

Improving Weathering Resistance of Flame-Retarded Polymers

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ABSTRACT: Most flame-retarded polymer products need to be highly durable throughout their service lifetime in many demanding applications areas such as construction, transportation, electric equipment, and textiles, where low flammability in combination with high resistance toward oxidative deterioration triggered by the action of light, heat, and/or mechanical stress is a mandatory quality. To achieve this, it is essential to better understand the overall interplay (both physical and chemical processes) between different components such as different flame retardant structures in their respective polymers and in the presence of coadditives such as processing stabilizers, antioxidants, light stabilizers, metal deactivators, filler deactivators, ultraviolet absorbers, and so on, in the flame-retarded polymer product. In this article, the key difficulties in improving weathering resistance of flame-retarded polymers are reviewed. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 925–944, 2013

KEYWORDS: degradation; flame retardance; photochemistry

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INTRODUCTION

It has been generally accepted that the growth and fast development of polymer industry would not have been possible without various types of plastic additives. Many of today's bulk polymers are difficult to process without additives, other vital polymer properties need to be enhanced, and undesirable properties need to be mitigated or even eliminated to meet different end application requirements. Typically, plastic additives either improve or preserve key properties of almost all polymer products such as their mechanical and visual properties and they also importantly guarantee their long-term durability under service conditions. In many cases, additives open new application fields for polymers as they overcome weaknesses such as retardation against flammability, color, electrical conductivity, softness, and so on. As a consequence of this, additive systems are becoming technically more challenging and they are offering more value. New specialized additive formulations and chemistries are constantly being developed and have become the drivers to meet future challenges of plastic materials.

When dealing with fire retardancy of polymeric materials, a number of issues have to be simultaneously taken into consideration. Such considerations are the burning/combustion characteristics of the polymer substrate, its fitness to a particular type of flame retardant, the compatibility of the selected flame retardant with the host polymer, the flame retardant's interaction

with other additives in the formulation (potential synergistic, antagonistic or additive effects of flame retardants with other essential plastic additives), its cost, required loading, and thermal stability. Meanwhile, safety, health, and environmental aspects and life cycle assessments also play an increasingly important role during the selection process and development of suitable flame retardant structures.

Recently, numerous studies have shown that various flame retardant families often exhibit an antagonistic effect with heat and light stabilizers, that is an adverse interaction between various flame retardant types and conventional stabilizers has been observed that significantly reduces the service lifetime of the flame-retarded product. Therefore, special care has to be taken when formulating additive systems to guarantee sufficient weathering resistance in combination with flame retardant efficacy over the whole expected service lifetime of the polymeric articles. The correct selection of the flame retardant type and heat/light stabilizer combinations is dictated by the polymer substrate used, potential fillers, the interaction between various components in the formulation, intended end application requirements, and predicted exposure to heat, moisture, and light of the plastic material during its final utilization.

The key difficulties in the stabilization of flame-retarded polymers are reviewed below with regard to components (stabilizer systems, coadditives, fillers, metal deactivators, filler

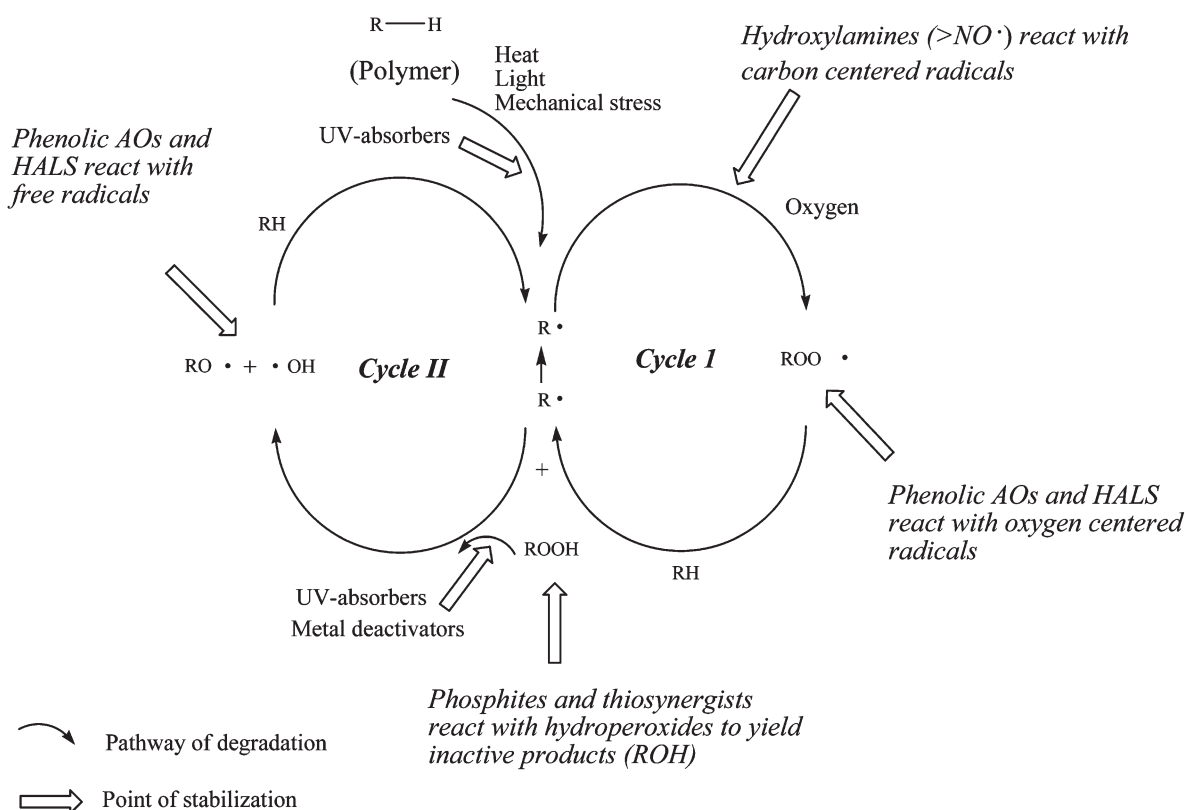


Figure 1. Auto-oxidative degradation cycles of polymers and interruption points of various additives.

deactivators, compatibilizers, etc.) and their mutual interactions with focus on environmentally friendly flame retardants such as phosphorus and nitrogen-based halogen-free flame retardants, inorganic-, and nanocomposite-based flame retardants. Processing and long-term thermal stabilization of flame retarded polymers are discussed, and past and present efforts of improving the light stability of flame-retarded polymers are reviewed. The new trend of using multifunctional additives that simultaneously provide two or more value adding functions such as weathering in combination with flame retardant efficacy is also discussed.

POLYMER DEGRADATION AND STABILIZATION

Although the focus of this review is on improving light stability of flame-retarded polymers, the principles of oxidative degradation and stabilization have to be discussed. Moreover, sufficient processing and long-term heat stability are, in general, prerequisites for achieving light stability in the presence of light stabilizers.

Principles of Oxidative Degradation

Most polymeric materials and all commodity plastics exposed to heat and sunlight are stabilized to suppress the deleterious effects of prolonged exposure to oxygen, ultraviolet (UV) radiation, and moisture on the polymer backbone.¹⁻⁴ To inhibit or delay those degradation reactions that lead to irreversible changes in chemical composition, morphology, molecular

weight, and molecular weight distribution are of primary importance. Polymer degradation occurs during the entire life cycle of the polymer product, from “cradle-to-grave” through an auto-oxidative free radical chain reaction process that can be divided into two cycles. A simplified auto-oxidation process of polymers and the points at which different stabilizers interfere, retard, and control the degradation process are shown in Figure 1.

This auto-oxidation process involves the generation of free radicals followed by propagation reactions that lead to the formation of hydroperoxides and ketone carbonyl species during the first degradation cycle I. The energetic free radicals and atmospheric oxygen trigger the polymer degradation, whereas the formed hydroperoxides and ketone species are believed to accelerate the photo-oxidation process of the polymer in the second degradation cycle II. The accumulated light-absorbing carbonyl chromophores in turn give rise to chain scissions via the classical Norrish I and Norrish II reactions of aliphatic ketones.⁵ These (photo)oxidative-induced changes are partially responsible for premature material failure owing to the loss of mechanical properties (impact strength, E-modulus, and elongation at break), worsening of visual properties (discoloration, cracking, etc.), and finally loss of overall value. The sensitivity to oxidation depends on the chemical structure of the polymer and of all other ingredients such as additives, fillers, metal ions, share of recycled material, type of pigments, flame retardants which may accelerate or delay (photo)oxidation. For example,

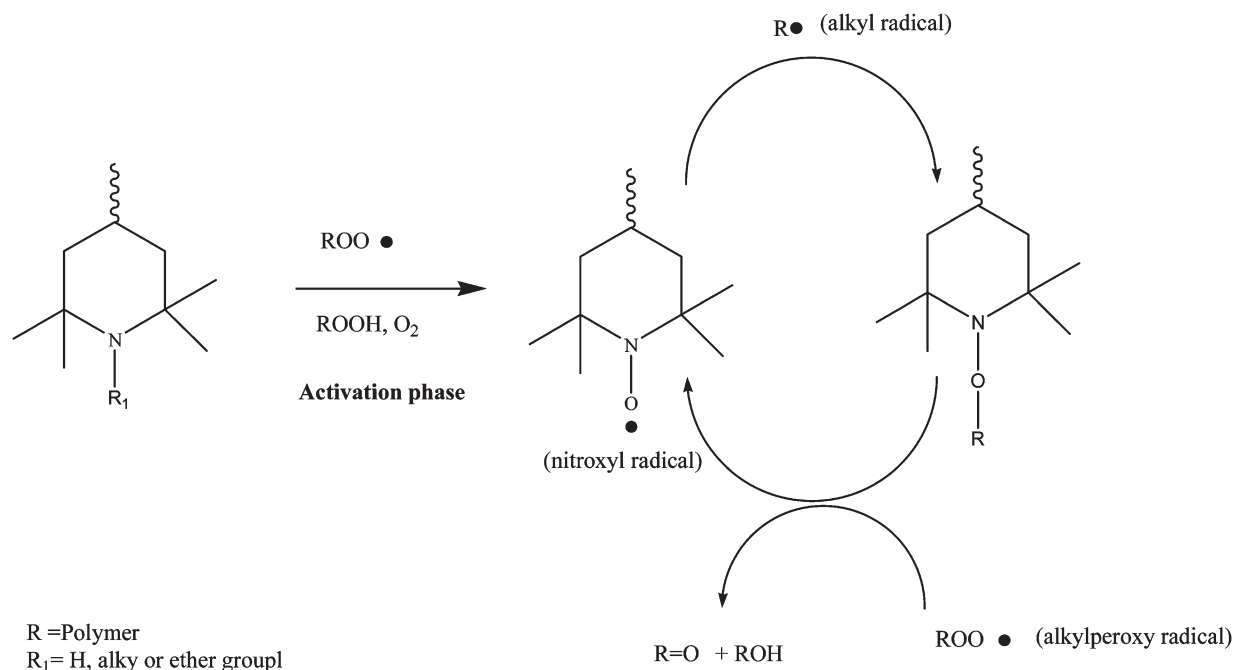


Figure 2. Mode of action of HALS.

