Macromol. Symp. **2005**, *225*, 147-164

Organic Phosphites as Polymer Stabilizers

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Summary: The antioxidative action of phosphonites and phosphites depends on their structure, the nature of the polymer to be stabilized and the aging conditions. Phosphorus compounds can act in different ways: as hydroperoxide decomposers (secondary antioxidants), as free-radical scavengers (primary antioxidants), as well as metal-complex forming agents. The stabilizing action of phosphites and phosphonites is due to three basic mechanisms: oxidation by hydroperoxides, substitution by alkoxyl radicals and hydrolysis to acidic phosphorus compounds and phenols. Modification of phosphites with additional functional groups such as hindered amine moieties leads to new stabilizing properties. An intramolecular synergistic effect is observed.

Keywords: degradation; stabilization

Introduction

The protection of organic material against oxidative degradation processes during fabrication, processing, storage, or end-use is a prerequisite to their successful application. It is evident from the enumeration of the deterioration processes that different additives, especially inhibitors of oxidation processes, must be used to protect organic materials and to guarantee a sufficient performance during their envisaged application.

Organic phosphites and phosphonites mostly in combination with hindered phenols and hindered amines are widely used as polymer additives for the stabilization against degradation during processing and long-term application. According to the general autoxidation process (Scheme 1) different radicals and hydroperoxide are formed. Sterically hindered phenols react beside other stabilizers as primary antioxidants by scavenging mainly alkylperoxyl radicals under formation of hydroperoxides (Scheme 2). These hydroperoxides can be efficiently decomposed by phosphorus antioxidants thus giving a synergistic effect with the former.

DOI: 10.1002/masy.200550712

$$\mathrm{RH} \longrightarrow \mathrm{R\bullet\ (RO\bullet,\ ROO\bullet,\ HO\bullet,\ HOO\bullet)}$$

$$\mathrm{R\bullet} + \mathrm{O_2} \longrightarrow \mathrm{ROO\bullet}$$

$$\mathrm{ROO\bullet} + \mathrm{RH} \longrightarrow \mathrm{ROOH} + \mathrm{R\bullet}$$

$$\mathrm{ROOH} \longrightarrow \mathrm{RO\bullet} + \mathrm{OH\bullet}$$

$$\mathrm{RO\bullet} + \mathrm{RH} \longrightarrow \mathrm{ROH} + \mathrm{R\bullet}$$

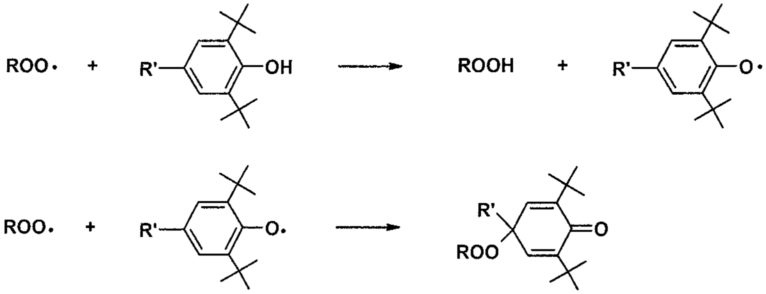
$$\mathrm{HO\bullet} + \mathrm{RH} \longrightarrow \mathrm{R\bullet} + \mathrm{H_2O}$$

$$\mathrm{ROO\bullet} + \mathrm{ROO\bullet} \longrightarrow \mathrm{O_2} + \text{inactive products}$$

$$\mathrm{R\bullet} + \mathrm{ROO\bullet} \longrightarrow \mathrm{ROOR}$$

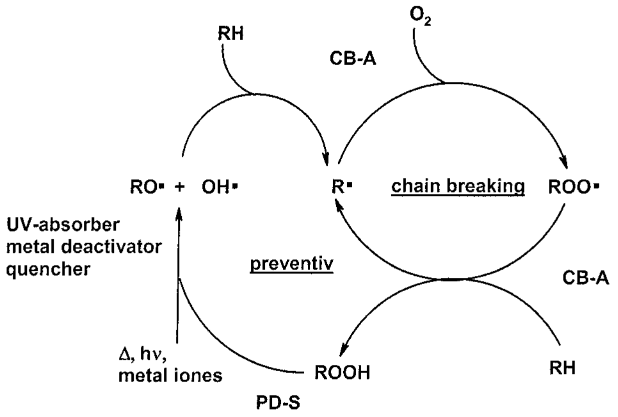
$$\mathrm{R\bullet} + \mathrm{R\bullet} \longrightarrow \mathrm{R\text{-}R}$$

Scheme 1. Mechanism of autoxidation of hydrocarbons and polymers.[1]



Scheme 2. Action mechanism of phenols.

The possibilities of the interference of stabilizers in the autoxidation process is demonstrated in Scheme 3.

