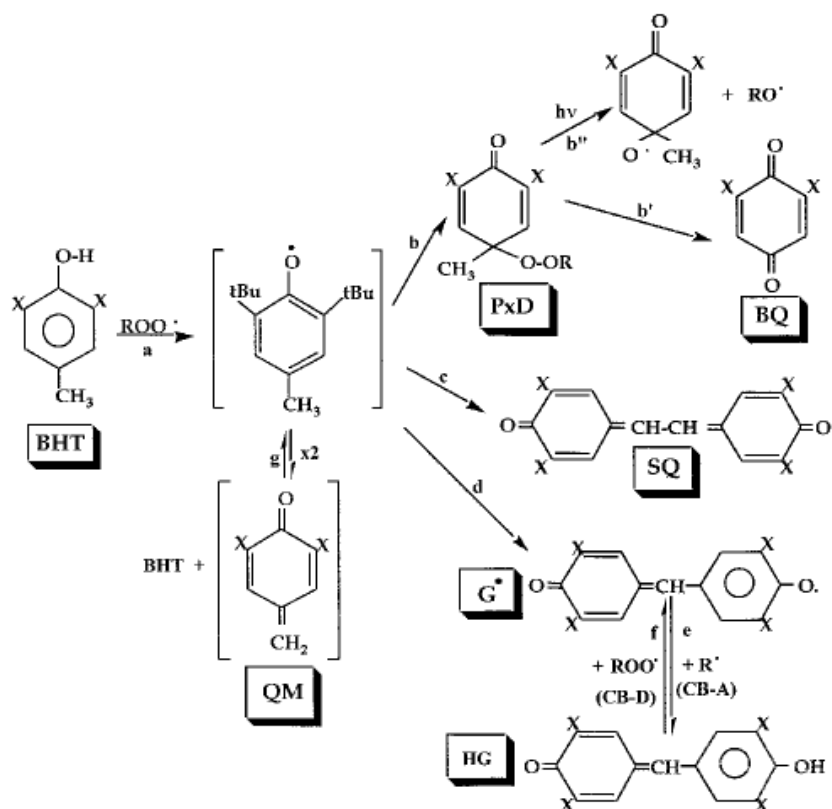
Note: Polymer processed in an internal mixer at 190 °C. melt flow index (MFI) measured at 230 °C and 2.16 kilogram.



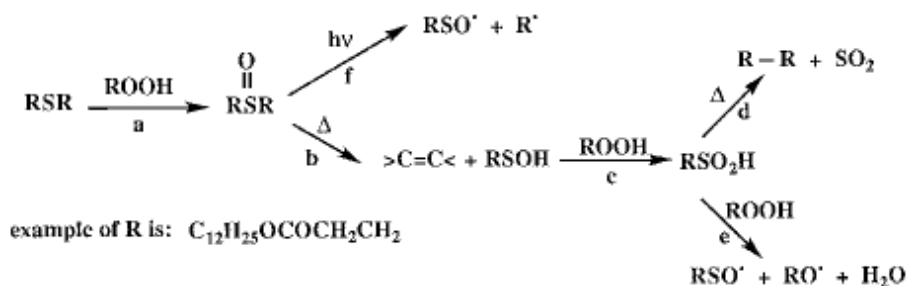
SCHEME IV: Chain-breaking mechanism and competing chain reactions. AH is an antioxidant and RH is a polymer substrate.



SCHEME V: Peroxide decomposition by phosphites.



SCHEME VI: Oxidate transformation products formed during the antioxidant action of BHT.



SCHEME VII: Simplified reaction scheme for the antioxidant mechanism of simple alkyl sulfides.

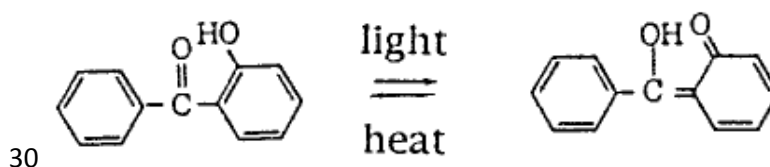
UV STABILIZERS:

There are two classes of UV stabilizers used in PEs: UV absorbers and hindered-amine light stabilizers (HALS). A common UV absorber is Chimassorb 81 (or Cyasorb 531), which is chemically known as 2-hydroxy-4-n-octyloxybenzophenone. These additives absorb UV radiation in the range of 300-360 nm, the spectral region of sunlight most damaging to polymers. The damaging radiation that is absorbed usually dissipates harmlessly as heat. In benzophenones, a six-membered ring can form through hydrogen bonding between the hydrogen atom of the hydroxyl group and the oxygen atom of the carbonyl group. The absorbed UV energy is dissipated by a keto-enol tautomerism of this hydrogen-bonded molecule. Ultraviolet absorbers of the benzophenone class are often used in formulations that contain sulfur-containing antioxidants because there is no antagonism between these additives.

Hindered-amine light stabilizers have become increasingly important in the UV stabilization of PE and have generally displaced UV absorbers. The first widely used HALS was Tinuvin 770 chemically known as bis(2,2,6,6-tetramethyl-4-piperidinyl)sebacate. Newer oligomeric HALS such as Chimassorb 944 LD have greater retention in the polymer and have largely replaced the older monomeric-type HALS. HALS inhibit photooxidation in PE extremely well. For instance, at concentrations as low as 0.5 wt %, they can provide the same protection as 1 wt % of a typical UV absorber. The mechanism by which HALS function involves their oxidation to a nitroxyl radical that scavenges alkyl radicals. This reaction then produces hydroxylamines that can react with peroxy radicals and, in turn, regenerate nitroxyl radicals. This cycling of nitroxyl radicals accounts, in part, for the high effectiveness of HALS, even at low concentrations.

UV Absorbers:

There are many kinds of photostabilizers that protect plastics from degradation by light, especially harmful UV light. A UV absorber is added to various plastics to keep the bulk and surface of plastic materials protected from light. It can absorb light with a wavelength of about 290 to 310 nm by transferring a hydrogen atom and then releasing the energy as heat according to Equation 30.



This additive contains both a functional group absorbing UV light and a labile hydrogen closely positioned to the group. UV absorbers having the following fundamental skeletons are mentioned as examples (Structures 6-8).