polystyrene, polymethylmethacrylate, or polyesters are quite stable, whereas polypropylene and other polyolefins such as polybutadiene are very sensitive to (photo)oxidation.¹

Primary Antioxidants

The harmful degradation process needs to be controlled and inhibited by the addition of various antioxidants that preserve the properties and prolong the service lifetime of the polymeric product. There are mainly two types of antioxidant categories that interfere with the two auto-oxidation cycles, that is primary and secondary antioxidants. The most common primary antioxidants are based on sterically hindered phenols such as 2,6-di-tert-butyl-4-methylphenol (BHT), AO-1, AO-2, and AO-3. These hindered phenols interrupt the first degradation cycle by scavenging alkoxy and peroxy radicals formed during auto-oxidation cycle by offering an externally and more easily abstractable hydrogen than those from the polymer backbone itself.^{6,7} Consequently, when a hydrogen radical is donated, it neutralizes alkoxy and peroxy radicals that otherwise would continue the chain reaction of auto-oxidation. The high ability of phenolic compounds to quench peroxy radicals arises because of both their acidity (ability to donate protons) and their delocalized π -electrons characteristic of aromatic rings. Naturally occurring phenols, such as α -tocopherols (E-Vitamin) are also known to be effective antioxidants for polyolefins.⁸ The sterically hindered phenols provide protection to the polymer both during processing at high temperatures and in the end application as a long-term thermal stabilizer. A number of publications on the mechanism of stabilization for sterically hindered phenols have been published during the last decades.^{1,6} Aromatic amines such as diphenylamines are another class of efficient primary antioxidants, interrupting the first degradation cycle also by H-donation. The aromatic amines are mainly used in stabilization of elastomers and in less color critical applications.

Secondary Antioxidants

The classes of phosphite stabilizers (PS-1 and PS-2) act as secondary antioxidants that decompose unstable hydroperoxides prior to their homolytic cleavage into nonreactive and stable products. Thus, they are converted to the corresponding alcohol whereby the hydroperoxide decomposer is simultaneously oxidized to phosphate.⁹ The phosphites effectively compete with the thermolysis of the hydroperoxide groups and therefore effectively suppress the formation of alkoxy and hydroxyl radicals in the second auto-oxidative cycle. It is a common practice to use phosphites in combination with phenolic antioxidants, whereby the synergistic phosphite/phenol blend effectively inhibits both of the auto-oxidation cycles I and II, as shown in Figure 1, owing to their different and complementary stabilization mechanisms. In addition, various organosulfur compounds such as esters of the 3,3-thiodipropionic acid can also play an important role as hydroperoxide decomposers. Initially, the thiodipropionic acid ester reacts with hydroperoxides and forms sulfoxide and sulfone which undergoes thermolysis to give finally sulfuric acid derivatives. The produced sulfuric acids further catalyze hydroperoxide decomposition. More recently, a number of multifunctional stabilizers have been developed that contain both sterically hindered phenol and sulfur moieties within the same structure.² In addition to phenolic antioxidants, phosphites and sulfur compounds phosphonites, hydroxylamines, and lactones may be used in certain combinations.¹

Light Stabilizers

The protection mechanism of UV absorbers (UVA-1, UVA-2, UVA-3, and UVA-4) is essentially based on their ability to absorb the harmful UV radiation and to dissipate the absorbed energy as heat so that UV light does not trigger photo-oxidation of the polymer backbone. Thus, to protect polymers (or even brominated aromatic flame retardants) from the negative

influence of light, UV absorbers such as benzophenones, benzotriazoles, cinnamates, and hydroxyphenyltriazines may be used. Hindered amine (light) stabilizers (HA(L)S) such as LS-1, LS-2, LS-3, and LS-4 are based on sterically hindered piperidines or piperazines. The main representatives are derivatives of 2,2,6,6-tetramethylpiperidine or *N*-substituted molecules (alkyl, alkoxy, and acyloxy). HA(L)S do not absorb radiation. Their effectiveness is owing to their quenching and radical scavenging ability (Figure 2).

The superiority of hindered amine light stabilizer (HALS) and related compounds over other classes of light stabilizers in various polymers, including polyolefins, has been well established. First, in contrast to HALS additives, various UV absorbers perform poorly in thin sections such as films, tapes, sheets, and fibres as high concentrations of UV absorbers and sufficient thickness of the polymer are required before enough absorption takes place to effectively retard photodegradation. HALS form nitroxyl radicals which act as radical scavengers to inhibit degradation of the polymer. Owing to this radical scavenging mechanism, HALS do not only provide light stability (photo-oxidation) but also contribute to long-term thermal stability (oxidation) of the polymer. Significant levels of (photo)oxidative stabilization are achieved at relatively low concentrations owing to the fact that HALS are regenerated rather than consumed during the stabilization process. Since the introduction of hindered amine stabilizers as light stabilizers, the chemistries have been refined and nowadays HALS additives having increased resistance to acids and improved compatibility with the polymer matrix are available.¹⁰ In addition, today there are a number of HALS additives ranging from oligomeric, polymer-bound, to high-molecular weight HALS additives.¹¹ The better understanding of the influence of the molecular weight accounts for the application of HALS blends.^{12,13}

Meanwhile, information on the light efficacy of various HALS is available in the literature, whereas information of property–structure relationship on the light efficacy of different NOR compounds is more scarce. When ranking the best light stability efficacy in a series of 4-benzoate-substituted 2,2,6,6-tetramethylpiperidines, the obtained ranking was $N-O-COCH_3 < N-COCH_3 < N-H < N-O$.¹⁴ A recent patent application reveals that certain NOR derivatives are able to protect polypropylene films beyond 5000 h of artificial weathering against polymer degradation.¹⁵ Furthermore, a recent study that compares the efficacy of alkoxyamine-based HALS (NOR-1, NOR-2, and NOR-3) with the secondary HAS (>NH) LS-1 suggests that the nitroxide-based NOR compounds may be able to retard the chain oxidation by scavenging polymer alkyl radicals before the formation of polymeric hydroperoxides POOH.¹⁶

Metal Deactivators

These organic compounds are capable of forming co-ordination complexes with various metal ions such as Ti, Fe, and Al that may be present in the polymer matrix. These traces of metal ions would otherwise promote polymer degradation via metal-activated oxidation. The metal deactivators have typically multiple co-ordination sites that are capable of effectively entrapping the pro-oxidant metal ions.¹⁷

Filler Deactivators

One of the most common ways to modify thermoplastics is compounding them with various immiscible minerals to improve mechanical properties such as E-modulus or to reduce the cost of the formulation. Usually, the inorganic filler content in the blend is between 20 and 40 wt %. In most cases, the inorganic fillers such as talc, chalk, wollastonite, and glass are compounded with the polymer by melt blending in a twin-screw extruder to provide characteristics to suit a particular application. In thermoplastics, it has been recognized that various fillers can, in many cases, have a significant effect on the thermal and photochemical stability of the polymer material. Here, the surface activity, size and shape, hydrophilicity, and spectral characteristics of the fillers play a vital role. The filler–stabilizer interaction can be especially problematic owing to the absorption/desorption processes of stabilizers onto filler surface whereby the polymer itself may be depleted from stabilizer and the destructive polymer degradation sets in. Although the mode of interaction between the filler and the antioxidant is not fully elucidated, presumably fillers to a different degree possess active sites at which certain constituents are adsorbed from the polymer in its melt state. Mechanodegradation through high filler loadings contribute to the formation of additional radicals during processing that accelerate the consumption of stabilizers.

Coatings, filler deactivators, or coupling agents are used to block the surface of the filler and to render it inactive toward stabilizer sorption. Available coating agents and filler deactivators are based on fatty acids, siloxanes, titanates, acrylates, amphiphilic copolymers, epoxides, and many more.¹⁸

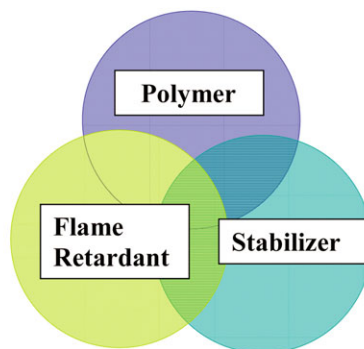
FIRE RETARDANT CONCEPTS AND FIRE TESTING

Flame retardants represent a substantial share of additives used in polymers and are one of the fastest growing areas of additives. Fire retardants are incorporated into the polymer and fulfill the essential function to protect the organic materials, for example in construction, textiles, furniture, transportation, or in electrical and electronic applications from being ignited. Various flame retardants, depending on their nature, can inhibit or suppress accidental fires or flame spread either chemically and/or physically in the solid, liquid, or gas phase. Classical flame retardant systems for polymers are based on halogenated, phosphorous, nitrogen, silicon-containing or inorganic (metal hydrates and nanocomposites) additives that are used alone or in combination with synergists. The most common flame retardants today are still halogenated (brominated) compounds with about 30% market share. Key parameters to estimate fire behavior of flame-retarded products are based on ignitability, flame spread, heat release as a function of time, smoke production, toxic or corrosive gas emissions, and charring rate. The most common small scale flammability tests includes the cone calorimeter test (ASTM E 1354), the UL94 vertical burn test (UL 94, Underwriters Laboratories, Northbrook, IL, 1991), DIN 4102-test, and assessment of limiting oxygen index (LOI).¹⁹