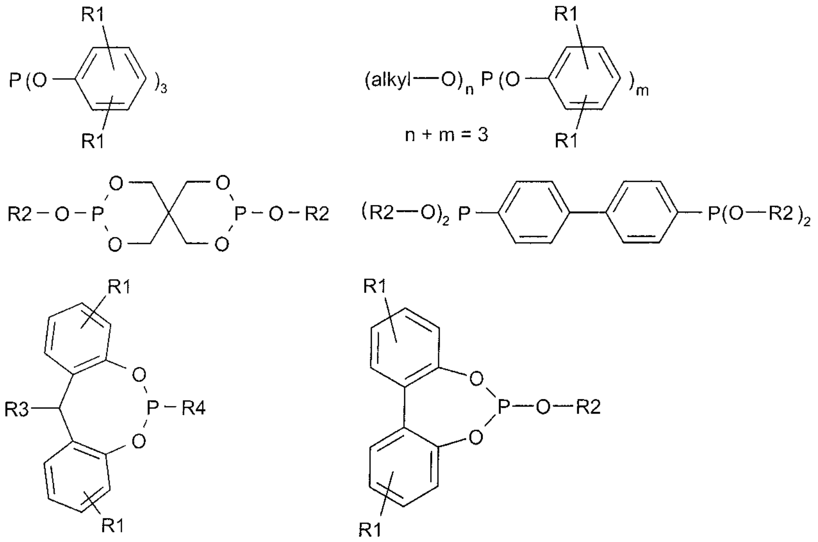


CB-A: Primary Antioxidant, Hindered Phenols
Arylamines, Hindered Amines
Benzofuranones, Hydroxylamines

PD-S: Secondary Antioxidant (stoechiometric)
Phosphites
Thiopropionates

Scheme 3. Role of stabilizers in the autoxidation process.

Among a variety of additives applied to stabilize polymers effectively against oxidative deterioration, esters of phosphorous and phosphonous acid hold a special position due to their multivalent properties. Typical examples of trivalent phosphorus stabilizers commercialized as well as some derivatives which have been studied repeatedly in the literature are listed in Scheme 4.



R1 = alkyl, aryl substituted alkyl, R2 = 2,4-disubstituted aryl, alkyl, aminoalkyl, R3 = H, alkyl, R4 = F, O-aryl, O-alkyl

Scheme 4. Basic structure of common commercial phosph(on)ites.

Although phosphorus antioxidants are generally applied in combination with hindered phenols and other stabilizers, the sterically hindered aryl or aryl alkyl phosphites and phosphonites are under some conditions active by themselves and able to partially substitute phenols. Besides the high overall stabilizing effect as antioxidants, trivalent phosphorus compounds have a positive effect on the color stability of polymers and act as metal-complex forming agents blocking polyvalent metal ions which cause chain initiation and branching by reaction with hydroperoxides or other labile bonds in organic substrates. Moreover, most of the phosphites are quite compatible with polymers, have a low volatility and tendency to bloom out and show a low sensitivity towards molecular oxygen at ambient temperature.

Mechanisms of Antioxidant Action of Phosphites and Phosphonites

The oxidation and stabilization of various organic materials, especially of commercial polymers, have been repeatedly reviewed. [2,3,4]

Among the stabilizers used, phosphites or phosphonites play a crucial role in the processing stabilization of a variety of polymers. This practical importance of phosphorus stabilizers has induced numerous studies to mechanistic problems of their antioxidant action. The results of these investigations have been summarized by various authors including ourselves. [5,6,7,8,9,10,11]

Phosphites and phosphonites can act by a number of different mechanisms dependent on their structure, the structure and morphology of the substrate to be stabilized, and the application conditions. As a consequence the efficiency also of phosphorus compounds as stabilizers against oxidative degradation processes is essentially determined by their ability to disturb the free radical chain mechanism of the autoxidation (Scheme 1) by removal or deactivation of the chain propagating radical species and/or by non-radical decomposition or blocking of radical precursors or initiators.

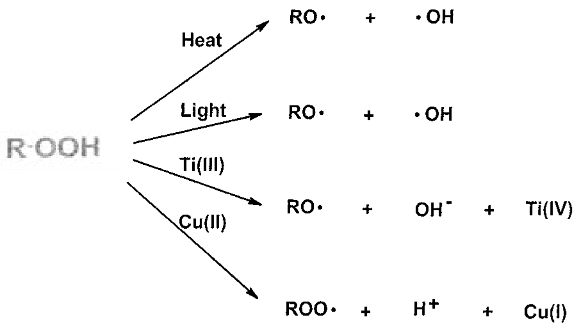
Phosphites and phosphonites can act as antioxidants by three basic mechanisms:

1) Decomposition of hydroperoxides, thus preventing the branching of the oxidation chain reaction.
2) Trapping of alkoxyl radicals by aryl phosphites, giving rise to a radical substitution reaction under release of antioxidatively acting aroxyl radicals.
3) Hydrolysis of aryl phosphites under formation of phenols and phosphonates.