These three absorbers can absorb wide ranges of UV and visible light as shown in Figure 5

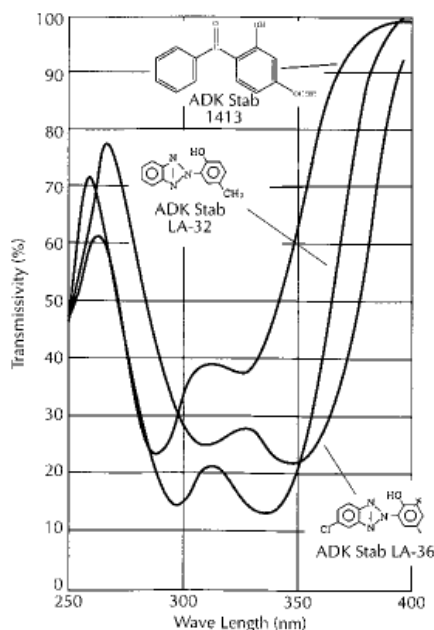
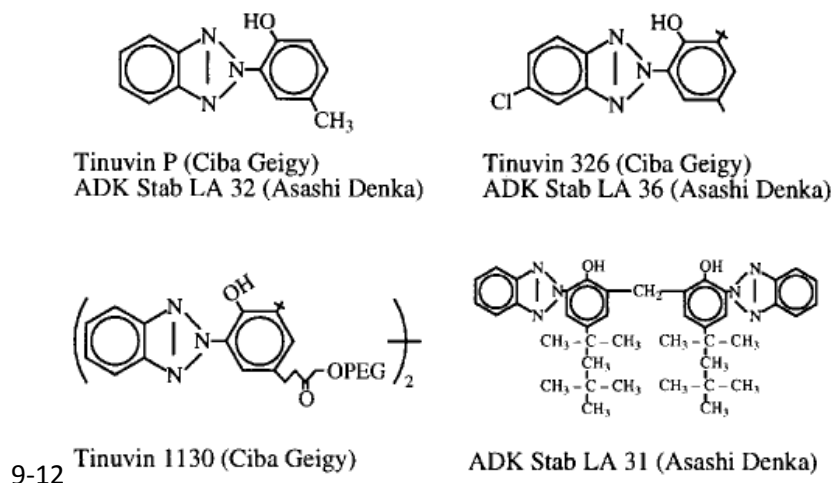


Fig. (5): UV spectra of representative UV absorbers.

A benzotriazole absorber has a wider absorption range compared with a benzophenone absorber and absorbs a little visible light. It offers no initial coloration and stabilizes color shade for long periods. Commercial products of benzotriazoles are illustrated as shown in Structures 9-12.



A benzotriazole absorber shows high synergism with hindered amine light stabilizers (HALS) and is used in various plastics such as polyolefins, polycarbonates, and polyesters, because it inhibits fading of pigments and dyes.

UV absorbers often evaporate during processing if they have low molecular weights. In addition, benzophenone and benzotriazole absorbers also lose their functions through oxidation because they belong to kinds of phenols and consequently are sensitive to oxygen and peroxy radicals (RO₂·).

PIGMENTS:

Carbon black is probably the most common pigment and UV screener used in PE. Usually added in concentrations between 2 and 3 wt %, carbon black protects against UV light. When compounded into LDPE, carbon black can inhibit thermal oxidation for ~30 h at 140 °C. Its effectiveness as an antioxidant increases with the amount of chemically bound oxygen. Unpaired electrons have been detected in carbon black particles suggesting that they act as a radical trap. Furthermore, carbon black can be an effective hydroperoxide decomposer. Because of its acidic nature, carbon black decomposes hydroperoxides into non-radical products. The pigments used in HDPE bottles and bags are often based on inexpensive metal oxides. For instance, the most common pigments (brown, grey, and orange) are based on various iron oxides and hydrates that act as prooxidants or prodegradants at high temperatures (200 °C) encountered during processing. Inorganic green pigments are usually based on chromium(III) oxide, which readily catalyzes the thermooxidative degradation of HDPE even in trace quantities.

Common Additives Used in polyethylene:

Silica is commonly used as an antiblocking agent for LDPE film-grade resins. The silica is usually diatomaceous earth (e.g., Celite) that creates little mounds (asperites) on the surface of the LDPE film and reduces sticking or blocking between adjacent film surfaces. Erucamide, chemically known as cis -13-docosenamide, is a fatty acid amide $\text{CH}_3-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_{11}-\text{CO}-\text{NH}_2$ commonly used in LDPE film to provide "slip." Erucamide, which is incompatible with PE, migrates to the surface of the LDPE film over ~24 h. It is essentially a surface-active molecular lubricant used to lower the film's coefficient of friction (COF), allowing adjacent surfaces to slide smoothly over one another and bags to slide smoothly in automatic operations such as form, fill, and seal.

Erucamide is an unsaturated compound highly susceptible to oxidation. The oxidation of erucamide can occur before it is incorporated into the polymer during storage at ambient temperatures. This degradation leads to yellowing of the erucamide because nitrile compounds form. Moreover, erucamide can degrade significantly during compounding at processing temperatures that exceed 200 °C. The consequences of erucamide degradation are a rancid odor from the film, lower slip performance because the amide degradation products are not effective slip agents, and printing problems with PE film.

CONCLUSIONS

It is important to evaluate additives for the purpose intended. A degrading polymer does not always result in limited use. The evaluation of polymer degradation is carried out by observing chemical and physical changes of a material's properties (see Table 6). Degradation occurs during processing or use with the corresponding estimation procedures established. Processing degradation can be evaluated by measuring the melt flow index under actual processing conditions. Degradation during use, however, is generally evaluated according to accelerated methods by means of a weather-o-meter for weather resistance and an oven for heat. There is no absolutely reliable evaluation method. The data obtained should be interpreted by understanding the merits and defects of the

method and instrument used. The evaluation results also depend on the atmosphere or environment of the experiment as well as the shape and thickness of the materials tested.

TABLE 6. Evaluation of Polymer Degradation

Item measured	Properties evaluated
<i>Physical</i>	
Density	Cleavage of principal chain, crystallinity
Degree of gelation	Crosslinking
Viscosity of solution	Molecular weight
Contact angle, reflection factor	Condition of surface
Modulus of elasticity	Mechanical property
Elongation	Mechanical property
<i>Chemical</i>	
Formation of oxygen-containing Group (carbonyl, peroxy)	Degree of oxidative degradation
Free radical, exiting species	Process of degradation

Additives are used to preserve the properties of polymers that were designed to meet certain specifications. Antioxidants are comprised of various chemistries that perform by different mechanisms. Understanding the chemistry combined with the judicious selection of the appropriate additives for a product's use is the key to success.

Part II: Compounding

COMPOUNDING PRINCIPLES & PRODUCT PROBLEMS RELATED TO COMPOUNDING:

Additive Feeding

Additives must be precisely weighed for the compounding extruder with a continuous feeder.