PHOTOSTABILIZATION OF FLAME-RETARDED POLYMERS

When dealing with challenges such as providing fire/flame protection in combination with weathering resistance to polymers,

a) Interplay



b) Durability of Flame Retarded Polymer

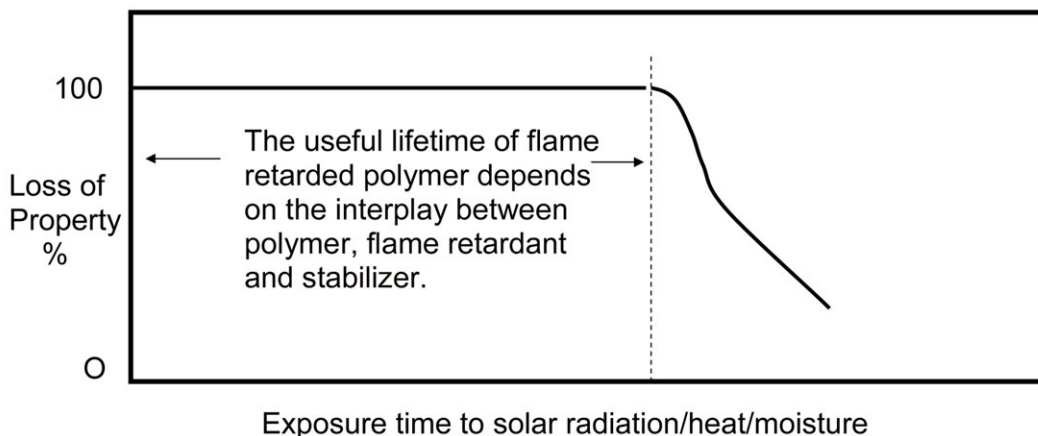


Figure 3. (a) The interplay between polymer, flame retardant, and stabilizer. (b) The useful lifetime of flame-retarded polymers may be drastically reduced owing to antagonism between FR and stabilizer, traces of metals, deactivation of HALS by acid species, hydrolysis of FR, adsorption of stabilizer onto filler surface, decomposition of FR owing to lack of UV stability, uneven distribution of FR or stabilizer in the polymer matrix, so on. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

one needs to take into account that the flame retardant might degrade independently (e.g., aromatic brominated flame retardants are not UV stable and release bromine and aromatic radicals that initiate photo-oxidation of the host polymer). Also, traces of metal impurities in filler-based flame retardant systems function as prodegradants by promoting hydroperoxide decomposition to free radical products that cause premature polymer failure. In addition, ammonium-modified clay nanocomposites are prone to Hofmann elimination reactions during polymer processing whereby flammable and volatile olefins and amines will be released. Phosphorus-based flame retardants may hydrolyze during polymer weathering whereby polyphosphoric acids decrease HALS activity through protonation. There might also be a direct interaction between the polymer and the flame retardant owing to poor compatibility and solubility or an interaction between the flame retardant and the stabilizer additives. For instance, the inclusion of filler-based flame retardants may lead to adsorption/desorption of stabilizers and antioxidants on the filler surface whereby the thermal and photostability of the polymer may be drastically reduced (the host polymer will be depleted of stabilizer owing to stabilizer sorption onto the high energy surface of various flame retardant fillers) or in the case of aromatic brominated flame retardants the formed acidic

vapors may deactivate the HALS through ammonium salt formation whereby again the polymer service life will be significantly reduced as shown in Figure 3.

Thus, certain flame retardant types may cause difficulties in regard to the durability of polymeric materials as a result of their reactivity and crossreactivity with other additives such as stabilizers and fillers. Overall, the demands on flame-retarded products and their performance are becoming ever more stringent owing to higher service-life expectations, new more challenging applications and standards, tougher legislation and regulations, lower cost requirements, and above all the request for flame retardant formulations with better toxicological and environmental profiles.

Brominated Flame Retardants and Their Impact on Polymer Stability

The mode of action of brominated flame retardants is based on thermally induced release of bromine radicals at the site of the flame zone. It has been established that the relative efficacy of halogenated flame retardants increases with decreasing thermal stability. However, a drawback of conventional brominated flame retardants such as tetrabromobisphenol A or brominated diphenyl ethers, besides environmental concerns, is that they

have a tendency to undergo dehydrobromination reactions already during polymer processing (temperature range, 210–250°C) and when subjected to UV irradiation during end use. The dehydrobromination reaction involves the homolytic cleavage of the C–Br bond, leading to the formation of bromine and aromatic radicals that will induce photolytic and thermo-oxidative reactions in the polymer matrix, that is thereby accelerating the degradation by “feeding” the auto-oxidation cycle with radicals. For polypropylene, it has been observed that the rate of formation of photoproducts is dramatically enhanced in the presence of decabromodiphenylether and antimony oxide compared to a virgin polypropylene sample.^{20–22} Similar results have also been recorded for halogen flame-retarded polystyrene²¹ and polyethylene (HDPE, LDPE).²³

In addition, hydrobromic acid is formed when the bromine radicals abstract hydrogen from the polymer backbone itself. The formed halogenated acid vapors are in turn known to impair the performance of HALS additives through the formation of an amine salt through protonation of the amine.²⁴ The amine salt inhibits the oxidation of HALS to the nitroxyl radical that is mandatory for polymer stabilization to take place. On top of this, the resulting amine salt is less thermally stable than the corresponding amine and it may even lead to the total decomposition of the HALS skeleton during processing.²⁵ Aliphatic bromine compounds are, in this respect, less detrimental than aromatic ones.²⁶ Studies have shown that even very weak acids such as those generated from sterically hindered phenolic stabilizers²⁷ may partially deactivate the HALS and that also bromine radicals may react with the nitroxyl radical of the 2,2,6,6-tetramethylpiperidine light stabilizer.²⁸

Several strategies and attempts have been made to circumvent the antagonistic effect between brominated flame retardants and HALS derivatives to secure high weathering resistance of halogen flame-retarded polymers. Mainly, four different strategies have been tested: (1) the use of acid scavengers such as tin malates or antiacids such as ZnO, calcium stearate, and Mg(OH)₂²⁹; (2) the use of traditional UV absorbers or pigments as UV filters³⁰; (3) microencapsulation of the brominated flame retardant³¹; and (4) utilization of low interacting HALS derivatives where the HALS moiety has been replaced with *N*-alkoxy or *N*-acyloxy hindered amines.³² The most successful approach of these aforementioned strategies has been the development of alkoxyamine (NOR) derivatives that exhibit lower basicity compared to conventional HALS and which are already in a more active oxidation state than classical HALS derivatives for polymer stabilization.^{33–35} In addition, good results have been obtained by combining NOR compounds with UVA. The primary benefit of UVA is that it provides an UV screen for the aromatic brominated flame retardant besides the polymer itself, thus inhibiting the generation of bromine radicals and hydrobromic acid.³⁰ Further study has shown that UL94 V-0 rating can be achieved with NOR and a halogenated system.¹⁹ Thus, the NOR additives do not only improve the UV stability and long-term stability of polymers, but also exhibit a strong synergistic effect with brominated flame retardants. As an example, a commercial multicomponent system consisting of brominated flame retardant/antimony oxide, NOR light stabilizer, and

selected pigment has been successfully developed for stadium seats made out of polypropylene. This FR/NOR light stabilizer formulation for PP copolymers survives 4000 h of artificial weathering (ASTM G26, spray), whereas the similar formulation with conventional FR/HALS light stabilizer combination fails already after about 800 h.³⁵ In addition, it has been proposed that the detrimental interaction between brominated flame retardant and HALS can be partially circumvented by microencapsulation of the halogenated flame retardant.³⁶

Phosphorus- and Nitrogen-Based Halogen-Free Flame Retardants

Ammonium polyphosphate (APP), which is available in different crystal modifications and with coatings (e.g., melamine and silicone) or in an encapsulated form, decomposes by exposure to fire or heat to ammonia, polyphosphoric acid, and phosphorus oxides. In the presence of a char-forming agent, for example a polyol, an intumescent barrier via phosphoric ester intermediates is formed. APP-/pentaerythritol-based intumescent flame retardants do not significantly accelerate the degradation of unstabilized PP.^{37,38} However, the APP-based intumescent flame retardant is susceptible to photodegradation as such. Therefore, it can be concluded that two separate processes take place, that is (1) photo-oxidation of the intumescent flame retardant and (2) photodegradation of the polymer matrix. Other studies have shown that the activity of HALS is somewhat reduced likely through protonation by the polyphosphoric acid. It is, however, less severe than with brominated flame retardants. On the other hand, the efficacy of an UV absorber is increased through the polyol present in the flame retardant combination.