Furthermore, they are able to complex metal residues and to react with molecular oxygen dissolved in the polymer.

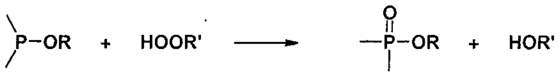
Hydroperoxides formed in the autoxidation process decompose easily by different influences (heat, light, metal ions) to form highly reactive radicals leading to a chain branching and an accelerated polymer degradation (Scheme 5).

All phosphites and phosphonites are mainly regarded as preventive antioxidants decomposing hydroperoxides in a non-radical way. This results in a suppression of the radical chain-branching step. However, this reaction has no influence on the rate of autoxidation at low temperatures at which hydroperoxides do not homolytically decompose.



Scheme 5. Decomposition of hydroperoxides.

The reduction of hydroperoxides by organic phosphites and phosphonites gives alcohols and the corresponding phosphates or phosphonates [12] and is determined mainly by polar and steric effects of the groups bound to phosphorus (Scheme 6). It decreases with increasing electron-acceptor ability and bulkiness of substituent groups in the sequence [5]: Aryl phosphonites > alkyl phosphites > aryl phosphites > hindered aryl phosphites.



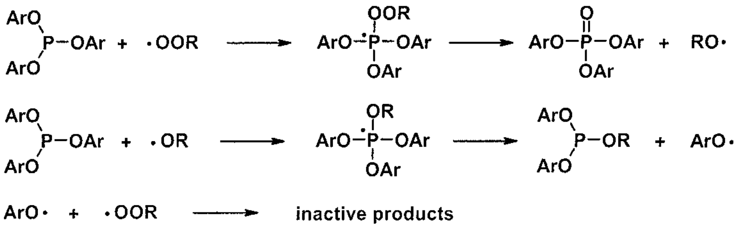
Scheme 6. Hydroperoxide decomposition by phosph(on)ites.

Five-membered cyclic phosphites (1,3,2-dioxaphosphole and 1,3,2-dioxaphospholane derivatives) are able to catalyze the ionic decomposition of alkyl hydroperoxides. [13,14,15] Six- and higher-membered cyclic phosphites are not capable of decomposing hydroperoxides in a catalytic way. [15,16]

In order to act as chain-breaking antioxidants, stabilizers must match two basic requirements:

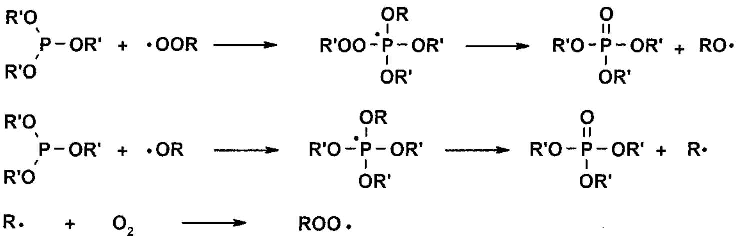
1) They must be able to compete effectively with the substrate RH for chain-propagating radicals.
2) They must form an efficient chain-terminating agent as a result of its radical scavenging reaction.

Aryl phosphites, particularly those based on sterically hindered phenols, show both an efficient competition with autoxidation chain propagating reactions (Scheme 2) by trapping ROO• and RO• radicals and formation of relatively stable aroxyl radicals which are not able to propagate the oxidation chain-reaction (Scheme 7).[5,6,7,8]



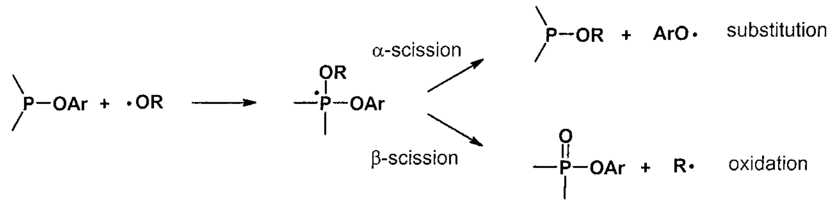
Scheme 7. Radical trapping reactions of aryl phosphites.[5]

Alkyl phosphites are not chain-breaking antioxidants. They trap oxyl radicals under release of new, active radicals propagating the oxidation chain-reaction (Scheme 8). Therefore, at low temperatures, these compounds even act prooxidatively. The same is true for both alkyl and aryl phosphonites.[17]



Scheme 8. Reactions of alkyl phosphites with oxyl radicals.[5]

Both aryl phosphites and alkyl phosphites are oxidized by ROO• radicals in a first reaction step affording the corresponding phosphate and RO• radicals. These radicals can react in a second step with the parent phosphite in different ways. Only aryl phosphites which react with alkoxyl radicals by substitution releasing chain-terminating aroxyl radicals can act as primary antioxidants (Scheme 9). In this case the intermediate alkoxyphosphoranyl radicals undergo α-scission, whereas ß-scission leads to oxidation of the phosphite and formation of chain-propagating alkyl radicals (Scheme 5).[5]



