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Antioxidants for Industrial Applications

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Abstract. The thermooxidative degradation of organic materials as well as its inhibition by classical and nonclassical antioxidants are briefly outlined.

1. Introduction

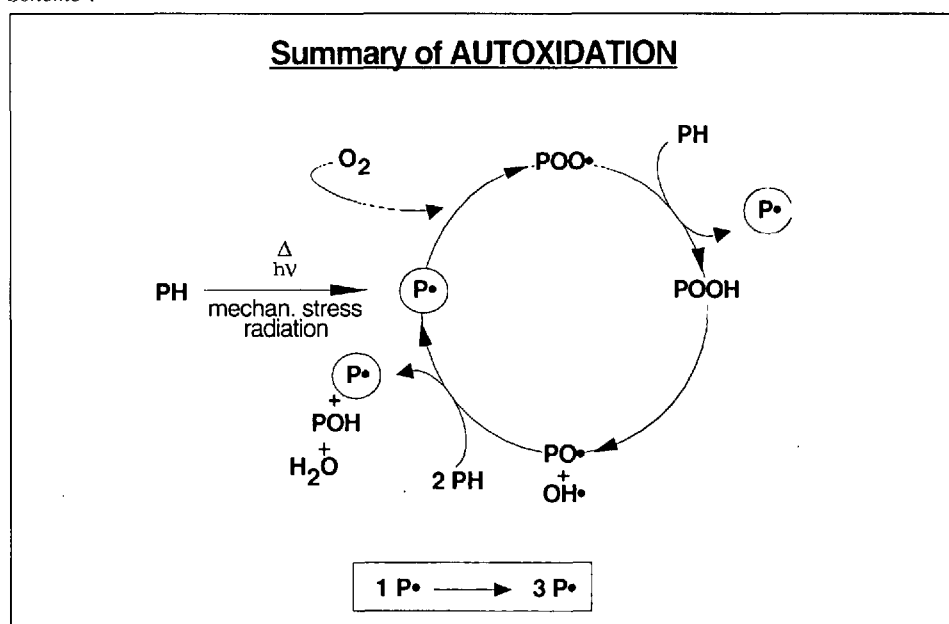
Antioxidants are chemical additives, used at concentrations of between 0.05 and 0.5%, which protect organic materials (e.g. polymers, lubricating oils, fats, etc.) against oxidative degradation during their production, processing, final use, and recycling [1].

Thanks to the fact that polymers, as unstable as polypropylene, can be stabilized in an industrially feasible manner, they have found a wide range of applications in our daily life. Since the beginning of industrial polyolefin production, *Ciba* has been the primary partner for the stabilization of such plastics (polyolefin production ca. 60 mio t in 1993), and now *Ciba* has a worldwide leading technical position in this field.

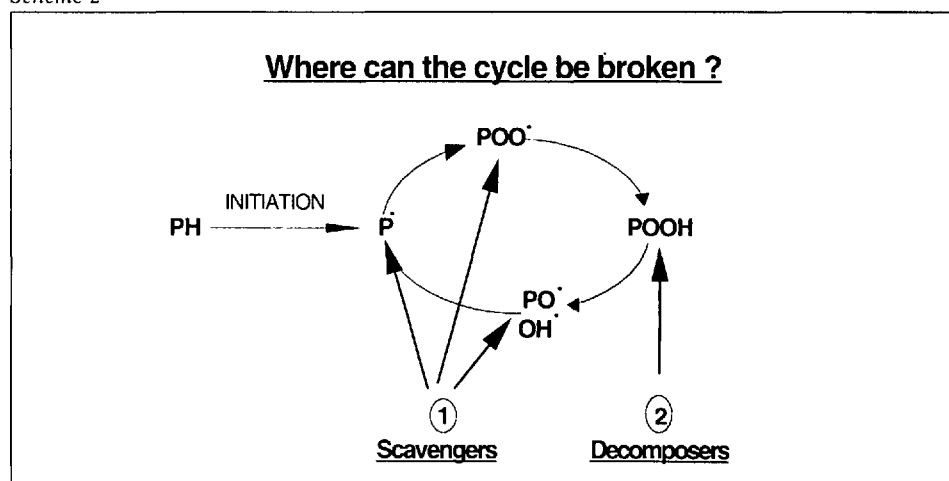
2. Autoxidation

Under the combined action of heat and mechanical stress, or the influence of catalyst residues, organic materials are able to form carbon-centered radicals $P\cdot$. In the presence of O_2 these radicals react very rapidly to afford the corresponding peroxiradicals $POO\cdot$, which will further abstract H-atoms from the substrate. The