The photochemical behavior of polypropylene formulations containing 0.5 wt % HALS as light stabilizer and as flame retardant either octabromodiphenyl ether (OBDE)/Sb₂O₃ or APP has been studied under artificial accelerated conditions.³⁹ The formulation with OBDE showed significant surface degradation (the appearance of surface cracks by light microscopy at 100-fold magnification was used as the criteria of surface degradation) already after 400 h irrespective of the presence of 0.5 wt % of HALS, whereas the APP/HALS system was stable up to 1800 h of artificial light exposure. On the other hand, the reference polypropylene/HALS sample without any flame retardant lasted for 2500 h under similar experimental conditions. However, in case of artificial weathering, hydrolysis of APP may occur and it results in reduced fire retardancy as the formation of the intumescent network is disturbed already after 210 MJ/m², corresponding to 1 year in mid-Europe.⁴⁰ A similar result was found in EVA/PA-6/PP-blends.⁴¹

As red phosphorus is mainly used in engineering plastics (polycarbonate, polyamide, and polyester), the influence on light- and long-term thermal stability is less critical. From the stabilization point of view, it is important to stabilize red phosphorus against phosphine formation through moisture which is achieved by microencapsulation⁴² or by adding salts such as copper acetate.⁴³

Nitrogen-containing flame retardants are a class of various materials among which are well-known halogen-free commercial products, namely APP, melamine cyanurate (MC), melamine

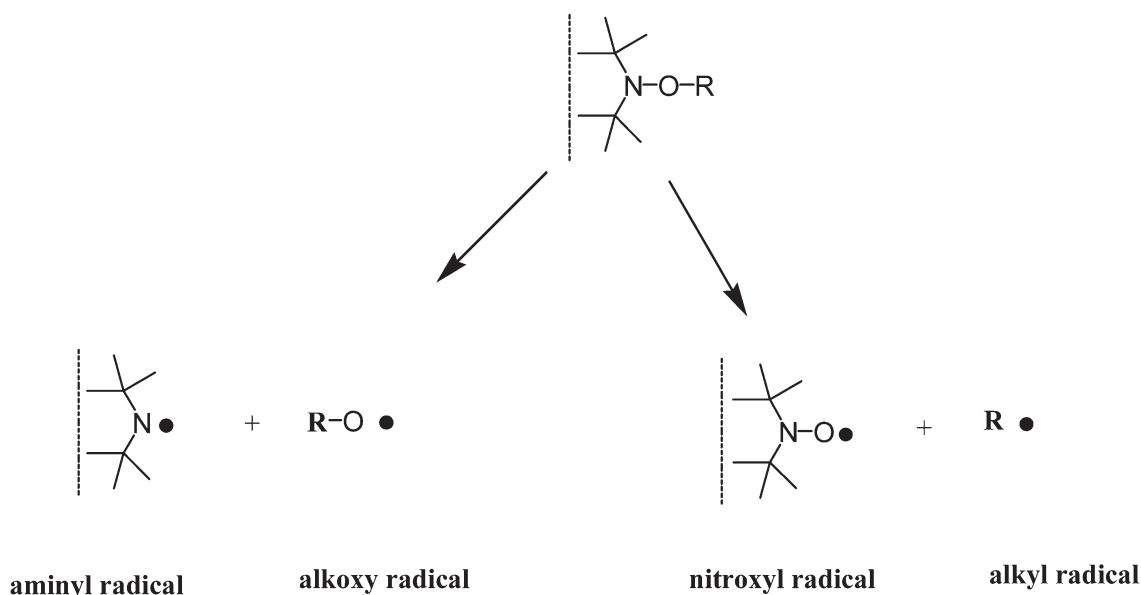


Figure 4. Thermolysis of alkoxyamines to aminyl, alkoxy, nitroxyl, and alkyl radicals.

borate, and melamine (poly)phosphate. MC is a 1 : 1 adduct of melamine and cyanuric acid. MC decomposes endothermically into its components and melamine decomposes further to nitrogen-containing gases such as noncombustible ammonia. Stabilized polyamide MC formulations did not lose their fire retardancy after artificial weathering (210 kJ/m²); however, some blooming of MC was detected.⁴⁰ Melamine phosphates did not reveal any antagonistic effect with HALS in artificial weathering experiments.⁴⁴ Actually, even a slight improvement could be found owing to a pigment effect of the flame retardant.

The processing stability of MC-containing polyamide has been shown to be improved by addition of sulfates (e.g., magnesium-sulfate⁴⁵) or metal acetates (e.g., magnesium acetate⁴⁶). Bisphenol-A-diphosphate PC/ABS blend showed without UV stabilizer discoloration and surface cracks, it had, however, no influence on the flame retardancy after 210 MJ/m².⁴⁰

MC polyamide compounds, APP polypropylene, and melamine phosphate/polypropylene can be successfully recycled without significant loss of properties.⁴⁷ On the contrary, recycled PC/ABS flame retarded with organic phosphate ester lost already after the first recycling step flame retardancy, whereas its molecular weight and mechanical properties were still essentially unchanged.⁴⁸ In contrast, ABS with brominated flame retardants passed the UL 94 5VB test even after five extrusion steps.

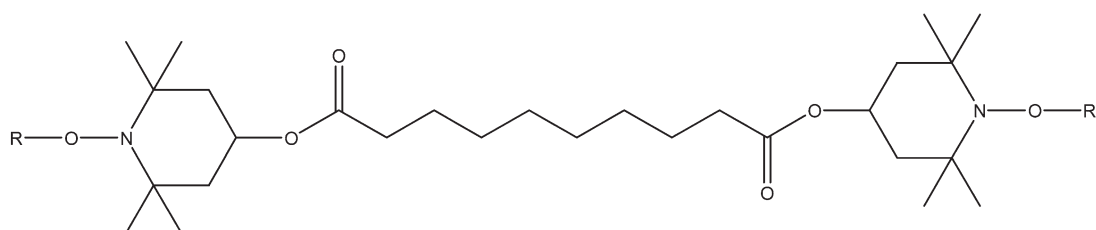
Nitrogen Flame Retardants Based on Dual Functional NOR Additives

It was earlier believed that the noninteractive NOR additive in the presence of brominated flame retardants contributed only to improved light stability and that it functioned as an FR synergist with halogenated flame retardants. More recently, it has been shown that in some polypropylene formulation, the NOR additive can successfully replace antimony oxide as a synergist for halogenated flame retardants. Later, it was discovered that

NOR additives, in fact, exhibit flame retardant and self-extinguishing properties in polypropylene films and fibres by themselves.^{49–52} Other advantages of NOR additives are that they are easily melt processable, they function at very low concentrations (ca. 1 wt %), and they do not weaken the mechanical or physical properties of the host polymer. In short, NOR provide flame retardancy in thin polypropylene/polyolefine sections in combination with inherent light stability properties. A disadvantage is that the NOR compounds alone do not achieve usual flame retardant standards such as UL 94 in polypropylene moldings and that they cannot be processed above 250°C without decomposition. In addition, several other chemical structures related to alkoxyamines are claimed to provide flame retardancy namely hydroxylamine esters,⁵³ hydroxylamines, and nitroxyl radicals.

The activity of alkoxyamines as flame retardants is based on the thermolysis of nitroxyl ethers which leads to the formation of either alkoxy and aminyl radicals or alkyl and nitroxyl radicals (Figure 4).

The N—OR and NO—R bond dissociation energies are of the same range. Alkoxyamine-derived radicals are very reactive and cause, on the one hand, degradation of polypropylene (and crosslinking of polyethylene) upon thermal activation. On the other hand, they are involved in the free radical chemical reactions during the combustion process.¹⁰ Overall, the flame retardant properties of different alkoxyamines mainly depend on three parameters: (1) thermal stability of NOR (homolysis of NO—R or N—OR), (2) molecular weight of NOR additive and its substitution pattern, and (3) reactivity of the radicals generated during decomposition. In the case of polypropylene, it is believed that the formed small polymer fragments of low molecular weight are rapidly withdrawn from the flame zone in the form of droplets that either drip off or are immediately consumed in the combustion process. It is even possible to



General NOR template

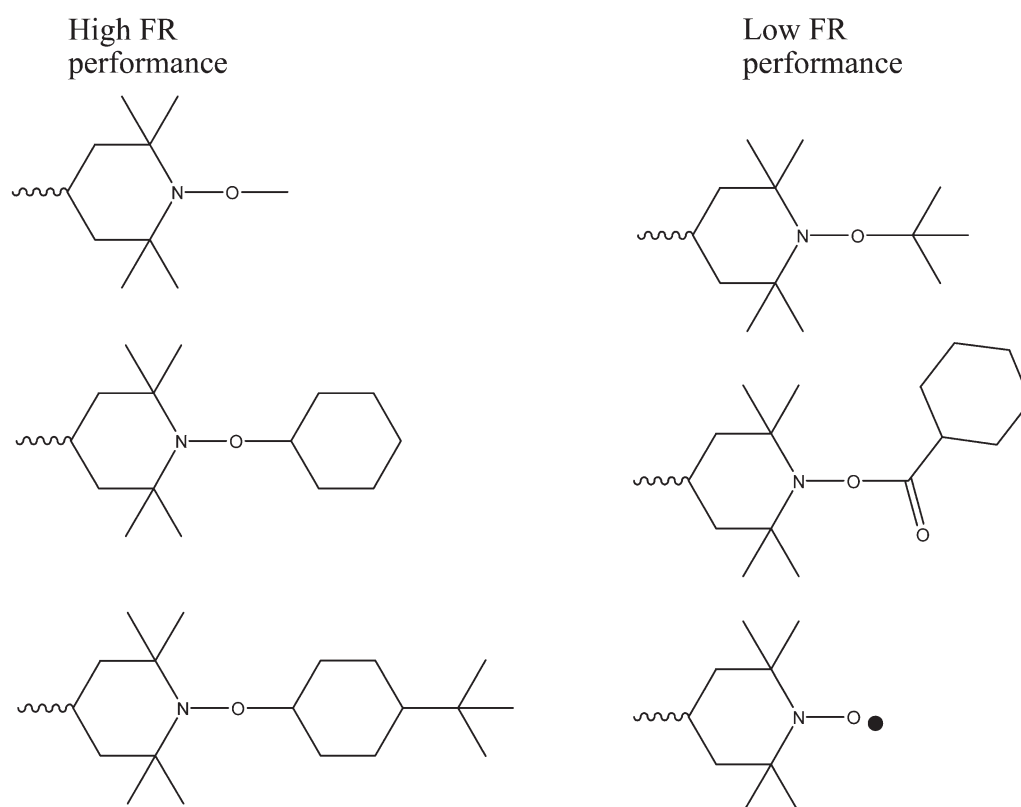


Figure 5. Flame retardant ranking of various NOR additives based on their performance in DIN 4102/B2 test in polypropylene films.

incorporate further flame retardant-active structures chemically in one molecule, for example in phosphorus-containing alkoxyamines.⁵⁴

However, the literature available on the role of various NOR structures on fire retardant efficacy is still very limited and mostly in the form of patents. A few examples of structure–property relationship of various NOR structures in flame-retarded polypropylene films are shown in Figure 5.