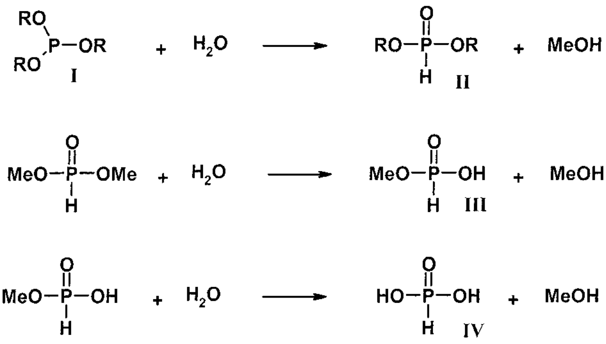
Scheme 9. Reactions of aryl phosphites with alkoxyl radicals.[5]

The efficiency of aryl phosphites as chain-breaking antioxidants is much lower than those of phenols.

The performance of phosphites as polymer stabilizers is strongly influenced by their hydrolytic stability, which has to be considered as a limiting factor for commercial applications of phosphites. Acidic products formed during hydrolysis can cause unwanted effects.[4,18] The storage and handling of these compounds may become difficult because the product mixtures tend to cake. Poor thermal stability can accompany the hydrolytic instability of phosphites and leads to the formation of "black specks" during processing of the polymer.[19] On the other hand, active stabilizing species, such as hindered phenols, can be released by hydrolysis of phosphites. It has been suggested that these phenols are the species responsible for the antioxidant activity of phosphites at higher temperatures. They can form synergistic mixtures with the parent phosphites or phosphorus-containing hydrolysis products.[20,21,22,23,24,25] Therefore it was emphasized that a high hydrolytic stability may not always lead to maximum performance. Release of antioxidatively acting secondary compounds from the phosphites by hydrolysis in combination with the other stabilizing mechanisms can contribute to better overall performance.[26]

Hydrolysis of phosphites (**I**) proceeds via phosphonates (**II**) and hydrogen phosphonates (**III**) to finally give phosphorous acid (**IV**) (Scheme 10).

The reaction of phosphites with water can be catalyzed either by acids or bases. Acid-catalyzed hydrolysis is the faster usually proceeding process. Hydrolysis of phosphites occurs with rates which depend on the structure in the same manner as given above for the oxidation. But even sterically hindered aryl phosphites hydrolyze during hydrocarbon oxidation at higher temperatures (>100°C) to give phenols and hydrogen phosphites which may further hydrolyze forming phosphorous acid.



Scheme 10. Hydrolytic pathway of phosphites.

Investigating the hydrolysis of various phosphites, the following sequence of hydrolytic stability was found: [27]

sterically hindered aryl phosphites > unsubstituted aryl phosphites > araliphatic phosphites > aliphatic phosphites.

In order to increase the hydrolytic stability of phosphites for application as polymer stabilizers three possible methods are proposed: [28]

1) Internal (a) or external (b) addition of basic components to the phosphites
2) Increase of steric hindrance around the phosphorus atom
3) Reduction of electron density at the phosphorus atom. [19]

In general, however, the demands for a good hydrolytic stability are contrary to the requirements for a high activity as hydroperoxide decomposer. Nevertheless, it has been stated that the development of phosphite antioxidants has to focus on the improvement in hydrolytic stability as well as performance. [18] A balance between hydrolytic stability and stabilizing performance has to be found.

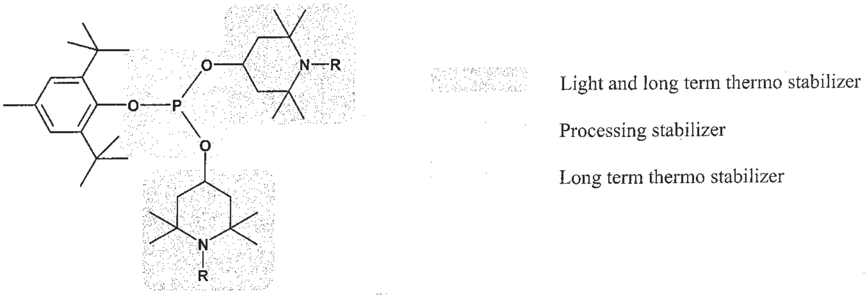
In this context we became interested in developing phoshorus stabilizers with improved antioxidative efficiency and high hydrolytic stability.

Synthesis and Performance of HAS-Phosphites

Phosphite antioxidants are generally synthesized according to a well-established method by reaction of phosphorus halides with alcohols or phenols [29] and by transesterification of simple phosphites.

Phosph(on)ites modified by additional functional groups should exhibit new stabilizing properties due to action mechanisms characteristic for these functional groups or to synergistic effects of these groups on the common phosph(on)ite stabilizer mechanisms.