Slip and lubricants such as calcium stearate are low-melting-point additives that melt before the polymer is fully plasticized. Thus, they lubricate the screw and consequently reduce dispersive mixing. To overcome this effect, these additives can be injected downstream of the main extruder with a side-stream extruder after plasticizing the polymer.

The additive's physical form is important to consider when compounding PE. Fine powders can create nuisance dust and also pose a dust explosion hazard. Major additive suppliers are now marketing low-dusting additives in a compacted or "prill" form. These compacted versions also improve feeding and metering consistency. For small amounts of different additives, a preblended additive package may improve accuracy and reduce cost. The major advantage of such preblends is

that the compounder need only control the feed rate of one additive rather than many. The preblended package consists of two or more additives in fixed ratios. The most commonly used preblend in the PE industry is produced by CIBA Corp. and is known as Irganox B900 (a 4:1 blend of Irgafos 168 and Irganox 1076). Another phenolic and phosphite preblend that is frequently used is Irganox B911 (a 1:1 blend of Irganox 1076 and Irgafos 168). Enichem recently commercialized preblends of Irganox 1076 with zinc stearate.

Dispersion:

Additives, such as antioxidants, should be distributed uniformly throughout the polymer, particularly as some downstream converting operations such as injection molding and rotomolding involve little mixing. Often, however, the distribution of additives in PE pellets is non-homogeneous with some pellets rich in additive and others having no detectable amounts. The reasons for this non-uniformity of additive dispersion include feeding problems in the additive extruders because of hopper “bridging” or barrel “plate-out,” surging of the polymer melt from the main extruder,

Ahmed M. Eltayef, POLYETHYLENE (Stabilization and Compounding), 2001

inadequate mixing of the melt, and inadequate post-blending. Indeed, some PE manufacturers do not add any antioxidants during extrusion (to allow controlled degradation to occur); instead, they add an antioxidant concentrate in pellet form to pelletized polymer.

Poor additive dispersion in pelletized PE can be readily checked by a simple test: exposure to iodine vapor. In this test, pellets rich in antioxidant are stained dark violet and pellets low in antioxidant are a light pink color. In this way, variations in antioxidant concentrations are easily discerned. This test relies on the affinity of iodine vapor with polar compounds such as phenolic antioxidants.

Carbon black is always introduced to the polymer from a concentrate (i.e., masterbatch). It is essential that a proper dispersion is obtained during compounding and that the average particle size is between 15 and 25 microns. In a good dispersion of carbon black in PE, a uniform, dark background with only some isolated agglomerates can be seen under 100X magnification on thin microtomed PE samples. A poor dispersion, however, has an almost clear background with numerous clusters visible.

Dispersion agents, based on silicon oil, are sometimes used with titanium dioxide pigments for a better dispersion in PE. These agents should be avoided, however, as they cause sealing and printing problems. Because silicon oil migrates to the PE film surface, a laboratory check can confirm its presence. The test involves swabbing the suspected area with cotton wool that is then extracted by a Soxhlet extractor. The extract is concentrated by rotary evaporation and the presence of silicon checked by atomic absorption spectrometry.

Interaction

Polymer Blending:

The term compounding also embraces the physical mixing of two or more polymers. For instance, a common blend is LDPE with linear low-density PE (LLDPE). Adding LLDPE can improve the toughness

and elongation of LDPE, making it possible to produce a significantly thinner film (downgauging) with strength and impact properties equal to or better than a thicker LDPE film. LDPE also improves the processability of LLDPE. Blends of LDPE with 10, 20, 30, and 60% LLDPE include pallet shrink wrap, briquette bags, horticulture bags, and microirrigation pipes, respectively. Other blends manufactured by PE producers are LDPE and butyl rubber, which imparts environmental stress-crack resistance to the former.

COMPOUNDING PRINCIPLES:

Compounding primarily involves the melt plasticization of a PE reactor product, generally accompanied by additives. The equipment and the compounding parameters employed depend on the operation's size and the desired end product properties. An intensive mixing device is often used with a plasticating extruder, followed by melt filtration, pelletization, and blending. Two types of processes are necessary for compounding PE and additives: distributive mixing and dispersive mixing. Distributive mixing is essential for homogenizing the polymer and for distributing the additive properly. Dispersive mixing is essential for carbon black, which tends to form agglomerates. Recirculating vortices in the melt produce distributive mixing, while high shear planes between the screw's channels give good dispersive mixing.

Continuous Mixers

For high production rates (e.g., 6-15 tonne/h), a combination of a continuous mixer and hot-melt extruder is recommended. Farrel Corp. in the United States is the largest manufacturer of continuous mixers for the PE industry. The Farrel continuous mixer (FCM) uses specially designed rotors, similar to those used in a Banbury, to convert the powder resin feed (i.e., fluff) into a molten polymer mass in the form of a ribbon (that feeds) into a hot-melt extruder. New continuous mixers made by Farrel are the 9UM and the larger 18UM, which can process up to 9 and 18 tonne/h, respectively. A scheme outlines the basic principle in Figure 6. These units consist of two stages, with a single screw pumping the polymer to the mixing elements that are housed in a clamshell-shaped barrel. The high throughput of large intensive mixers is achieved with short residence times at high temperatures. For a single-screw extruder, a temperature profile of 200-240 °C is generally used for PE. However, in large finishing equipment, temperatures from 260 °C upwards are used. Finishing line equipment is energy intensive as much of the heat required to raise PE's temperature to 260 °C is generated through the mechanical work input to the polymer which is powered by large electric motors (~ 0.2-0.3 kW/kg).

