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Plastics Additives Handbook

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because the hydroperoxides formed in PE are poor initiators of photo-oxidation [63]. Another reaction was proposed, instead, involving a six-member transition state and resulting in the formation of trans-vinylene groups and hydrogen peroxide (Reaction 27 in Scheme 2.6). The latter can decompose directly into hydroxy radicals if it possesses an excess of energy (Reaction 28). Alternatively, it can also yield free radicals on subsequent photolysis (Reaction 30 in Scheme 2.6) [63]. The possible contribution of CT complexes to initiation of photo-oxidation is still a matter of discussion [64, 65]. Considerations of the energy involved with a CT state led to an amendment of the first proposal [66–71]. Instead of CT complexes, corresponding exciplex formation polymer-oxygen has been envisaged. Nevertheless, the reactions and their products were still the same as those outlined in Scheme 2.6. More recently, the potential role of air pollutants in initiation of photo-oxidation has been examined [36–40].

The finding that ozone in ambient air has a determining role in initiating thermal oxidation of polymers such as PP and PE was of prime importance for understanding possible new mechanisms of photo-oxidation. However, initiation of photo-oxidation is more complicated and air pollutants other than ozone may also be involved, such as nitrogen dioxide and sulfur dioxide [36–40]. Comparing the mean monthly concentrations of the main air pollutants leads to the interesting finding that nitric oxide and sulfur dioxide vary considerably during the year, as does the concentration of ozone. Moreover, the concentrations of nitric oxide and sulfur dioxide are lowest in summer when the concentration of ozone is highest. It is only the mean concentration of nitric dioxide that remains relatively constant through the year. Therefore, initiation of photo-oxidation mainly by photolysis of nitrogen dioxide would be in agreement with the observation of a rather constant rate of photo-oxidation in artificial exposure devices such as the Weather-Ometer Ci 65. The considerable acceleration of degradation under exceptionally high concentrations of ozone could then be attributed to a complete change in mechanism. One such possibility is the passage from bulk initiation to surface initiation [39].

Photolysis of ozone yields a very reactive oxygen atom that can initiate an oxidative chain reaction as shown in Scheme 2.2. The same is valid for photolysis of nitrogen dioxide, also shown in Scheme 2.2. As a matter of fact, over the year, the mean concentrations of nitrogen dioxide in air are significantly higher than the corresponding concentrations of ozone.

Photolysis of ozone is a very effective process. It occurs not only with UV but also with visible light, up to 590 nm, with a quantum yield of 1. The situation is similar for nitric dioxide; photolysis occurs up to about 370 nm with a quantum yield of 1 and with decreasing quantum yields up to 420 nm. The subsequent reactions of the ground state oxygen atoms are typical hydrogen abstraction reactions as shown in Scheme 2.2. These reactions are limited by recombination of oxygen atoms with oxygen molecules; recombination of ozone with nitric oxide to yield oxygen and nitrogen dioxide has also been included in the limiting reactions in Scheme 2.2. It can also be seen as a neutral reaction, because if one active initiator molecule, ozone, disappears, another one, nitric dioxide, is generated.

The reaction of peroxy radicals with nitric oxide shown in Scheme 2.2 may have a determining role. It involves the normal chain carriers of polymer oxidation, i.e., the peroxy

radicals, and nitric oxide present as an air pollutant and resulting also from the photolysis of nitric dioxide [36–40].

In this way, a new potential initiator of photo-oxidation is produced, without interrupting the normal oxidation chain. In fact, the peroxy radical is transformed into a more reactive alkoxy radical. Through this catalytic cycle, the initiation reaction can itself be a chain reaction, superposed on the polymer chain oxidation and, at the same time, entangled with it.

The initiation by air pollutants just discussed most likely involves the surface layers of the polymer. Nevertheless, some reactions, especially those based on the catalytic cycle, can be very important for bulk oxidation [36–40]. This could explain the results of the photo-oxidation of LDPE films that show primarily surface oxidation but significant contributions from bulk oxidation as well, as reported previously [72, 73].