In the series of 1-*n*-alkoxy-4-(dodec-2-enyl)-2,2,6,6-tetramethylpiperidines, all of the compounds showed comparable or even higher efficiency than FLAMESTAB NOR116 (commercial product, supplied by BASF SE, structure attachment). The best flame retardant effect in this series was obtained for 1-methoxy-4-(dodec-2-enyl)-2,2,6,6-tetramethyl-piperidine. The results indicate that the flame retardant properties within the family of NOR compounds increased as a function of the thermal stability of the *N*-alkoxyamine additive.⁵⁵ Similar ranking results for NOR

efficacy as flame retardants can also be found in a recent patent application for new spiro-NOR-HALS derivatives.⁵⁶

Novel Multifunctional (1-Alkoxy-2,2,6,6-tetramethylpiperidin-4-yl)diazene Additives

Recently, it has been reported that (1-alkoxy-2,2,6,6-tetramethylpiperidin-4-yl)diazene (AZONOR) compounds provide, besides flame retardancy also, heat and light stability to polypropylene films and plaques.^{57–59} The AZONOR compounds are active at very low loadings of only 0.5 wt % and they have no detrimental effect on polypropylene appearance or its mechanical and processing properties. Moreover, they exhibit a synergistic effect with many conventional flame retardants such as brominated, inorganic, and especially phosphorous flame retardants.⁶⁰ Representative AZONOR structures are shown in Figure 6.

In the shown experiment, the various AZONOR compounds were the only ones at the concentration applied to provide flame retardancy in polypropylene plaques of 1 mm for more

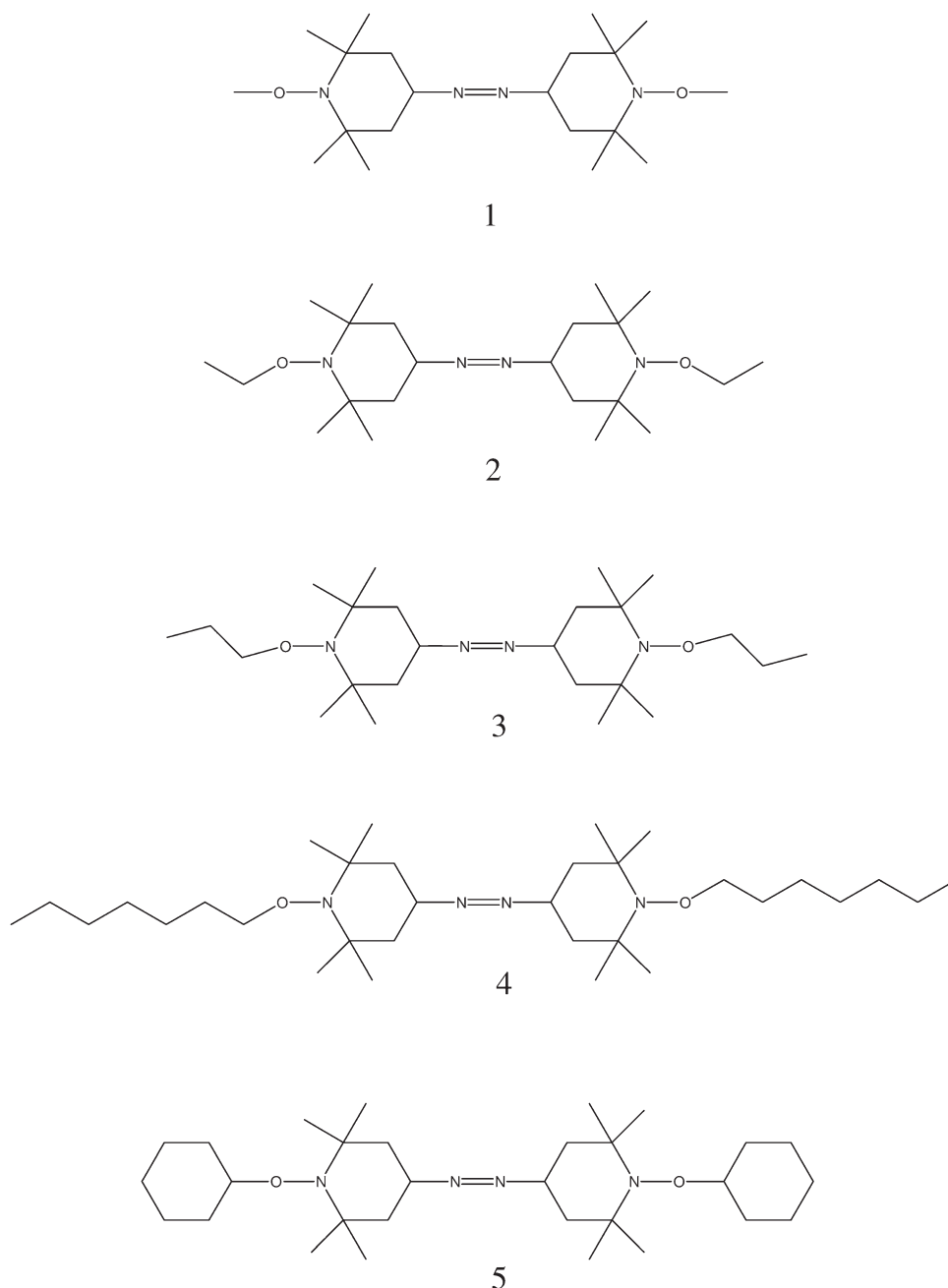


Figure 6. Various NORAZO structures.

than 2000 h of artificial weathering (WOM Ci 65A, BPT 63°C, 60% relative humidity, water spray) as summarized in Table I. Another bonus of AZONOR flame retardants was that no burning dripping could be detected.

Inorganic Minerals as Flame Retardants

Inorganic fillers such as $\text{Al}(\text{OH})_3$, $\text{AlO}(\text{OH})$, $\text{Mg}(\text{OH})_2$, layered silicates, and nanocomposites are widely used as efficient flame retardants of low cost. Metal hydrates provide effective flame retardancy by several routes including release of water at elevated temperatures, the dilution of fuel available to sustain combustion during fire, and providing a blanket that limits the oxygen available for combustion. Very high loadings of 40–60

wt % are required to achieve the desired level of flame retardancy, whereby polymer processing becomes difficult and mechanical properties may be negatively altered.

Fillers and Polymer Stability

The impact of various inorganic fillers on the stability of polymers is illustrated in the following examples: The long-term heat stability at 150°C in a forced air circulated oven for three talc-filled polypropylene grades decreased from 80 days (unfilled polypropylene, base stabilization package: 0.1 calcium stearate, 0.1 wt % AO-1, and 0.3 wt % PS-1 to 5–24 days) until embrittlement depending on the specific talc used. Thus, the contribution of talc to heat stability was always negative, even if the

Table I. Results of Flame Retardant Testing According to DIN4102/B2 Standard Before and After Artificial Weathering

Additives (wt %)	Before artificial weathering			After 2000 h of artificial weathering		
	Weight loss (%)	Burn length (mm)	DIN 4102 Pass/fail	Weight loss (%)	Burn length (mm)	DIN 4102 Pass/fail
Blank	100	100	Fail	Test failed before WOM test		
NOR371(2%)	n.d.	88	Fail	Test failed before WOM test ^{a)}		
NOR116 (0.5%)	49.4	80	Fail	Test failed before WOM test		
1 (0.5%)	n.d	31	Pass	Passed 2000 h of WOM		
2 (0.5%)	n.d	41	Pass	Passed 2000 h of WOM		
3 (0.5%)	5.2	27	Pass	Passed 2000 h of WOM		
4 (0.5%)	14	43	Pass	Passed 2000 h of WOM		
5 (0.5%)	8.9	37	Pass	Passed 2000 h of WOM		

amplitude was dependent on talc type.⁶¹ Similar results of decreased stability of talc and calcium carbonate-filled polypropylene composites have also been observed by other research groups.^{62–64} Experiments using talc-filled polypropylene samples containing a 1 : 1 mix of LS-1 and LS-2 as light stabilizers have also been carried out. The results from the artificial weathering experiments clearly show that talc also significantly decreases the light stability of polypropylene. The observed decrease in both heat and light stability has been mainly attributed to stabilizer absorption on the high energy surface of the filler. In addition, it was showed that heat and light stability of the composites could be improved by using a “filler deactivator” such as an oligomeric Bisphenol-A-glycidylether or by significantly increasing the amount of light stabilizer. The increase of stabilizer content may not be a feasible, economic, or practical solution to the stabilizer adsorption problem, whereas the filler deactivator route holds more promise. For instance, a number of filler deactivators or coupling agents have been successfully used to modify the filler surface and to improve the stability of the polymer. Suitable additives range from typical filler coatings (stearic acid, stearates), oligomeric epoxides, silanes, titanates, to functional polymers (e.g., polypropylene-*graft*-maleic anhydride or polypropylene-*graft*-acrylic acid). Encouraging results for using coupling agents with respect to improved heat stability of talc-filled polypropylene formulations have been recorded, that is certain amphiphilic coupling agents with hydrophilic ends prevent the undesired adsorption of stabilizers onto the filler surface.^{65,66}

Nanocomposites—Highly Dispersed Flame Retardants

In recent years, fillers in nanodimensions such as highly dispersed flame retardants, layered and fibrillated silicate clays, carbon nanotubes and nanofibers, calcium carbonate, metal oxides, or silica nanoparticles that function at low loadings of 2–5 wt % have been investigated. Researchers have focused their attention particularly on polymer-layered silicate nanocomposites. The clay-based nanocomposites are among the most examined owing to the relatively low price of clay minerals, their availability, and unique characteristics including their plate-like morphology with a high aspect ratio. The macroscopic phase behavior of polymer–colloid mixtures has been the subject of many

theoretical and experimental studies. The dispersion state of the nanoclay in the polymer matrix can be described by cluster, intercalated (distanced but yet parallel layers), or exfoliated (fully dispersed) structures. In each case, the polymer chains are differently arranged in the nanocomposite matrix and thus the composite properties are intimately linked to the macroscopic structure of the inorganic filler in the nanocomposite. In many cases, the most significant improvements in reinforcement, barrier, and flame retardant properties have been found for intercalated and/or exfoliated systems and therefore various ways to enhance the dispersibility have been the topic of great interest.^{67–72} Normally, polymers containing a small amount of nanofiller exhibit a significant decrease in peak heat release and mass loss during cone calorimeter experiments. The fire retardant effect has been attributed to the accumulation of inorganic particles at the surface of the composite with subsequent formation of a carbonaceous coating limiting heat and mass transfer. However, nanofillers rarely contribute, in their own right, to improvements in traditional fire tests such as UL-94 or LOI tests. Today, there is a consensus that nanofillers need a synergistic flame retardant to perform well in the aforementioned two fire tests. Recently, it has also been noted that nanocomposites prevent blooming by reducing environmental release of any additive present in the nanocomposite product.