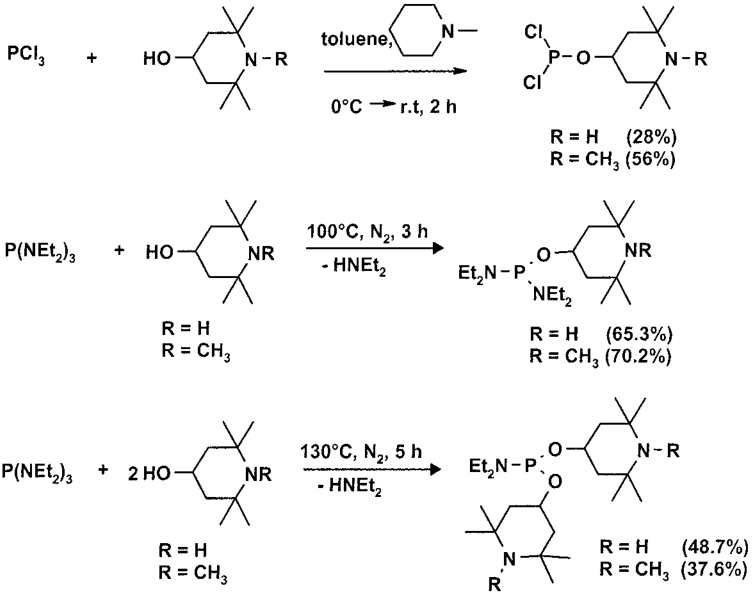
In order to design multifunctional stabilizers with hydroperoxide decomposing, radical scavenging, UV absorbing, photostabilizing and metal complexing abilities various active groups have to be combined in one molecule. Interesting in this context are aromatic phosphite esters bearing 2,2,6,6-tetramethyl- or 1,2,2,6,6-pentamethyl piperidinyl (*Hindered Amine Stabilizer*) groups which contain in their molecules hydroperoxide decomposing, chain breaking and light stabilizing moieties. For this purpose we tried to combine various phenols via phosphorus with hindered amine units (Scheme 11).



Scheme 11. Multifunctional stabilizer.

Some cyclic representatives of such *HAS-phosphites* have been described in earlier patents.[30] We synthesized and studied the stabilizing efficiency of some further HAS-phosphites and phosphonites.[31] For their formation different possibilities can be taken into account. So the reaction of phosphorous or phosphonous acid chlorides with 2,2,6,6-tetramethyl- or 1,2,2,6,6-pentamethyl-4-piperidinol (HA) leads to such products.[29,31d,32,33] This method is limited by the accessibility of the appropriate phosphorus acid chlorides.

Recently we have introduced the so-called phosphoramidit method [34] beside the usage of phophorus acid dichlorides of piperidine derivatives for the synthesis of HAS-phosphites (Scheme 12).[35,36]



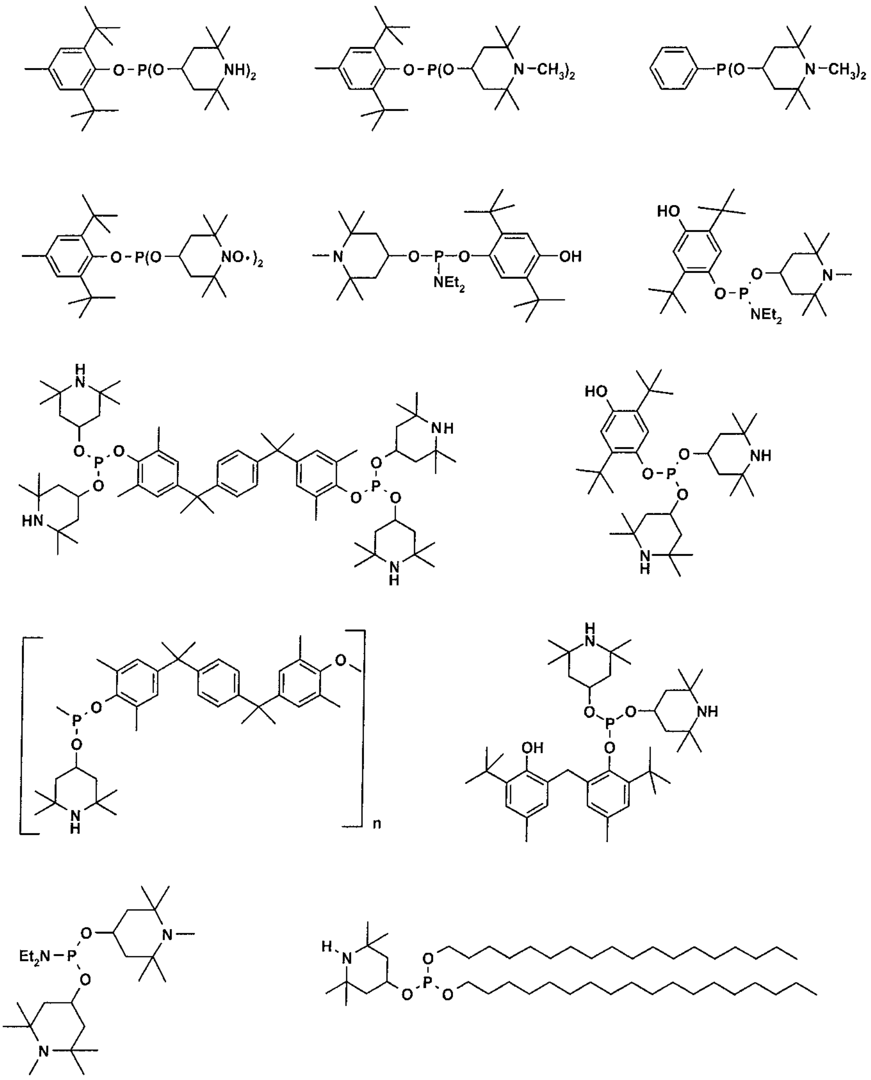
Scheme 12. Synthesis of HAS-Phosphite precursors.