It is thought that initiation by air pollutants is only one aspect of initiation of photo-oxidation. Initiation by catalyst residues (Ti) and direct initiation by HALS are additional modes. Furthermore, as already discussed, in PP, initiation by photolysis of tertiary hydroperoxides dominates after an initial period if the HALS concentration is not too high. Moreover, photolysis of hydroperoxides may also be important in PE in the presence of significant amounts of transition metals [70, 71].

The carbon radicals formed in the photochemical primary processes can react very fast with oxygen (Reaction 2 in Scheme 2.1). The alkyl peroxy radicals (RO_2°) formed this way play a key role as chain carriers because they abstract mainly hydrogen from the polymer and thus produce the polymer radicals necessary for the propagation of the oxidation (chain propagation, Reaction 3 in Scheme 2.1). In this respect, it should be noted that the reactivity of a specific substrate is not only a function of its structure, i.e., the ease of hydrogen abstraction. It is also determined by the solubility and the diffusion rate of oxygen. In semicrystalline plastics, the density of the crystalline phase is usually higher than that of the amorphous phase and almost impermeable to oxygen. Hence, oxidation occurs exclusively in the amorphous material. Poly(4-methyl-1-pentene (PMP) constitutes an exception in this respect: the densities of the crystalline and amorphous phases are almost identical at 60 °C; at room temperature, the density of the amorphous phase is even higher than that of the crystalline phase [74]. It has been found that isotactic PMP is more susceptible to oxidation than atactic PMP [75, 76]. This has been attributed to the fact that in isotactic PMP crystals, oxidation takes place preferentially at the chain folds because the tension resulting from the chain configuration reduces the oxidation activation energy [75] and also because the crystal dimensions are such that the crystalline regions are permeable to oxygen. For Poly-(1-butene) too, the activation energy of the oxidation reaction has been found to be lower for the isotactic than for the atactic polymer [77].

2.2.5.1 Photo-oxidation of PP

In PP, isolated hydroperoxide groups and sequences of hydroperoxide groups are formed in intermolecular (Reaction 31 in Scheme 2.7) and intramolecular (Reaction sequence 32 in Scheme 2.7) oxidation steps [78]. Therefore, after a short exposure period, during which the chromophores initially present become photochemically active, appreciable quantities of

Table 3.1 2003 World Market for Primary PVC Heat Stabilizers (thousands metric tonnes)

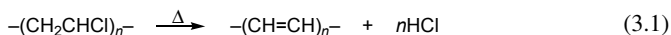
Type	United States	Western Europe	Japan	Rest of world	Total
Lead	14	84	50	197	345
Mixed metal	30	28	32	90	180
Organotin	36	18	12	9	75
Total	80	130	94	296	600

3.2 Chemistry of Degradation and Stabilization

Much of the stabilization technology for PVC was developed empirically, over a period of many years, without full knowledge of the chemistry that gave the observed results. However, extensive research now has yielded considerable amounts of detailed information about the mechanisms of action of stabilizers and the mechanisms by which the degradation of PVC occurs. In Sections 3.2–3.4 of this chapter, these mechanistic themes are emphasized in brief overviews of the topics discussed. Since the weatherability of PVC is addressed in depth in Chapter 2, the mechanisms of the photodegradation and air oxidation of the polymer are not considered here at all. Their chemistries are complex and incompletely understood. Nevertheless, thermal oxidative degradation [2, 3] and various aspects of photodegradation and photostabilization [2, 4–10] have been covered repeatedly in reviews.

Much more information is available in the literature about the mechanisms for the nonoxidative thermal degradation and stabilization of PVC. They have been of great interest to both researchers and technologists because of the low intrinsic stability of the polymer toward thermal dehydrochlorination and the attendant necessity of either preventing that process or avoiding its deleterious effects on polymer properties.