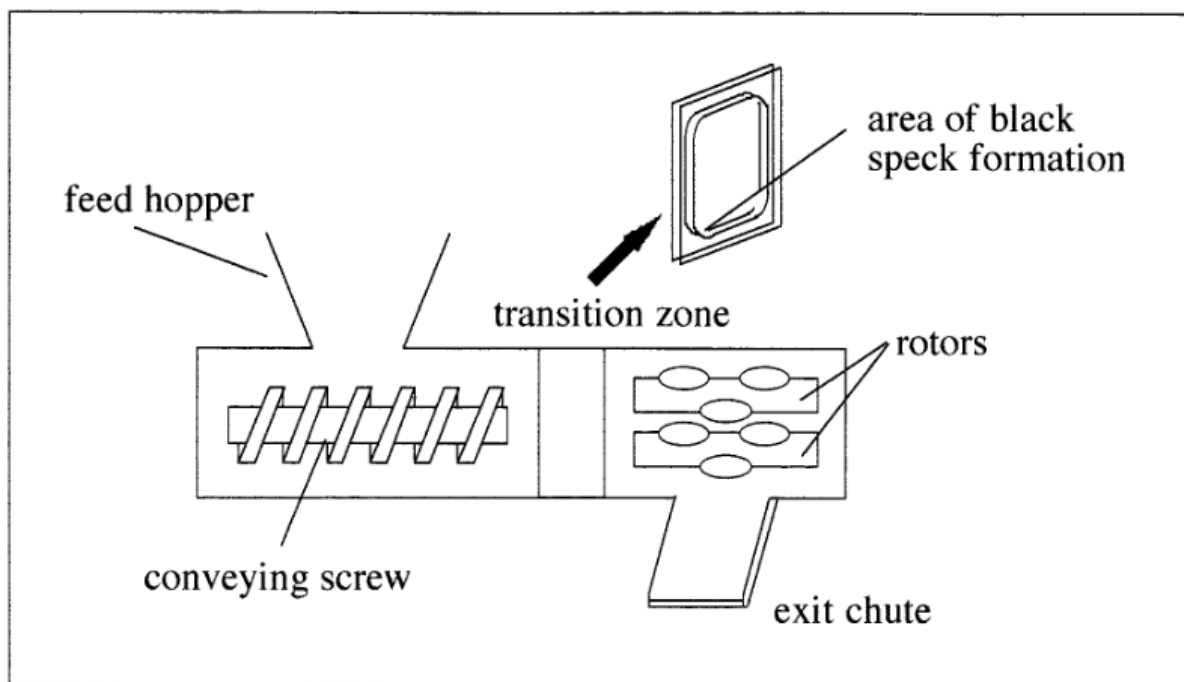


Fig.(6): Schematic showing how a continuous mixer operates. Note transition region where black specks can form.

Twin-Screw Extruders:

Twin-screw extruders, in contrast to single-screw units, have two screws mounted parallel in a single barrel with a figure-of-eight cross-section. These extruders provide intensive shearing and are well-suited for incorporating pigments. Twin-screw extruders fall into two categories: co-rotating and counter-rotating screws. The extent to which the screws intermesh further defines their classification. The screws can be non-intermeshing, partially intermeshing, or fully intermeshing. The most common high capacity twin-screw finishing extruders for PE are those produced by Werner-Pfleider Corp. and known as ZSK extruders. They have intermeshing, co-rotating, segmented screws that are self-cleaning. Because the segments are removable and interchangeable, they can be assembled in various ways to provide the desired combination of fluff feeding, melting, shearing, and metering zones.

Twin-screw vented extruders are used for phase separation between polymer and solvents or monomers. Stripping extruders are used in the Hoechst and Phillips HDPE processes to remove the solvent of polymerization. These intermeshing twin-screw extruders enable precise control of the polymer melt's temperature as only a small amount of polymer has contact with the barrel surface. Because the melt is spread out thinly over the barrel wall, the diffusion of volatiles from the polymer is facilitated. A volatile-rich layer is generated in the intermesh region. This partially filled region is vented to an atmospheric or vacuum con-denser. The screws are specifically designed to provide melt sealing and allow only a low degree of fill for each venting stage. Because vented extruders are expensive and have low throughput, pellet driers are often used instead. In the pellet driers,

volatiles are removed by passing dessicated air or nitrogen (to avoid polymer oxidation) through a bed of pellets.

Melt Filtration and Pelletization:

Polymer melts must be filtered to remove particulate contaminants. This is usually achieved with a breaker plate and wire-mesh screen. The breaker plate consists of a steel plate with numerous holes, and the screens are installed on the plate's upstream face. Usually, several progressively finer screens are used (e.g., a 40-mesh supporting an 80-mesh supporting a 200-mesh screen). When the pressure drop across the filter gets too high, the screen-pack assembly must be removed and cleaned. Automatic screens (e.g., HiTech) enable new screens to be inserted without interrupting the extrusion process. Other automatic systems have screens incorporated in a spur gear. This gear is periodically rotated to introduce clean screens into the melt stream as the preceding screens become plugged. The dirty screens can be replaced as they exit the melt stream.

Pelletization generally involves the extrusion of the polymer melt through a die plate, solidification (usually underwater), and the cutting of the polymer strands into pellets. The pellets are drained on a shaking screen and dried with hot air. Shaking and vibrating screens (e.g., Rotex[®] screens) are also used to remove irregular pellets, long strands, and fines.

Pellet Handling and Post Blending:

The usual mode of pellet transport in PE manufacturing plants is by high-velocity pneumatic conveying. Transfer lines can damage pellets from the high-speed interactions between the pellets and the pipeline. The result is fines, streamers, and other defects. Damage to pellets can be minimized by using large radius elbows (e.g., Hammertek[®] elbows), pipes with smooth joints, and moderate conveying velocities. Pellets are transferred from the compounding extruder to large bins where they undergo a mixing process known as post blending. The post-blending bins contain intricate internal structures to thoroughly mix the pelletized polymer. Excessive blending, however, can also lead to fines and streamers, especially for high Melt Index resins. To remove the fines, elutriators and aspirators are sometimes used. In some instances, the final blending stage plays a key role in end-product homogeneity (consistent product properties across a blend).

PRODUCT PROBLEMS RELATED TO COMPOUNDING:

Figure 7 shows the most common customer complaints received by PE producers, and all of these complaints can be related in some way to the compounding and stabilization process.

LDPE	HDPE
gels	black specks
odour	discolouration
haze	swell variation
wrong COF	poor pellet geometry
wet resin	metal contamination
blocking	high warpage

Fig. (7): Common customer complaints for low-density and high-density polyethylene. All are related to the stabilization and compounding process. COF, coefficient of friction

Gel Contamination:

Gels are the most common problem in compounding PE and the number one source of complaints for LDPE. Gels are small regions of loosely crosslinked polymer that generally form in an extruder during compounding. These gel particles are usually generated in dead-spots (i.e., stagnant regions where there is poor flow) in the extruder. Polymer that hangs-up in such areas experiences longer residence times, thereby depleting the antioxidant supply and promoting crosslinking. Gels are particularly undesirable in thin PE films where they can act as lenses and appear much larger than their actual size because of their distortion from the surrounding film. Gels causing imperfections in PE film are known descriptively in the industry as fisheyes and arrowheads depending on their appearance. Their occurrence in PE film may appear as isolated gel particles or as a cluster of gel particles. The latter is attributed to small pockets of degraded material that have “hung-up” in the extruder. These regions are periodically swept back into the mainstream and then become fragmented while passing through the extruder's narrow die gap. Gels can also act as stress concentrators and may cause “blow-outs” in bottles made from HDPE. Their rubbery nature allows them to elongate and squeeze through screenpacks, making them difficult to eradicate once formed.