Scheme 1

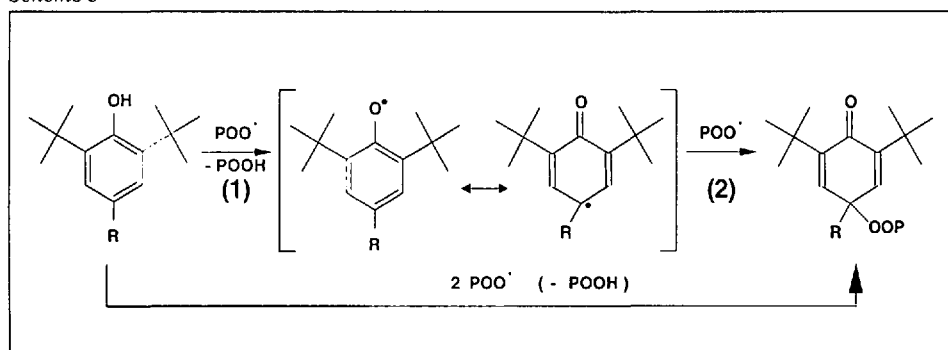


Scheme 2



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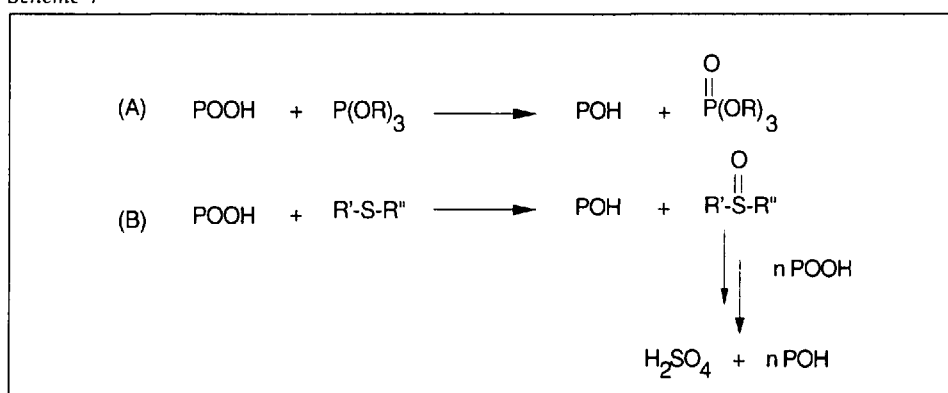
Scheme 3



resulting hydroperoxides POOH are very unstable species (weak O–O bond!), and can easily decompose to generate reactive alkoxy (PO•) and hydroxyl (OH•) radicals, both of which are capable of abstracting H-atoms from the organic material and initiating new chains. The balance of this reaction cycle is the net formation of three radicals from one. This is the start of a radical-chainreaction which is outlined in Scheme 1.

As a consequence of autoxidation, polymers undergo molecular structural changes (chain-scissions or cross-linking). This results in the loss of their mechanical properties (e.g. impact strength, elasticity, viscosity, elongation) and changes in physical appearance (e.g., discoloration, loss of gloss and transparency, formation of microcracks).

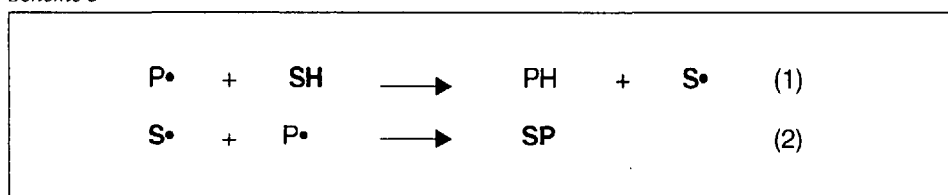
Scheme 4



3. Stabilization

To slow down or, better yet, prevent the deterioration of polymers [3], we have to intervene in the autoxidation chain mechanism (Scheme 1). How can this be done? The main two possibilities are outlined in Scheme 2:

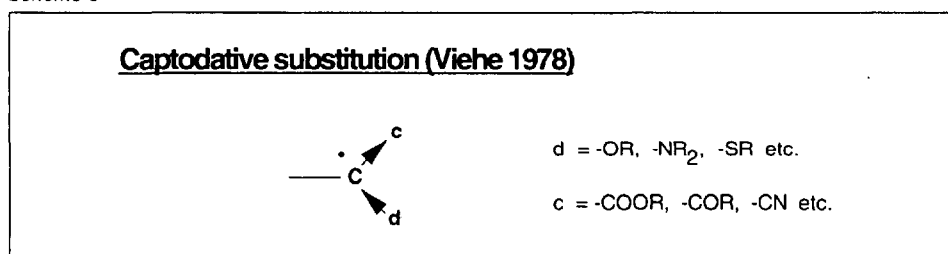
Scheme 5



1) *Scavengers* are radical-traps which react either with O-centered radicals (classical stabilizers) or C-centered radicals (nonclassical stabilizers).