The thermal dehydrochlorination of PVC forms conjugated polyene sequences (Reaction 3.1). They impart undesirable color to the polymer when the number of double bonds that they contain is sufficiently large. They also undergo very facile air oxidation [2], experience phototransformations [4, 5], are involved in crosslinking [2, 11], and serve as sources of numerous aromatic compounds when the resin is heated to higher temperatures (for example, during fires) [12–14]. Thus the prevention of thermal dehydrochlorination and the innocuous destruction of the polyenes that it forms are major keys to PVC stabilization under various conditions.

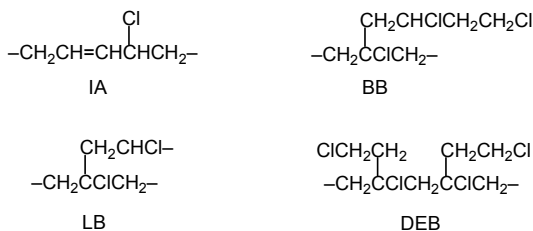


During the past 15–20 years, several general reviews of the nonoxidative degradation and stabilization of PVC have been published [2, 7, 15–21]*. Other recent surveys of these subjects that are more specialized are cited in [15]; older general reviews that still are useful [6, 8–11, 22] also are available. The material presented here can be regarded as a partial update for references [15, 18, 20, 21].

3.3 Mechanism of Thermal Dehydrochlorination

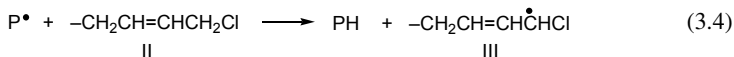
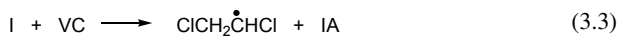
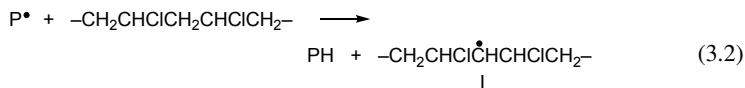
3.3.1 Thermally Labile Structural Defects

A considerable amount of published experimentation shows that the thermal stability of pristine PVC is much lower than it should be if dehydrochlorination began exclusively from ordinary head-to-tail monomer units [2, 11, 15, 18–20]. Anomalous structures (“structural defects”) having lower stabilities must therefore act as starting points for the sequential losses of HCl that generate polyene sequences. The nature and number of these structures was debated for several decades. However, it now is apparent to most researchers that the virgin polymer contains only four specific types of defect that make appreciable contributions to thermal instability. They are the internal allylic (IA), 2,4-dichloro-*n*-butyl branch (BB), long branch (LB), and 1,3-di(2-chloroethyl) branch (DEB) structures depicted here [23]. Their concentrations can be determined easily by ^1H and ^{13}C NMR methods (the latter technique requires a prior dechlorination with Bu_3SnH [24]), and their mechanisms of formation (during PVC synthesis) are thoroughly understood.

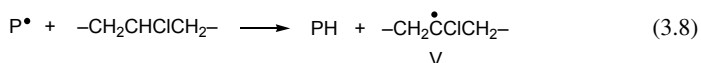
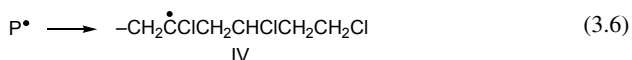


The principal route to IA involves the abstraction of methylene hydrogen from a finished monomer unit by a growing macroradical, P^\bullet (Reaction 3.2), followed by the transfer of a β chlorine atom to vinyl chloride (VC) monomer (Reaction 3.3) [25–27]. The initial abstraction can be either inter- or intramolecular [25–27]. Alternatively, IA results from another two-step sequence that starts with the transfer of hydrogen to P^\bullet from the chloromethyl component of long-chain terminus II (Reaction 3.4). Sequential head-to-tail addition of VC to the resulting radical, III, then forms structure IA (Reaction 3.5) [15, 26]. Chain end II, unlike IA, is known to have no substantial effect on thermal instability [15, 20].