The advantage of this methods is the convenient accessibility of building-blocks containing the HA and phosphite structure which can react with various alcohols or phenols to give HAS-phosphites. The reaction is more selective and the esterification can be carried out step-wise. Amine hydrochlorides function as catalysts. Using these different methods we synthesized a number of novel HAS-phophites in good yields. Some examples are shown in Scheme 13.

A remarkable property of these HAS-phosph(on)ites is their pronounced hydrolytic resistance.[37,38] Whereas common phosphorus(III) based stabilizers are more or less sensitive to hydrolysis, HAS-phosph(on)ites are stable even under conditions where sterically hindered aryl phosphites are completely hydrolyzed. This property may be ascribed to the amino function of the HALS group which neutralizes existing and formed acid and so suppresses acid catalysis of hydrolysis.

Due to the electron-donating property of the piperidinyl group, they also destroy hydroperoxides with higher rates than common aryl phosphites.[31d]

The outstanding and wide antioxidative efficiency of the multifunctional stabilizers of the HAS-phosph(on)ite type manifests itself especially in the stabilization of polyolefins against oxidative and thermal degradation and discoloration.[31-32]



Scheme 13. Novel HAS-phosphites synthesized.

In the thermo-oxidation of polypropylene, HAS-phosph(on)ites are better inhibitors than common phosphites and HAS compounds and surpass in many cases also the efficiency of phenols. They give rise to longer induction periods and lower oxidation rates after the induction periods. The superior inhibition efficiency of HALS-phosph(on)ites may be due to the synergistic cooperation of the hydroperoxide decomposing ability of the phosph(on)ite moiety and the chain breaking antioxidant activity of the hindered piperidinyl substituent.

The inhibition of the carbonyl formation in the thermooxidation of PP films in the presence of the new phosphorus compounds is shown in Figures 1 and 2. Interestingly compounds **1**, **2** and **5** bearing secondary and tertiary HAS moieties perform very well (Fig. 1). Especially long induction periods are also obtained with compounds **A3s4** and **Aes2** as demonstrated in Figure 2.

As it was shown in ref. 33, synergism between phosphites and HAS during thermo-oxidation of PP can be observed. It was explained by a protection of the polymer by the phosphite during processing and in the first stages of thermooxidation which gives time for the HAS moiety to form active nitroxyl radicals which are later effective during long term thermooxidation.

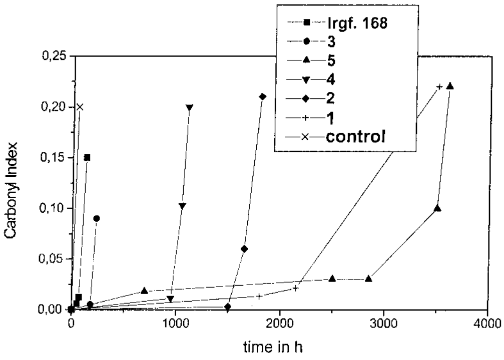
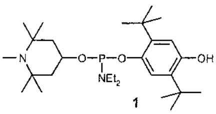


Figure 1. Thermooxidation of PP films at 100°C (film thickness: 0.1 mm, additives: 3.5 x 10^{-3} mol/kg).



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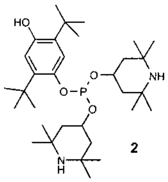

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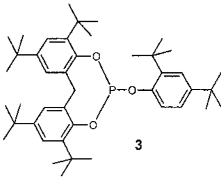

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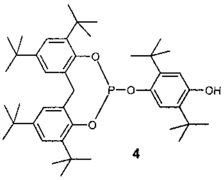

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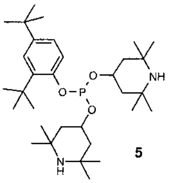

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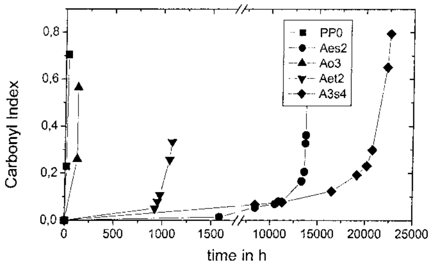

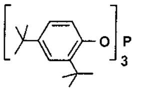

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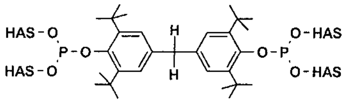
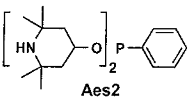
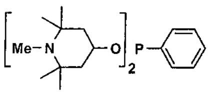


A3s4



Aes2



Aet2

Figure 2. Rates of thermo-oxidation of polypropylene films (0.2 mm) at 110°C containing 0.2% stabilizer.