2) *Decomposers* are capable of reducing hydroperoxides as well as peroxides to their stable parent alcohols or ethers.

Scheme 6

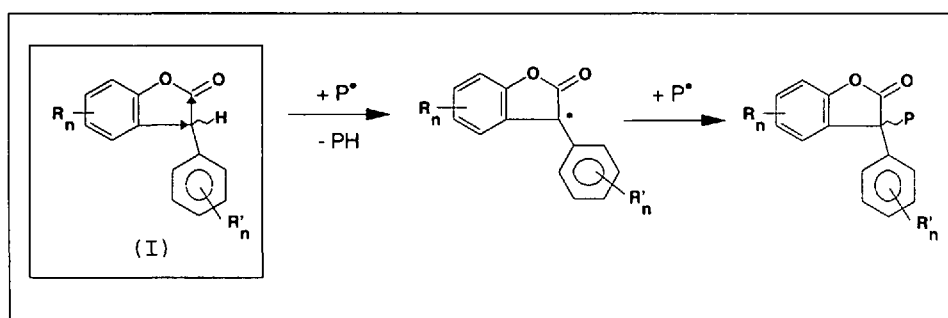


The classical *scavengers* (sterically hindered phenols and aromatic amines) are inhibitors, which trap O-centered radicals by donating a H-atom to alkylperoxy or alkoxy radicals. Scheme 3 illustrates the mechanistic action of sterically hindered phenols. In the first step (1), H-donation affords a stable phenoxyl radical (steric hindrance as well as electronic delocalization), which, in a second step (2), reacts further with another peroxy radical to give a 4-(alkylperoxy)cyclohexadienone.

Two of the main classes of *decomposers* comprise phosphites, which stoichiometrically reduce peroxides (A), and various sulfidic compounds, which act in a catalytic fashion (B; Scheme 4). In practice, *scavengers* and *decomposers* are used together.

The *scavenging of C-centered radicals* is a relatively new approach in the area of polymer-stabilization. This is of greatest importance in O₂-deficient environments (concentration of O₂ < 10⁻⁴ M), which are

Scheme 7



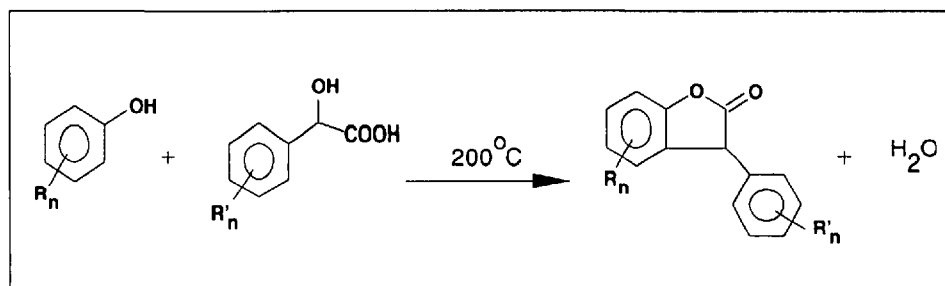
prevalent in modern processing (extruders). The ideal stabilizer (SH) should be capable of trapping two polymer chain radicals; the first by H-donation and the second *via* recombination (Scheme 5). Clearly, the radical formed from the stabilizer after H-donation (S^\bullet) must be more stable than the radical on the polymer chain (P^\bullet).

Ideally, such stability is achieved by a combination of three main factors: steric hindrance (kinetic stabilization), electronic delocalization (thermodynamic stabilization), and captodative substitution [4], which is the substitution of a C-center by both an electron-withdrawing (captor = c) and an electron-donating (dative = d) group (Scheme 6).