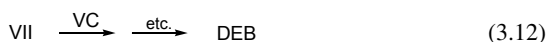
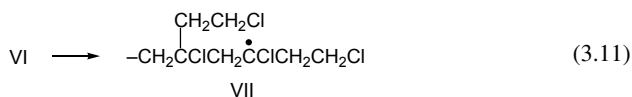
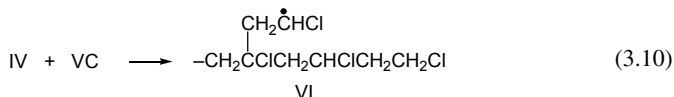
* A list of minor corrections for reference [20] is available from its senior author, who was not provided with proofs of the article prior to its publication.



The P^{\bullet} radicals occasionally rearrange by intramolecular hydrogen transfer to produce radical IV (Reaction 3.6). Head-to-tail propagation (Reaction 3.7) then produces branch structure BB [28]. Formation of the LB array results from a similar process (Reactions 3.8 and 3.9) that starts with an atom abstraction from an interior monomer unit [24, 29].



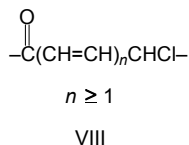
This step probably occurs most frequently in an intermolecular manner. However, in contrast, the doubly branched DEB structure arises from a mechanism (Reactions 3.6 and 3.10 to 3.12) involving two hydrogen transfers that are exclusively intramolecular [27].



The major reaction of P^\bullet is, of course, its addition to the monomer. Decreases of monomer concentration must, therefore, tend to increase the concentrations of all of the labile structures. The most prevalent of these defects is usually the BB grouping, whose frequency of occurrence was found to range from 1.0–2.4 per thousand monomer units in a series of suspension resins made isothermally at 40–82 °C [30]. The least abundant structure is the DEB one, which has been detected only in polymers that were synthesized at very low concentrations of VC [27]. Increases in the temperature of polymerization should tend to increase the amounts of the labile defects [26], an expectation borne out by experiment in the case of structure BB [30].

3.3.2 Hypothetical Labile Structures

Other anomalous groups have been suggested to affect the thermal stability in highly unfavorable ways. One of these groups is VIII, which supposedly is created by adventitious air oxidation [10].



However, its presence has been disproven by NMR measurements, whose sensitivity was greater than that required to visualize VIII at its proposed level of occurrence [15, 20]. According to other researchers, cisoid $-\text{COCH}=\text{CH}-$ structural defects are quite effective as true catalysts for the thermal dehydrochlorination of PVC [31, 32]. Yet high-field NMR studies have not revealed these groups in commercial polymers, and their proposed catalytic proficiency was not confirmed in a model-compound study [15].

The only important labile structure has been suggested to be the GTTG^- conformer (denoted by some workers as “GTTG”) of the *mm* triads in the ordinary *mmr* segments of the polymer [33, 34]. For many reasons that are detailed elsewhere [15], this proposal seems untenable. Further evidence against it came from a recent study which showed that the thermal stabilities of some PVCs with identical GTTG^- abundances were related directly (but inversely) to the concentrations of the IA, BB, and LB groups that the polymers contained [35].

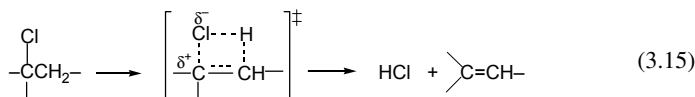
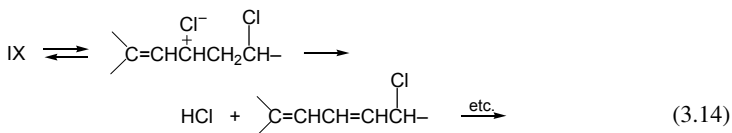
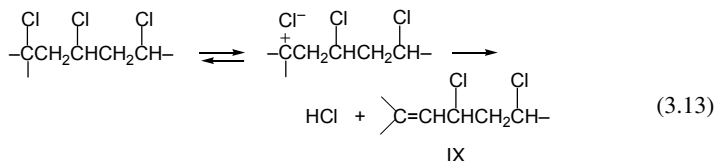
The foregoing comments should not be construed to mean, however, that ordinary monomer units, as a whole, do not initiate the thermal degradation of PVC. Because of their high concentration, relative to those of unstable defects, their net contribution to initiation actually may be quite significant, in spite of their low lability [15].