In Figure 3 the synergism is demonstrated by compound **AVIIIs**. Its efficiency is much higher than the efficiency of corresponding mixtures of single components which give only rise to an additive effect.

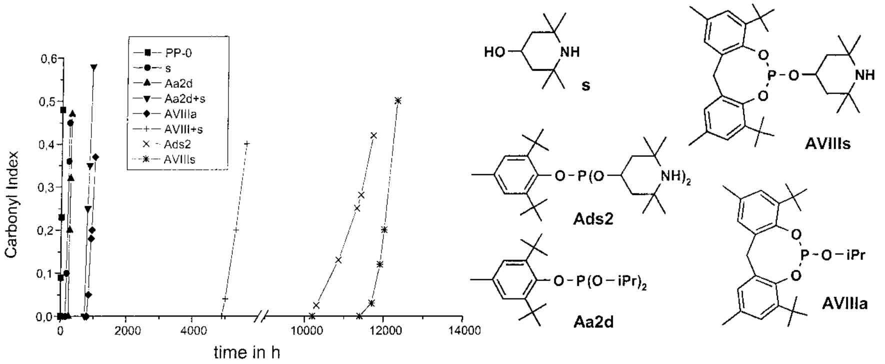


Figure 3. Rates of thermo-oxidation of polypropylene films (0.2 mm) at 100°C containing **s**, **Aa2d**, **AVIIIa**, **AVIIIs**, **Ads2** (3.56 x 10^{-3} mol/kg), **Aa2d+s** (3.56 x 10^{-3} mol/kg + 7 x 10^{-3} mol/kg) **AVIIIa+s** (3.56 x 10^{-3} mol/kg + 7 x 10^{-3} mol/kg).

Beside the efficiency of HAS-phosphites as thermo-stabilizers they also show the expected performance as photo-stabilizers (Fig. 4,5).

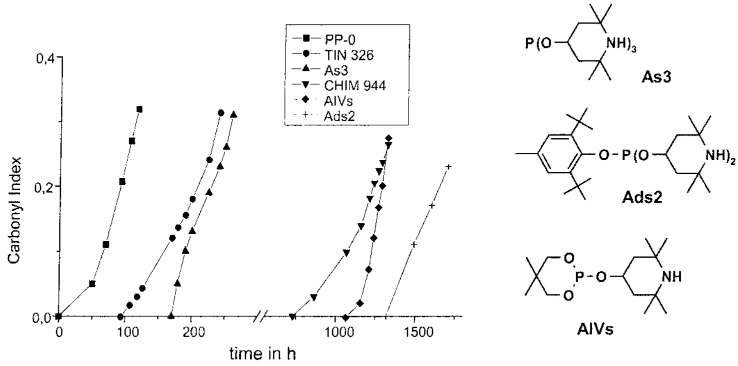


Figure 4. Rates of photo-oxidation of stabilized polypropylene films (0.2 mm) without **BHT** and calcium stearate. Concentration of additives 0.2 w%.

Under the conditions used the multifunctional stabilizer **Ads2**, and **Aes2** give a superior performance even surpassing the commercial high molecular weight HAS **Chimasorb 944** (Fig. 4) and **Tinuvin 770** (Fig. 5), respectively.

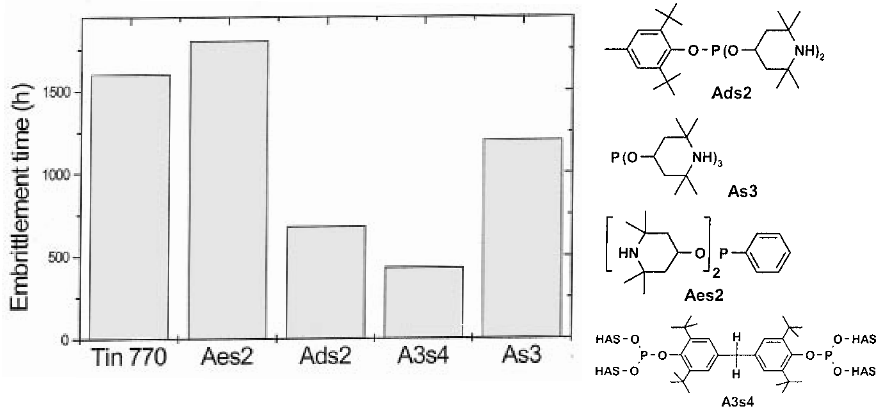


Figure 5. Photooxidation of Polypropylene 0.1 mm films stabilized with different HAS Phosph(on)ites; HAS = [HAS moieties] = 14 x 10^{-3} mol/kg; light intensity = 4.2 Wm^{-2}.