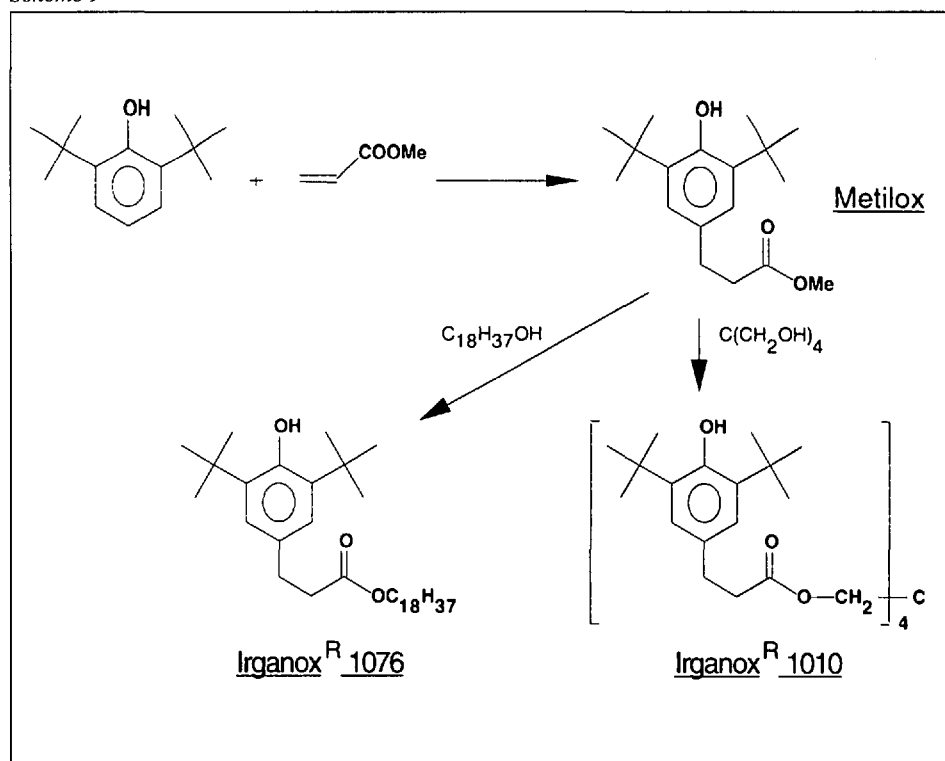
Benzo-furanones **I** fulfill all the aforementioned structural criteria. Their stabilizing action can be schematically shown as in Scheme 7. This new class of stabilizers **I** [5] is a major area of research in our laboratories in Marly/FR. We are optimistic that the first representative will be commercialized in the near future.

The first synthesis of such a benzo-furanone was – interestingly enough – described 100 years ago by A. Bistrzycki [6], a founder of the Chemistry Department of the University of Fribourg (Scheme 8).

Scheme 8



Scheme 9

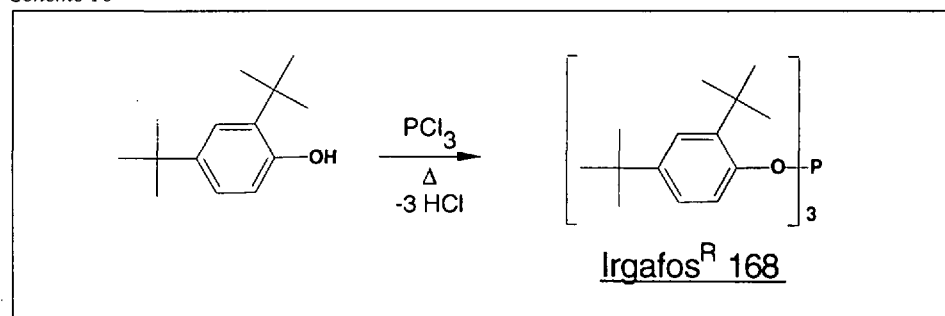


4. Ciba's Most Important Commercial Stabilizers

Our company actually produces a wide variety of phenolic antioxidants. Their chemistry is based on the addition product (*Metilox*) of 2,6-di(*tert*-butyl)phenol and methyl acrylate. Transesterification (Scheme 9) of *Metilox* affords the two most important commercial products, *Irganox*[®] 1076 and *Irganox*[®] 1010.

In addition, *Ciba* is one of the main producers, worldwide, of phosphite stabilizers. *Irgafos*[®] 168, obtained *via* the reaction of 2,4-di(*tert*-butyl)phenol with PCl_3 , is the most successful product in this domain (Scheme 10).

Scheme 10



5. Conclusion

The continuing trend to develop polymers exhibiting special properties, that can also be processed at higher speed and temperatures, leads to an ever-increasing demand for better-performing and more sophisticated stabilizing systems. Therefore, research in polymer stabilization has to continue and will allow further progress in the future.

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