3.3.3 Polyene Elongation

3.3.3.1 Ion-Pair/Quasiionic Mechanism

A huge body of evidence now supports a mechanism for the thermal dehydrochlorination of PVC that involves either ion pairs (Reactions 3.13 and 3.14) or a succession of four-center

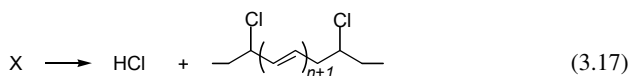
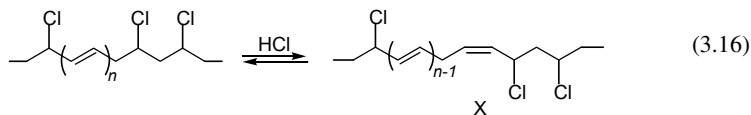
quasiionic eliminations, such as Reaction 3.15 [15, 20]. An ion-pair/quasiionic mechanism accounts, of course, for the relative instability of the defects discussed earlier, because their ionization can give rise to internal allylic or tertiary carbocations, all of which are more stable than the secondary carbocations formed from ordinary VC units.



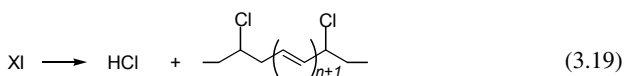
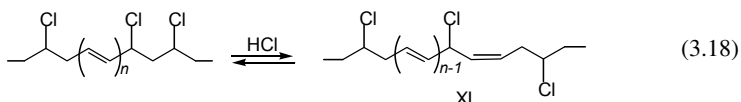
Bacaloglu and Fisch have asserted that an “ionic” mechanism cannot be operative [16, 36], but all of their arguments to that effect have been shown to be invalid [15]. Another case made against an ion-pair/quasiionic pathway [19, 37] is equally unconvincing [15].

3.3.3.2 Other Proposed Mechanisms

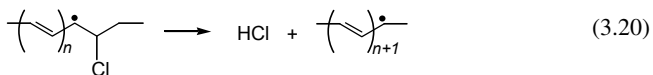
Bacaloglu and Fisch have stated that the *trans*-allyl chloride groups in PVC do not lose HCl at the temperatures where thermal degradation occurs [16]. To account for dehydrochlorination, these workers proposed a mechanism involving the HCl-catalyzed rearrangement of homoallyl chloride structures (Reaction 3.16), followed by the six-center concerted ejection of HCl from the resultant *cis*-allyl chlorides (Reaction 3.17) [36, 38–43].



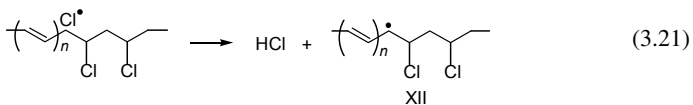
This scheme was ruled out, however, by a kinetic study with model compounds, which showed that the allyl chloride terminus of a PVC polyene sequence is the reactive site [44]. In response to this result, Bacaloglu and Fisch suggested an alternative pathway involving the six-center concerted dehydrochlorination of a *cis*-chloroallyl structure formed by rearrangement of the chloroallyl polyene end (Reactions 3.18 and 3.19) [16, 45, 46]. This mechanism also is inconsistent with the available facts [15], one of which is that, in the condensed phase, the thermal dehydrochlorinations of *cis*- and *trans*-allyl chlorides actually proceed at similar rates [15, 20].



There is considerable evidence to show that free radicals are created during PVC thermolysis [15, 20]. Thus, it is not surprising to find that several free-radical pathways have been suggested for the growth of PVC polyene sequences. One of these routes involves successive concerted losses of HCl from a polyenyl radical species, as in Reaction 3.20 [47]. This mechanism now has been excluded by an analysis based on the delocalization energies of polyenyl radicals and linear conjugated polyenes [15].