Various anti-gel additives for PE have been claimed in the patent literature based on radical trappers, metal phenolates, and polyethylene glycol. One compound, in particular, appears to be quite effective at preventing gel formation in LLDPE films. Kemamine AS990, although primarily intended as an antistatic agent, can passivate acidic residues and control gel formation through a poorly understood mechanism.

Black Speck Contamination:

Common sources of contamination in HDPE are black specks, local burnt regions within pellets. These are small areas of highly degraded polymer or degraded additive that have been carbonized because of excessive residence time, excessive shearing, or the presence of hot spots (localized high-temperature regions) in an extruder. As with gels, these black specks typically occur in low flow or stagnant regions in the extruder. In large hybrid processing equipment such as a 9UM mixer, the transition point between the melt pump screw and the mixing heads is usually a site where black specks are generated (see Figure 6). Black specks cause a major problem in the blow molding of natural or white bottles where they are aesthetically undesirable.

Black specks may also be caused by the charring of the additives present in PE (ironically, such additives as hindered phenols and hindered phosphites stabilizers). Antioxidant suppliers have addressed this problem with new additive systems. American Cyanamid developed Cyanox 2777, a blend of Cyanox 1790 hindered phenolic antioxidant and tris(2,4-di-*t*-butylphenyl)phosphite, which is claimed to be ideal for high-temperature processing conditions as it purportedly resists black speck formation. Ethyl Corp. released a new fluorophosphonite antioxidant system known as Ethanox 398, which exhibits high thermal stability (up to 287 °C) and outstanding resistance to charring. These features help prevent the black specks often encountered during high-temperature extrusion.

Extraneous Contamination:

Typical contaminants in commercial PE are degraded polymer, metal, sand, paper, and fiber. Degraded polymer contamination (known in the industry as burnt resin) is usually a translucent brown color and shatters under pressure. Often, such contamination may appear yellow or amber depending on the extent of degradation. In fact, under microscopic examination, a color gradient may be evident, indicating that the darkest side has been in direct contact with the extruder barrel wall. Paper and fiber often originate from bags and cardboard octobins used for packaging the resin or its additives. Metal contamination in HDPE (usually referred to as tramp metal) arises from the wearing of processing equipment such as extruder gates, granulators, aluminum adapters, frayed screenpack wire, welding slag, and attrition of pellet-conveying pipeline. Occasionally, metal shot contamination may be found after plant transfer lines are cleaned. Small fragments of metal can cause major problems in injection molding applications because they can plug precision injection nozzles. In addition, ferrous and ferric ions because of their multivalent nature act as oxidation catalysts in redox reactions and promote PE degradation.

Odor:

Odor in PE is generally associated with the polymer's oxidation, the additives, or both. Common causes of odor in HDPE are thermal oxidation of the fluff (or polymer powder) during storage before stabilization. In the Unipol process, in particular, the HDPE fluff is stored for some time (frequently at elevated temperatures) before compounding. The polymerization is generally performed at 90-100 °C, and the fluff leaves the reactor at ~80 °C. Because of its low thermal conductivity, fluff can remain at 60-70 °C for many days. 35 During this time, hydroperoxide groups can form in PE, which

when compounded, can decompose to give odorous, oxygenated species such as alcohols, acids, aldehydes, and ketones. HDPE made with Ziegler catalysts employ triethylaluminium (TEAL) as cocatalysts. After polymerization, these resins are purged with steam to strip and deactivate the TEAL. Incomplete deactivation, however, can contribute to odor forming in the polymer after compounding. A further source of odor in HDPE can originate from calcium or zinc stearate additives degrading. These metallic stearates can deposit on the extruder screw during compounding. The stearates undergo thermal decomposition to yield stearic acid that, after further oxidation, produces odorous aldehydic products. This phenomenon is also encountered by the PE processor, where degraded stearic acid can foul nip rollers and build-up on internal bubble cooling systems used to produce high molecular weight HDPE film.

In LDPE, compounding can liberate some bound chain-transfer agents. The chain-transfer agent is used to regulate the polymer's MW during polymerization and in the process is incorporated onto the chain. These transfer agents are usually based on ketones such as methyl ethyl ketone (MEK); thus, LDPE made using an MEK transfer agent may have some ketonic odor. Because LDPE is branched, it is more susceptible to oxidation during compounding than HDPE. This is because hydrogens at tertiary carbons have a lower bond dissociation energy than other hydrogens in PE's structure and, thus, are likely to be the first extracted by propagating radicals. Such oxidation can be associated with long residence time and high-temperature compounding conditions. Often, odor in LDPE is attributed to the oxidation of the fatty acid amide slip agent. Various workers have reported that fatty acid amide slip additives can cause film odor, usually when these additives are stored for too long or extruded under conditions where the compounds can oxidize. This oxidation produces aldehydic and nitrile species that are rancid-smelling compounds.

Specialty additives are available for binding PE odors that could otherwise taint delicate matrices such as spring water. The best known odor-absorbing additive for PE is Abscents by UOP Corp., which is based on an aluminosilicate zeolite. These compounds are effective at concentrations as low as 500 ppm and can be incorporated by standard melt-compounding.

Pellet Geometry:

Poor pellet geometry is the term that describes any deviation in pellet shape from that which is standard or desired. Polymer pellets are usually 3-4 mm i.d. and cylindrical, cubical, or spherical shaped. The shape of pellets can influence their behavior in extruders and injection molding machines. There are many variations of poor pellet geometry, including match-sticks, jackstraws, bullet-heads, shorts, tails, streamers, fines, and angel hair (see Figure 8).