The influence of nanosized silica on the oxidative and photo-oxidative stability has been studied by several authors. The results vary somewhat depending on the silica used in terms of particle size, pore, and surface morphology, purity in terms of metal residues (Ti, Al, Fe), Bronsted and Lewis acid sites, and controlled antioxidant absorption/desorption characteristics. It has been shown that various antioxidants are absorbed on the silica surface with different strengths depending on their chemical structure, that is studies have shown that light stabilizers, for example Chimisorb 944 (HALS-x) are more strongly adsorbed on the silica surface than hindered phenols such as butylated hydroxyl toluene (BHT) or (AO-1). When either of the antioxidants was used as a single stabilizer together with silica in LDPE, a reduction of stabilization performance was recorded. This phenomena was attributed to the deactivation of the antioxidant through immobilization of the active groups of

stabilizers molecules such as —OH , >NH , or >NO at the filler surface. Although interestingly it was noticed that when both HALS and hindered phenol additives were present in the silica/LDPE formulation, a strong synergistic effect was observed, that is leading to an enhanced level of stabilization. This in turn was ascribed to controlled release of the phenolic antioxidant through displacement from the silica surface by the more strongly adsorbing HALS.⁷³ Another study revealed that metal ion (Al, Ti, Fe) impurities in silica significantly accelerate the degradation process by catalyzing the breakdown of formed hydroperoxides at already very low loadings of silica. Studies have shown that the drawback of metal ion contaminants can be circumvented by using appropriate metal deactivators such as 1,2-bis(3,5-di-tert-butyl-4-hydroxyhydro-cinamoyl)hydrazine (MD-1).

As mentioned earlier, layered silicates have been evaluated as cost effective, environmentally friendly additives for reducing flammability, and for improving physical properties of various polymers.^{74–83} The clay-based nanocomposites are among the most examined owing to the relatively low price of clay minerals, their availability, and unique characteristics including their plate-like morphology with a high aspect ratio. Again, layered silicates from natural sources (e.g., montmorillonite) may contain evenly distributed metal ions as contaminants that are known to have a negative effect on polymer stability. Polymer compatibility with the surface of the clay platelets is crucial for obtaining sufficient dispersion of the nanoparticles in the polymer matrix. For instance, Seo et al.⁸⁴ prepared polyurethane nanocomposites by utilizing silanol surface-modified clays that reacted with NCO groups of polymeric 4,4'-diphenyl methane diisocyanate (MDI) whereby an exfoliated structure was obtained that resulted in enhanced mechanical properties at a clay loading of 3 wt %. Camino and coworkers⁸⁵ have shown that in the case of modified nanodispersed clay in polyurethane formulations, improved flame retardant properties can be reached for both intercalated and exfoliated structures. In general, it is difficult to obtain a homogeneous dispersion of nanoparticles in a polymer by using existing/traditional compounding techniques owing to the strong tendency of fine (nano) particles to agglomerate. One widely explored route to gain better interaction between the clay–polymer interfaces is to modify the nanoparticle surface by treatment with surfactants such as alkyl ammonium surfactants with long alkyl tails. In this case, the amount of organic material within the clay can be very high (ca. 40%), and therefore, the stability of this organic part of the surfactant cannot be neglected. At normal polymer processing temperatures of above 200°C, the thermal stability of the ammonium salts is too low. Most of the ammonium structures tend to undergo Hofmann elimination reactions whereby volatile and flammable olefin and amine derivatives are released. In fact, the thermal degradation of ammonium salts starts already at 180°C and is furthermore reduced by catalytically active sites on the aluminosilicate layer.⁶⁹ Hydrophobic polymers such as polyolefins often require, on top of the organic modification filler, a substantial amount of an additional compatibilizer such as polypropylene-*g*-maleic anhydride (PP-*g*-MAH). These lower molecular weight compatibilizers usually exhibit an inferior oxidative stability compared to the parent polymer and,

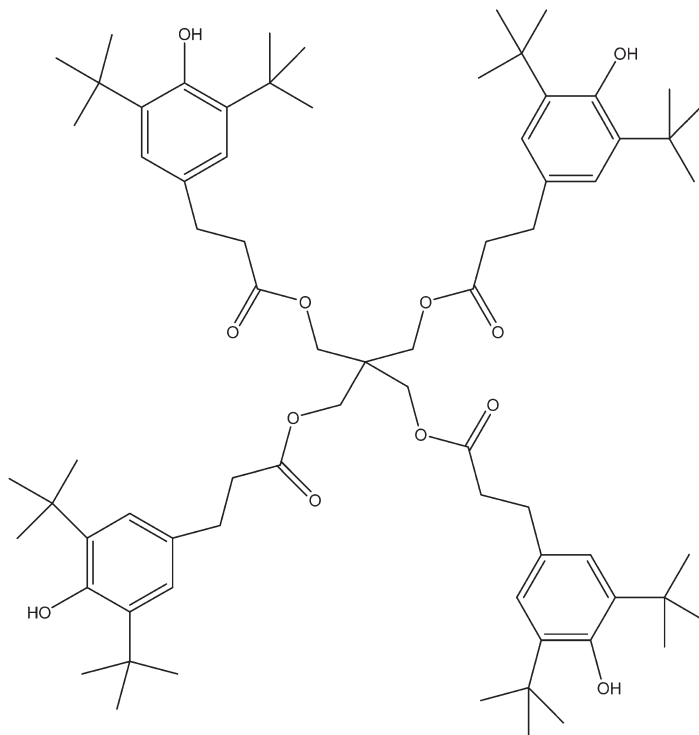
therefore, reduce the long-term performance of polymer nanocomposites.⁷⁴

In many cases, nanocomposites based on organically modified montmorillonite show in comparison to neat polymer a dramatic reduction of long-term stability,^{71–73} for example the long-term thermal stability of a stabilized polypropylene at 135°C is reduced from more than 40 days to only 15 days in the presence of 5% organically modified clay. Noteworthy is that the nanocomposites' higher propensity to photo-oxidation also leads to faster discoloration and deterioration of mechanical properties. For instance, according to the artificial weathering experiments, polypropylene montmorillonite-based nanocomposites (stabilized with antioxidant) degrade under exposure to UV light much more rapidly than virgin polypropylene.^{81,86} The photo-oxidation of EPDM montmorillonite nanocomposites drastically reduced the induction time of photo-oxidation in the presence of the nanoclay and the effect was enhanced in the presence of an exfoliated nanocomposite structure.⁸² The photo-oxidation of syndiotactic PP/synthetic clay (fluorohectorite modified by octadecylammonium) nanocomposites showed that the nanoparticles were catalyzed the decomposition process.⁸³ The presence of PP-*g*-MAH as compatibilizer accelerated the degradation furthermore. In natural clays, iron impurities play an active role in the dramatic modification of the oxidation kinetics.⁷⁴ Similar results of fast photo-oxidative degradation have also been found for polyethylene/montmorillonite nanocomposites. The reason for the more rapid degradation has been attributed to the adverse role played by the thermal decomposition products of the alkyl ammonium surfactant (Hofmann elimination reaction), the photo instability of compatibilizers such as PE-*g*-MA, and negative contribution from exfoliated structures.^{87–89} The influence of the nanocomposite substrate is furthermore of importance, for example EVA or polystyrene shows less acceleration of degradation than LDPE.^{90–94} In addition, for nanodispersed hydrotalcite in polypropylene⁹⁵ for CaCO₃ and SiO₂ nanoparticles,⁹⁶ for EPDM nanocomposites synthesized from layered double hydroxides,⁹⁷ and for boehmite, modified by long-chain alkyl benzene sulfonic acid in isotactic PP and in syndiotactic PP⁹⁸ a similar phenomenon of accelerated photo-oxidation has been recorded.

Only in some rare cases such as polyamide-6⁹³ and PE/PA-6 blends,⁹⁴ an improvement in (photo)oxidative stability in the presence of nanoclays could be detected.

Overall, it seems that in the case of filled polymers that the dilemma of the adsorption of stabilizers (in particularly for exfoliated structures) and the level of metal impurities need to be carefully addressed to achieve sufficient long-term heat and light stability of flame-retarded products. The conventional approach of melt blending of stabilizers into the nanocomposite during their production is insufficient. Thus, for example PP stabilized with 0.05% phenolic antioxidant and 0.05% phosphite achieves only a life time of 1.8 min (fluorohectorite) or 2.3 min (montmorillonite) at 190°C. However, through proper stabilization including filler deactivators, the oxygen induction time (OIT) value can be prolonged to more than 90 min.⁹⁹ With similar systems, the long-term thermal stability can be raised again to the values of unfilled materials; however, a higher stabilizer loading is compulsory.