The rather good efficiency of HAS-phosph(on)ites in the photo- and thermo-stabilization of polymers could be related to a special type of synergism which might be called "intramolecular synergism", since mixtures of individual components with appropriate structural elements give only additive or less pronounced synergistic effects.

Whereas most HAS-type stabilizers do not efficiently act under thermo-oxidative and processing conditions, the HAS-phosph(on)ites show just here their advantages. This could be demonstrated for polypropylene[39] and LLDPE[38], where the HALS-phosph(on)ites effectively contribute to melt flow and color stabilization during processing. Furthermore it was shown that HALS-phosphites with pentamethyl-piperidinyl groups exhibit an extraordinary good compatibility with LLDPE and are not at all prone to plate out. Their solubilities in the polymer were determined to be an order of magnitude above the usual application levels.

HAS-phosphites **9** and **14** have been tested for their color stabilizing ability of PP during processing (Fig. 6). The color stabilizing ability of compound **14** worsens after the first extrusion as a result of the presence of discoloring quinoid structures formed from the aromatic phosphites during the course of the processing procedure.

The aliphatic phosphite **9**, however, performs very well and is well comparable with the commercial phosphonite **PEPQ**, even after the fifth extrusion. This is also true for the melt flow stabilization of PP as demonstrated in Fig. 7. Again HAS-phosphite **9** behaves very well whereas the aromatic phosphite **14** gives slightly worse results. Both show almost the same performance as the commercial phosphonite **PEPQ**.

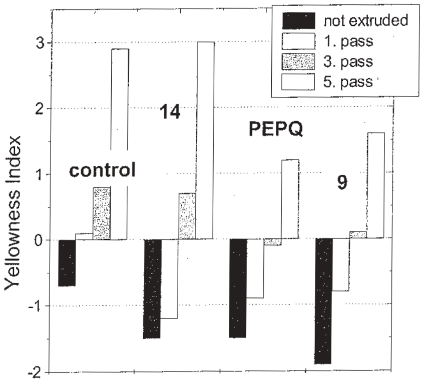


Figure 6. Multiple Extrusion at 270°C, Yellowness Index after 0,1,3,5 passes, 0.07% stabilizer basic stabilization: 0.07% Irg 1076 + 0.1% Ca stearate; *performed by Clariant Huningue S.A.

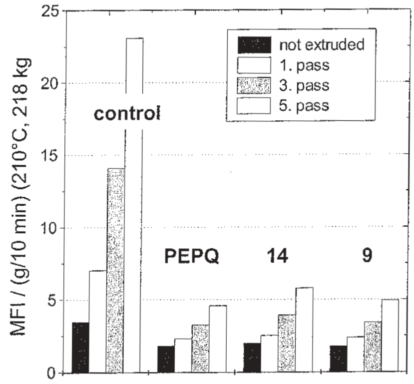
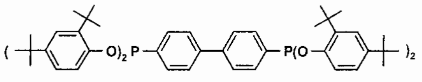
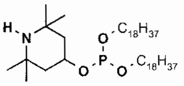


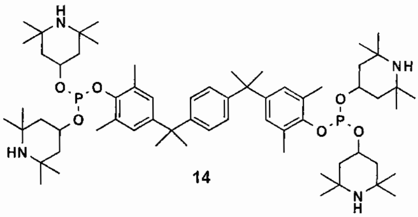
Figure 7. Multiple extrusion at 270°C, MFI (g/10 min), 210°C, 2.18 kg, 0.04% stabilizer basic stabilization: 0.07% Irg 1076 + 0.1% Ca stearate; *performed by Clariant Huningue S.A.



PEPQ



9



14

From the results of Figures 6 and 7 it can be concluded that especially the HAS-phosphite **9** is efficient during the processing of PP. The long aliphatic chains provide a high compatibility with polyolefines.

In general, it can be summarized that the functionalized phosphites are effective as multifunctional stabilizers by intramolecular synergism. It seems today that HALS-phosph(on)ites due to their high efficiency and wide applicability could complete the scale of commercial stabilizers in future.

Acknowledgment

The authors are grateful to SUMITOMO CHEMICAL COMPANY LTD., CLARIANT HUNINGUE S.A., BASF Schwarzheide GmbH, and the "Fonds der Chemischen

Industrie" for financial support of this work. Furthermore, this work was involved in a project of the "Sonderforschungsbereich 0287" of the DFG. We also thank CLARIANT HUNINGUE S.A., MITSUI PETRO-CHEMICALS CO. and HÜLS AG for the kind donation of chemicals.

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