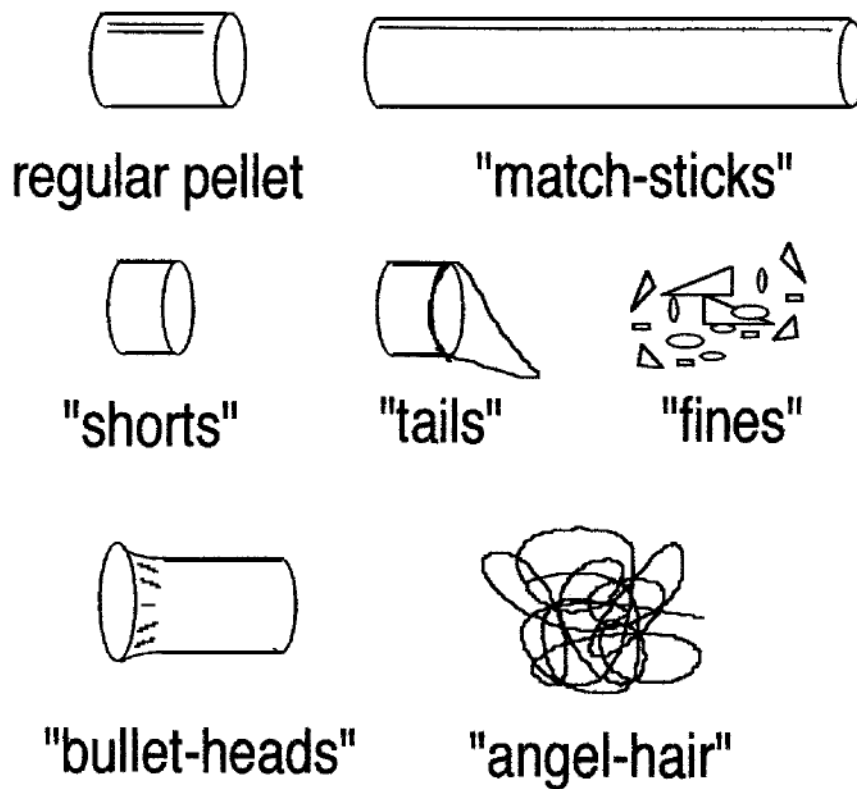


FIGURE 8: Diagram illustrating some variations of poor pellet geometry of compounded polyethylene.

Uniform pellet size is important for uniform feeding and melting in the downstream conversion steps. In film-grade resins, non-uniform pellet size may cause surging of the melt, leading to bubble instability. Excessive fines tend to accumulate in the hopper and feed throat of extruders as a result of static and, periodically, such deposits fall into the hopper causing bridging problems and non-uniform melting.

In commercial PE production, the melt is generally extruded through a die plate containing scores of bored holes and then cut into pellets underwater by rotating knives. If the pellets stick to the cold face of the die plate then pellet freeze-off can occur, resulting in plastic deformation of the solid pellet at one end to produce bullet-heads; pellets that are flat at one end. Matchsticks are extra long pellets, up to 3 cm long. Jack-straws are even longer, generally more than 3 cm. Poor cutter alignment produces under-sized pellets known as shorts. Streamers and angel hair generally form in the pneumatic conveying pipelines. Because of their high transfer velocities, the pellets in contact with the pipe wall begin to melt from the high frictional forces. Elbows, in particular, are regions where these streamers tend to form. Shotblasting of transfer lines (to roughen the internal surface) and rounding off sharp corners can reduce streamer formation.

Poor pellet geometry generally results from knives misaligned with the die plate, blunt cutting edges, poor heat distribution in the die plate (leading to pellet freeze-off), the cooling water too warm, insufficient or excessive melt back-pressure, poor die plate geometry, a dirty die plate, or pellet conveying problems.

A new heated die plate designed for pelletizing PE underwater was recently developed by Werner & Pfleiderer and reportedly prevents pellet freeze-off. The die plate features a series of slots, each feeding up to 20 or 30 holes and having its own heat channel, either steam or hot oil. The heat channels run parallel to the melt channel, reportedly providing better heat distribution and, consequently, more uniform pellet sizes.

Recent advances in hardening steel blades with carbide coatings means that die plate cutters have a long life and improved pellet geometry. For instance, granulator knives that resolve chipping and fracturing problems found with traditional carbide materials have been reported based on ferro-titanium carbide composites consisting of an impact-resistant, hard layer of silicon carbide diffusion bonded to a tool steel body.

Color:

During PE compounding, the natural pellets are frequently discolored, usually yellowing, although pink and grey hues can also develop. In nearly all cases, the discoloration is related to the additives present.

The most well-known origin of discoloration in PE is the yellowing imparted by stilbene quinone compounds that are the rearrangement products (usually dimers) of hindered phenolic antioxidants. These compounds are highly conjugated and can yellow PE at low concentrations by virtue of their high extinction coefficients. The most notorious antioxidant that forms stilbene quinone compounds is BHT, which is no longer used prevalently in the PE industry. Irganox 1076 also forms yellow transformation products but to a lesser extent. Figure 9 shows the common conversion products of Irganox 1076, which can cause yellowing. Biscinnamate and the conjugated and unconjugated bisquinonemethide of Irganox 1076 are the primary dimers responsible for yellowing PE. Quinone-related yellowing can be confirmed by exposing the PE sample to strong UV light causing the quinones to break down and the yellowing to disappear.

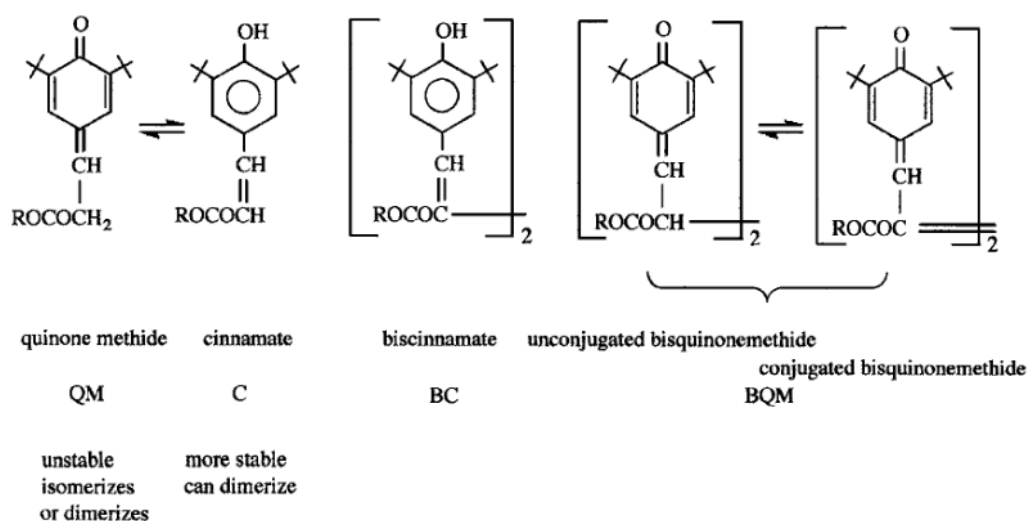


Fig.(9): The common conversion products of Irganox 1076 causing polyethylene to yellow.