AO-1: Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, 1,1'-[2,2-bis[[3-[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropoxy]methyl]-1,3-propanediyl] ester (CA: 6683-19-8)



AO-2: Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, octadecyl ester (CA: 2082-79-3)

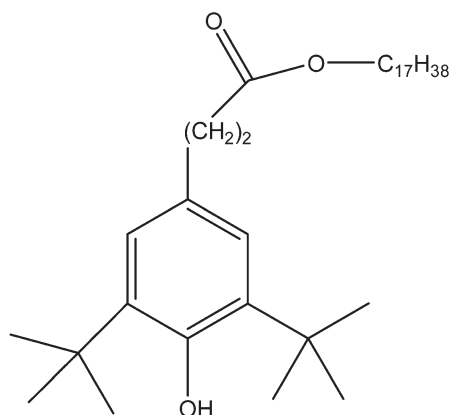


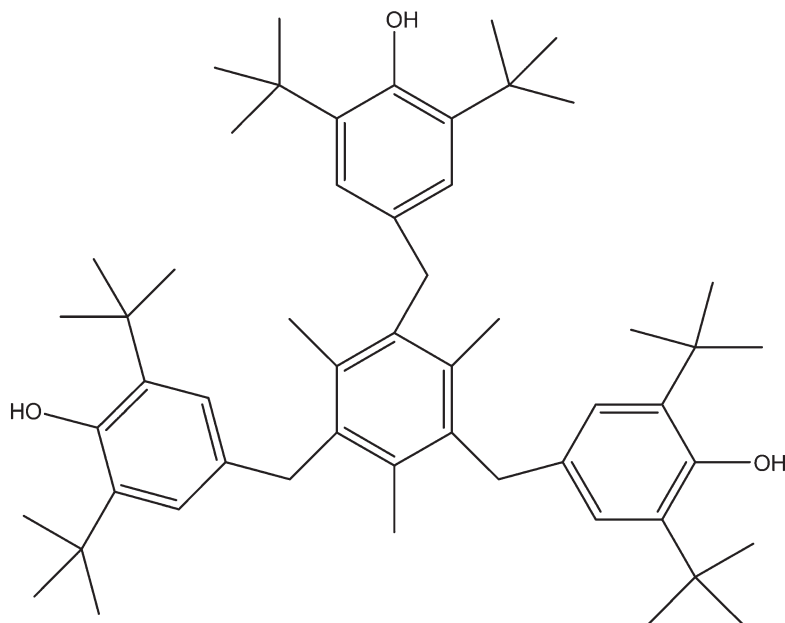
Figure 7. Structures and chemical names of stabilizers.

Recently, it has been demonstrated that by using a polymeric glycidyl group containing copolymer at a loading ranging between 0.3–2 wt % as filler deactivator not only the thermal stability (OIT) could be improved from 30.3 to 96.6 min but even also the tensile impact strength value increased from 128 to 178 kJ/m² for the polypropylene-based nanocomposite formulations.¹⁰⁰

In general, polymer nanocomposites exhibit inferior light stability owing to the sorption of stabilizers or owing to metal ion-

induced hydroperoxide decomposition. This can be partially circumvented by the use of UV absorbers and/or metal deactivators. Thus, UV absorbers of benzotriazole, benzophenone, or hydroxyphenyltriazine structures extended decisively the lifetime of linear low-density polyethylene (LLDPE) nanocomposite films. However, a metal deactivator alone outperformed the UV absorber in these experiments, indicating that the influence of metal impurities is also very crucial,^{90,101} whereas the combined effect of both UVA and metal deactivator only marginally improved the photostability of the LLDPE nanocomposite.

AO-3: Phenol, 4,4',4''-[(2,4,6-trimethyl-1,3,5-benzenetriyl)tris(methylene)]tris[2,6-bis(1,1-dimethylethyl)- (CA: 1709-70-2)



PS-1: Phenol, 2,4-bis(1,1-dimethylethyl)-, 1,1',1''-phosphite (CA: 31570-04-4)

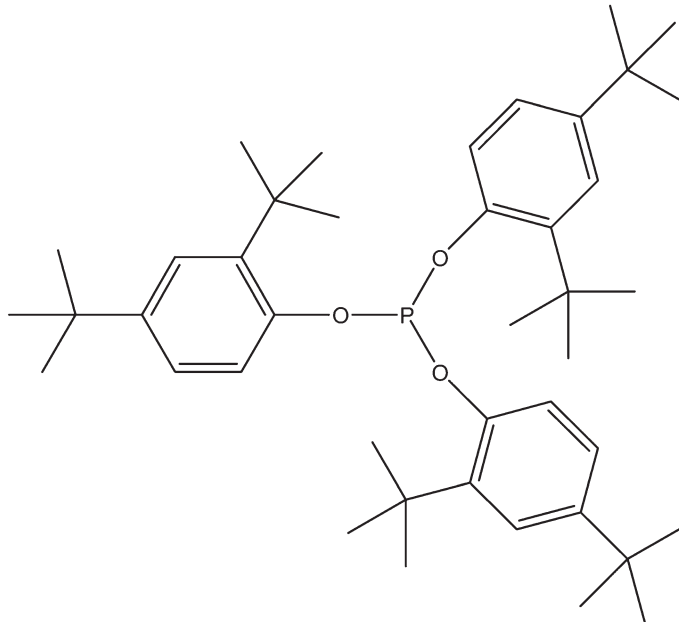
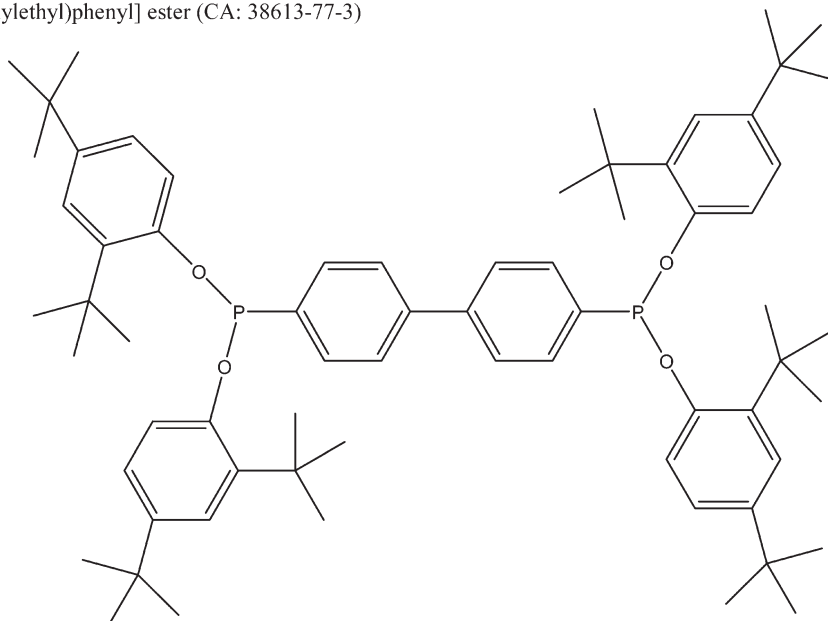


Figure 7. (Continued).

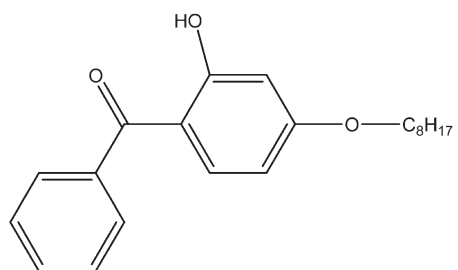
In addition to polyolefins,¹⁰² it has been experimentally demonstrated that polyamide nanocomposites can be synergistically stabilized by low- and high-molecular-weight light stabilizers in combination with processing and long-term heat stabilizers.

Alternatively, high light stability of nanocomposites can be reached with appropriate filler deactivators, that is the time until 50% retained tensile impact strength was raised from 1100 up to 2100 h in the presence of a filler deactivator. Artificial

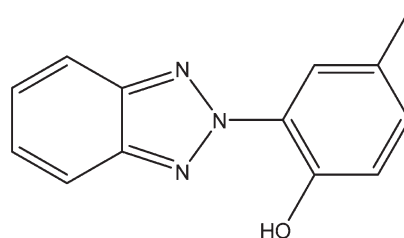
PS-2: Phosphonous acid, P,P'-[[1,1'-biphenyl]-4,4'-diyl]bis-, P,P,P',P'-tetrakis[2,4-bis(1,1-dimethylethyl)phenyl] ester (CA: 38613-77-3)



UV-1: Methanone, [2-hydroxy-4-(octyloxy)phenyl]phenyl- (CA: 1843-05-6)



UV-2: Phenol, 2-(2H-benzotriazol-2-yl)-4-methyl- (CA: 2440-22-4)



UV-3: Phenol, 2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylpropyl)- (CA: 25973-55-1)

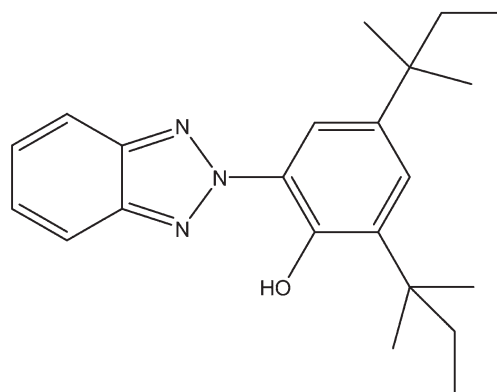
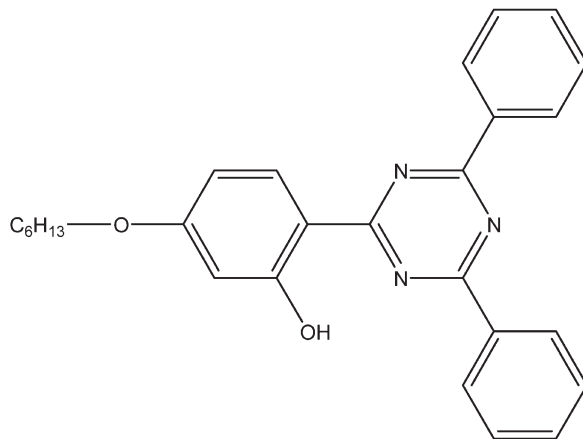
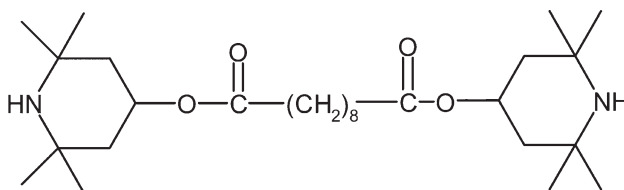


Figure 7. (Continued).