Another common route by which yellowing or pinking occurs is by the interaction between bridged phenolic antioxidants such as Isonox 129 and catalyst residues such as titanium and vanadium ions. In this reaction, intensely colored metal phenolates form. Although these species appear bright orange or red when produced in solution, they are reduced to subtle hues of yellow and pink when diluted in the polymer. This interaction has been widely studied by Pospisil. Pink discoloration can also occur in HDPE containing high levels (e.g., greater than 2%) of the antioxidant Permanax[®] WSP because of this additive's intrinsic pink color.

Yellowing also occurs during storage of PE pellets in rail cars before delivery to the processor. In this case, the yellowing is from a complex interaction between the hindered phenolic antioxidants, iron compounds from the container walls, and condensation of moisture.

Generally, discoloration is more pronounced in thick sections or in bulk rolls of film because of the greater optical path length and the contrast that is apparent on the butt end of a roll of film. In many cases, discoloration, although developed during compounding, becomes evident only when the pelletized material is converted to a product. For instance, in thick-wall sections, such as large-part blow molding (LPBM) of containers for dangerous liquids, yellowing is often apparent. This yellowing usually results from the stearates that are present as processing lubricants in the high molecular weight HDPE formulation.

Compounding with high levels of silica antiblock (e.g., 1%) in LDPE can result in grey discoloration. Yellowing in LDPE can arise as a result of excessively high compounding temperatures. A grey discoloration has also been observed in HDPE containing Irganox 1010 and DHT 4A (an acid scavenger based on synthetic hydrotalcite), although the mechanism of this interaction is unclear.

Strategies for combating discoloration in PE are prevention, neutralization, and masking. Prevention relies on careful formulation, control of extrusion parameters, and an inert atmosphere during compounding to prevent chromophores from forming at the onset. Novacor Corp. produces a high molecular weight HDPE blow molding grade resin with good color by compounding under a nitrogen blanket.

Neutralization methods rely on compounds such as phosphites and phosphonites that render colored species colorless.

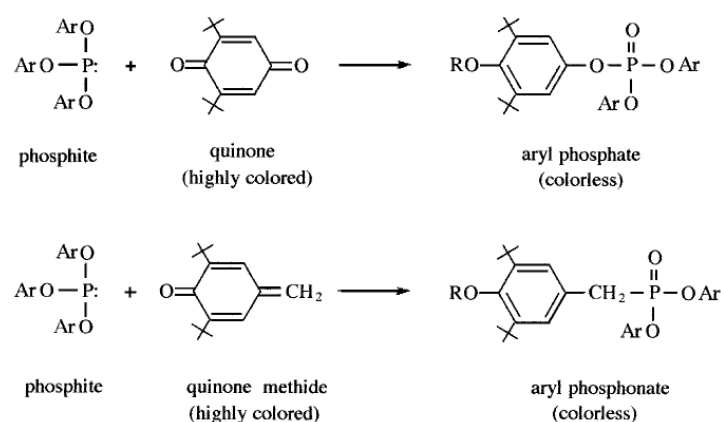


Fig.(10): Reactions of phosphite stabilizers with highly colored dimeric oxidation products of phenolic antioxidants to yield colorless products

Figure (10), shows the reaction of Irgafos 168 with highly colored quinoidal conversion products of phenolic antioxidants to yield colorless products. Sandostab PEPQ chemically known as tetrakis (2,4-ditertbutylphenyl) 4, 4'-biphenylene diphosphonite is a diphosphonite used to maintain PE color during processing. A newer class of additives for neutralizing color in PE is based on calcium lactate and calcium stearoyl 2-lactylate. These lactate-based compounds were recently commercialized by the Patco Additives Division of the American Ingredients Co. They reportedly preserve polymer color by acting as acid neutralizers and chelating with pro-degradant metal ions. Strong reducing agents such as sodium sulfite have also shown neutralizing behavior in PE.

PE discoloration can be masked with optical brighteners such as Uvitex OB, which mask yellowing by emitting into the blue spectrum. An optical brightener can be used to mask the stearate-induced yellowing in high molecular weight HDPE for LPBM by using concentrations as low as 50 ppm (see Figure 11). This level offsets the additive's high cost.

<p>Large bore pipe resin* (% w/w)</p> <p>base resin: HDPE, MFI(21 kg) = 15, D = 0.951 g/cm³</p> <p>pigment: carbon black (2.5%)</p> <p>antioxidant: Irganox™ 1010 (0.1%)</p> <p>processing stabilizer: Irgafos™ 168 (0.1%)</p> <p>lubricant: calcium stearate (0.3%)</p> <p>*such as Hoechst GM 5010</p>	<p>High-temperature pipe resin* (% w/w)</p> <p>base resin: HDPE, hexene copolymer, medium density</p> <p>pigment: carbon black (2.5%)</p> <p>antioxidant: Irganox™ 1010 (0.1%)</p> <p>high-retention antioxidant: Irganox™ 1035 (0.25%)</p> <p>acid neutralizer: calcium stearate (0.25%)</p> <p>*such as Neste NCPE 0909</p>
<p>Heavy-duty sack resin* (% w/w)</p> <p>base resin: LDPE, MFI (2 kg) = 0.4, D = 0.920 g/cm³</p> <p>antioxidant: Irganox™ 1076 (0.1%)</p> <p>processing stabilizer: tris nonyl phenyl phosphite (0.15%)</p> <p>antiblock: silica such as Superfloss™ (0.2%)</p> <p>slip agent: oleamide such as Crodamide™ O (0.05%)</p> <p>*such as ICI XDF 333</p>	<p>HMW blow moulding resin (% w/w)</p> <p>base resin: butene copolymer MFI (21 kg) = 9, D = 0.952 g/cm³</p> <p>antioxidant: Irganox™ 1076 (0.25%)</p> <p>processing stabilizer: Ultrinox™ 626 (0.15%)</p> <p>lubricant: calcium stearate and zinc stearate (0.15%)</p> <p>optical brightener: Uvitex™ OB (0.005%)</p>
<p>Cable insulation resin (% w/w)</p> <p>base resin: hexene, medium density</p> <p>antioxidant: Permanex WSP (0.3%)</p> <p>processing stabilizer: Ultrinox™ 626 (0.2%)</p> <p>metal deactivator: oxalybis(hydrazide) (0.1%)</p> <p>ESCR modifier: butyl rubber (0.5%)</p>	<p>HMW grocery sack resin* (% w/w)</p> <p>base resin: butene copolymer MFI (21 kg) = 9, D = 0.952 g/cm³</p> <p>antioxidant: Irganox™ 1076 (0.25%)</p> <p>processing stabilizer: Irgafos™ 168 (0.15%)</p> <p>lubricant: calcium stearate (0.15%)</p> <p>*such as Alathon™ 5005</p>
<p>Yellow gas pipe resin* (% w/w)</p> <p>base resin: HDPE, MFI(21 kg) = 12, D = 0.952 g/cm³</p> <p>pigment: cadmium sulphide/barium sulphate (1%)</p> <p>antioxidant: Santonox™ R (0.1%)</p> <p>UV stabilizer: Chimassorb™ 81 (0.3%)</p> <p>*such as Hoechst GM 505</p>	<p>Cling film* resin (% w/w)</p> <p>base resin: LDPE + LLDPE blend</p> <p>antioxidant: Irganox™ 1076 (0.1%)</p> <p>lackerifier: glycerol monooleate or polyisobutylene (2%)</p> <p>anti-gel agent: Kemamine™ AS990 (0.1%)</p> <p>*such as Glad™ Wrap</p>