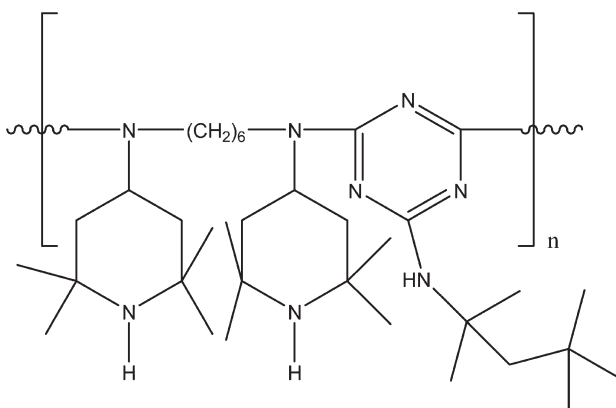
UV-4: Phenol, 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-(hexyloxy)- (CA: 147315-50-2)



LS-1: Decanedioic acid, 1,10-bis(2,2,6,6-tetramethyl-4-piperidiny) ester (CA: 52829-07-9)



LS-2: Poly[[6-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidiny)imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidiny)imino]] (CA: 71878-19-8)



LS-3: Butanedioic acid, polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidineethanol (CA: 52722-86-8)

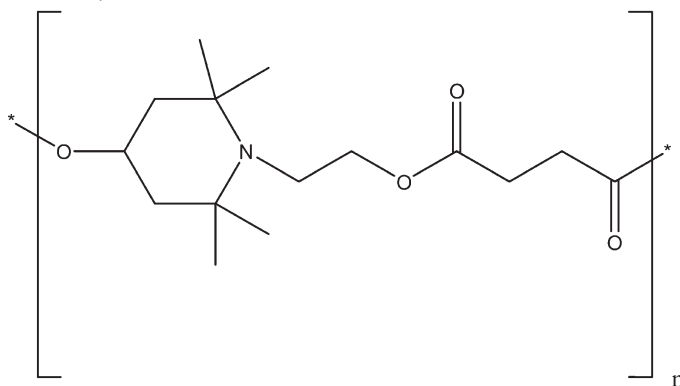
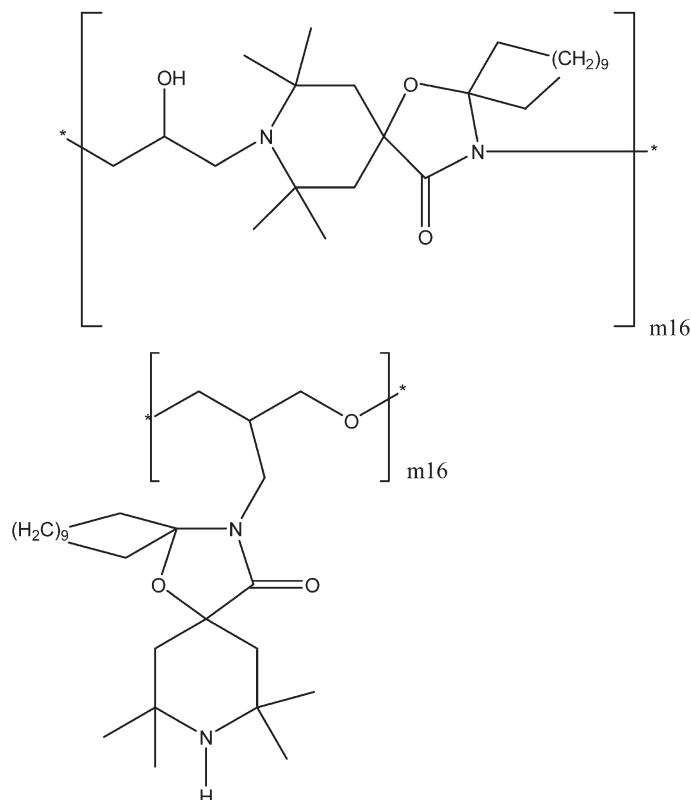
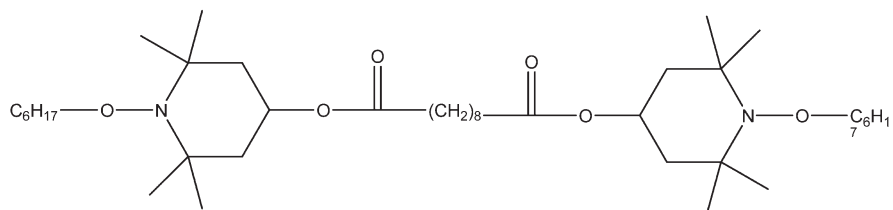


Figure 7. (Continued).

LS-4: 7-Oxa-3,20-diazadispiro[5.1.11.2]heneicosan-21-one, 2,2,4,4-tetramethyl-20-(2-oxiranylmethyl)-, polymer with 2-(chloromethyl)oxirane (CA: 237081-56-0)



NOR-1: bis (1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl) sebacate (CA: 129757-67-1)



NOR-2: 1,6-Hexanediamine, N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)-, polymer with 2,4,6-trichloro-1,3,5-triazine, reaction products with N-butyl-1-butanamine and N-butyl-2,2,6,6-tetramethyl-4-piperidinamine (Chimassorb 2020) (CA: 192268-64-7)

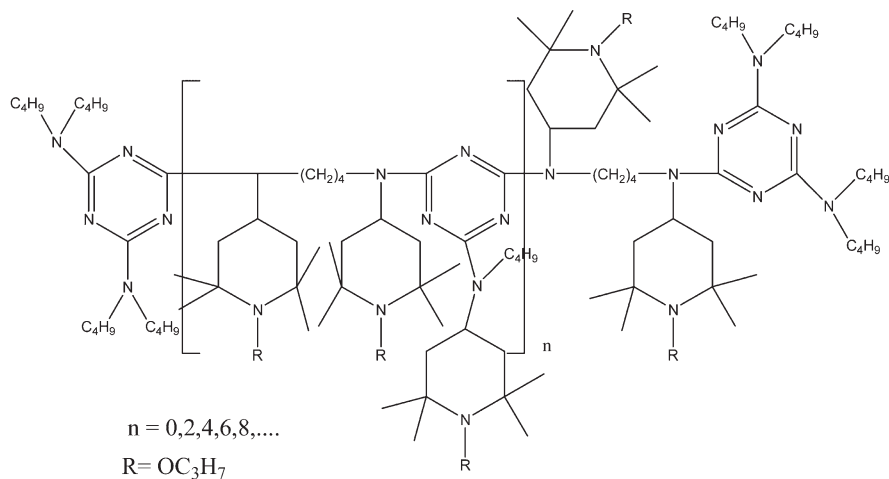
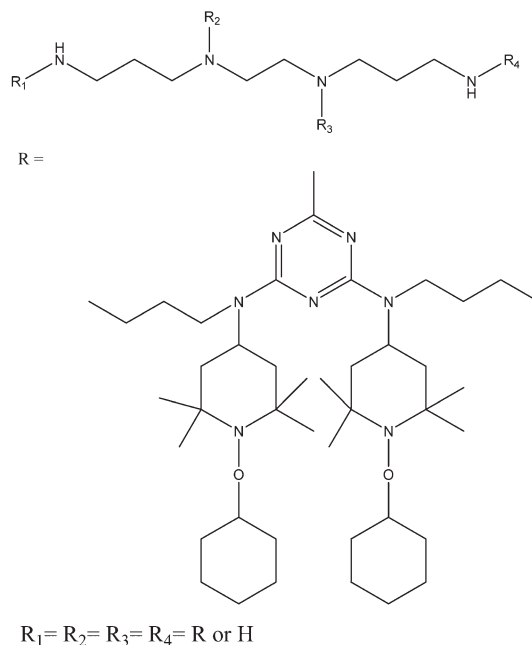


Figure 7. (Continued).

NOR3: 1,3-Propanediamine, N,N"-1,2-ethanediylbis-, reaction products with cyclohexane and peroxidized N-butyl-2,2,6,6-tetramethyl-4-piperidinamine-2,4,6-trichloro-1,3,5-triazine reaction products (CA: 191680-81-6)



MD-1: Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, 2-[3-[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropyl]hydrazide (CA: 32687-78-8)

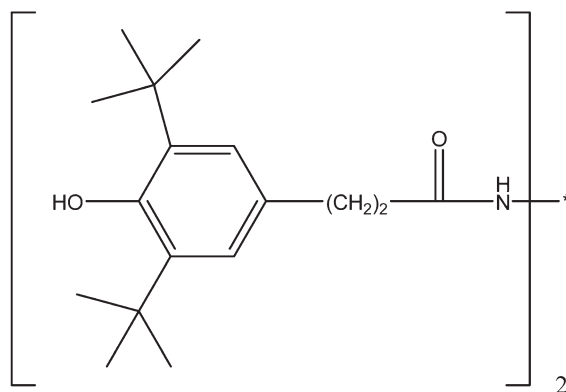


Figure 7. (Continued).

weathering of these stabilizer compositions reveals that the filler deactivator contributes by itself to the extended light stability and retention of mechanical properties.^{64,71} Further improvement of light stability was possible by introducing an UV absorber.

SUMMARY AND OUTLOOK

Most flame-retarded polymer products need to be highly durable throughout their service lifetime in many demanding applications areas such as construction, transportation, electric equipment, and textiles, where low flammability in combination with high resistance toward oxidative deterioration triggered by the action of light, heat, and/or mechanical stress is a manda-

tory quality. To achieve this, it is essential to better understand the overall interplay (both physical and chemical processes) between different components in the flame-retarded formulation during processing, use, and when subjected to various factors of weathering. Thus, increased knowledge of the interactions between different flame retardant structures in their respective polymers and in the presence of possible coadditives such as processing stabilizers, antioxidants, light stabilizers, metal deactivators, filler deactivators, UV absorbers, and so on, is needed. As opposed to brominated flame-retarded materials where these issues have been clarified for the most part, the impact of so-called "green" halogen-free flame retardants on the weathering resistance of polymers has been studied to a lesser extent and therefore it is less known. Phosphorus- and nitrogen-based

flame retardants seem to influence the (photo)oxidative stability of polymers less than brominated compounds and they show no or less antagonism with HALSs. On the other hand, the experimental results obtained for plastic-containing mineral fillers as flame retardants suggest that some improvements in the long-term properties have been achieved by using filler deactivators, compatibilizers, and metal deactivators. However, there is still a general lack of information regarding interference of mineral fillers, especially for exfoliated nanofillers, with commercially available stabilizers. Some recently developed flame retardants based on alkoxyamines even combine flame retardancy and light stabilizer functionality in the same molecule. Despite the fact that some insight has already been gained of parameters affecting the overall stability of flame-retarded polymers, more research is needed to further improve the durability of flame-retarded products.

STRUCTURES OF STABILIZERS

The structures and chemical names of stabilizers are shown in Figure 7.

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