Fig.(11): Typical formulations of commercial grades of polyethylene. MFI, melt flow index; D, density; HMW, high molecular weight; and ESCR,

Rheology:

PE from the reactor generally undergoes changes in its rheological properties during compounding. HDPE can undergo chain scission and crosslinking reactions during melt processing. These reactions are competitive, and the net change in the melt flow index is dictated mainly by the extruder's oxygen content and the polymer's degree of unsaturation. In the presence of oxygen, macroalkyl radicals rapidly convert to peroxy radicals and, thus, macroalkyl recombination reactions (which lead to crosslinking) are negligible. However, the oxygen level should be fairly low in an extruder, and the high consumption rate means that the oxygen concentration decreases rapidly as the polymer melt moves through the extruder. With Phillips-type HDPE, crosslinking is generally favored, whereas Ziegler-type HDPE mainly undergoes chain scission during melt processing. Phillips HDPE has a terminal vinyl group on each polymer chain. This vinyl group concentration decreases during melt processing. The predominance of crosslinking reactions in Phillips HDPE can be explained by alkyl radicals added to the carbon-carbon double bonds. A melt flow drift across compounding can also indicate poor oxidative stability. For instance, if significant oxidation occurred before compounding (during fluff storage, for example), an appreciable increase in MFI may be observed across compounding.

The molecular weight distribution (MWD) of PE (especially the high MW component) can greatly affect its swell characteristics. Thus, certain grades of polyethylene, such as those used in the blow molding of consumer bottles, have constant swell from one batch to the next. High swell is undesirable because it leads to parison problems (i.e., instability). Similarly, if the swell is too low, it can cause poorly formed bottle handles. High variation of swell from batch to batch and within a batch are most undesirable because then the tooling (e.g., die-gap) of the blow molding machines and processing conditions (e.g., temperature profile) must be adjusted constantly to compensate for the varying swell. Swell variation can be decreased by either running the extruder at high throughput (and hence high shear rates) or by extruding the polymer in the absence of antioxidant and in the presence of air (known as tailoring). Both these techniques lead to controlled scissioning of the polymer chains, in which the longer chains are statistically more likely to undergo cleavage. As a result, the polymer's MWD is narrowed, the swell is lowered, and the swell variation is reduced.

PROCESS CONTROL IN COMPOUNDING:

Polyethylene compounding facilities usually depend on regular process control measurements of the compounded product to operate efficiently. One common requirement for process control is to determine if the correct levels of additives are present in the polymer. These tests must yield a quick, reliable result so that feedback can be given to the compounder, allowing process corrections to be made mid-stream. To this end, many sophisticated techniques are employed. The level of antioxidant in the final polymer can be determined by testing the oxidative induction time (OIT), as measured by differential scanning calorimetry. A low OIT value indicates additive feeding problems, additive degradation, or the antioxidant's lack of uniformity. The level of nitrogen-containing additives such as HALS and erucamide can be determined by nitrogen pyrochemiluminescence (e.g., using an Antek Nitrogen Analyzer). The carbon black content of the compounded PE can be determined by dynamic thermogravimetry, for which a small quantity of polymer is heated in

nitrogen until 650 °C in a thermal balance followed by admission of oxygen until 800 °C. Similarly, the antiblock content of compounded LDPE is determined by gravimetry after furnace ashing in air.

Another critical parameter for control during compounding is PE's rheological characteristics. The MWD and swell behavior can be determined by capillary rheometry, which forces the molten polymer through an orifice under varying pressure (e.g., Zwick on-line melt indexer). Another technique based on rheometry (e.g., Rheometrics RMS800 rotational rheometer instrument) uses a parallel plate geometry and measures PE's dynamic shear modulus. This value can be related to the melt elasticity and the amount of warpage the HDPE will undergo on cooling from the melt.

The gels generated during compounding can be assessed by blowing film from a composite production sample acquired by diverting a trickle feed stream from the main production stream. This film can then be inspected by a real-time gel counter (e.g., Intec² automatic gel detector) that classifies and quantifies the gel particles by their size and abundance. Gel particles can also be detected in PE before pelletizing occurs. The Advisor² defect monitor by Flow Vision Inc. can simultaneously classify up to four different gel defects as small as 50 microns in PE melt at commercial production rates.

To classify and quantify contamination in PE, a representative quantity of resin (e.g., 100 kg) is usually run through an extruder fitted with a 100-mesh screenpack, acting as a filter and collecting and concentrating any particulate contamination in the resin. Subsequently, the contents of the screenpack can be analyzed by various methods (e.g., microscopy after xylene vapor exposure) to facilitate identifying the contamination source.

Release checks on pelletized PE product are also undertaken to determine if the resin has any objectionable odor. These tests are generally performed by a group of people who sniff the resin. However, this method can be quite unreliable because of the subjectivity involved and the problems with olfactory fatigue. There are also questions about the health risks of this test. Recently developed, faster, more accurate methods use a semiconductor-based odor meter (e.g., Cosmos Odor Meter) for detecting and quantifying odor from LDPE pellets. The response of this instrument correlates well with PE odor intensity as assessed by human subjects. By fitting a hypodermic needle to this hand-held device, the headspace of bagged PE product stored in warehouses can be sampled to assure quality.

Commercial color sorters, employing electro-optic sensors that can discriminate between natural and colored pellets, are increasingly used in the PE industry. These machines can highlight the presence of discolored pellets and other contaminants arising from compounding disruptions. They can also be used to upgrade batches containing occasional colored pellet contamination, thereby increasing the prime stock and decreasing the amount of off-specification resin produced. For instance, transfer lines are not always properly purged and cleaned and natural resin can be contaminated by a small quantity of black pellets. Similarly, natural pellets that have yellowed can be sorted at high production rates (e.g., 10 tonne/h) to upgrade the off-specification material.