Another hypothetical radical process, exemplified by Reactions 3.21 and 3.22, follows a chain mechanism wherein the chain-carrying intermediates are polyenyl radicals and chlorine atoms [48, 49]. Quantitative arguments based on energetics and the very low reaction selectivity of Cl have sufficed to rule out this process as a route to polyenes, though a similar scheme may lead to the formation of isolated alkene units throughout the polymer matrix [12, 15, 20].

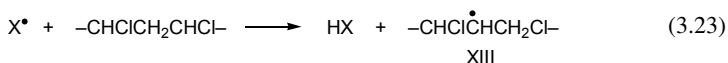


The sequential dehydrochlorination of polyenyl cation radicals (polarons) also has been propounded as a mechanism for polyene growth [50]. For various reasons, this possibility seems unlikely to be important [15, 20]. However, cation radicals are key reactants in another stage of the degradation, as the following discussion will show.

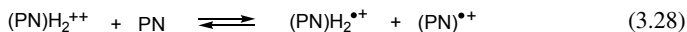
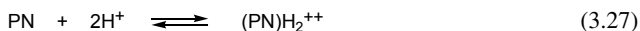
3.3.3.3 Autocatalysis

In an early stage of thermal dehydrochlorination, the labile structural defects present originally in PVC are destroyed. Since the polyenes that they initiate contain only an average of 3 to 20 double bonds [2], one might expect the degradation to stop or slow considerably when the extent of reaction still is low. Nevertheless, if some of the HCl being generated is allowed to remain in the system, dehydrochlorination does not decelerate but may increase greatly in rate [51]. This autocatalytic behavior is a very important aspect of the thermal degradation of PVC. Its onset is accompanied by an increase in the number of polyene sequences [52], a result which shows that it involves the initiation of polyene growth from monomer units that were stable theretofore. Hydrogen chloride also may catalyze either the growth of existing polyenes [53] or reactions that inhibit cyclizations which shorten polyene lengths [20]. Initiation from labile defects (especially chloroallylic structures) is promoted by HCl, as well [18, 20].

A very recent study [54] led to a comprehensive explanation of the autocatalytic effect. This explanation was supported by two principal findings: autoacceleration requires the presence of both polyenes and HCl, and it is inhibited by free-radical scavengers (including metallic mercury, a trap for chlorine atoms) that have no effect on the rate of the polyene growth reaction [54]. In the first stage of the mechanism for autocatalysis, HCl reacts with PVC polyenes (PN) to form free-radical intermediates (X^\bullet). These abstract methylene hydrogen from an ordinary monomer unit (Reaction 3.23), and the resultant C-centered radical experiences thermal β scission (Reaction 3.24) in order to form a IA defect. Rapid dehydrochlorination of that structure then starts the growth of a polyene sequence in the usual (nonradical) way. The chlorine atom created in Reaction 3.24 can serve as X^\bullet in Reaction 3.23 and thus continue a radical chain that leads to additional IA groups.



The nature of the initial X^\bullet species is not entirely clear. However, there are a number of reasonable possibilities for which support has been found [54]. One of these is the delocalized cation diradical formed in Reaction 3.26. It results from the thermal excitation of the protonated polyene produced in Reaction 3.25, and it owes its stability to the presence of two orthogonal π -electron systems that are generated by rotation about a C-C bond. Other X^\bullet candidates are the delocalized cation monoradicals formed in Reaction 3.28 from a neutral polyene and the doubly charged product of Reaction 3.27.



A further possibility for X^\bullet is a chlorine atom resulting from the homolysis of an allylic C-Cl bond in a cation radical species. This option is now considered to be the most probable one, as the others fail to account for the ability of mercury to prevent the autocatalysis [54] rather than just to make it less pronounced.

3.4 Thermal Stabilization

3.4.1 General Mechanisms

When PVC is subjected to heat under nonoxidizing conditions, two major types of stabilization can be envisaged. One of these tends to prevent alterations in the molecular structure of the polymer and, therefore, can be characterized as “chemical” stabilization. The other type is concerned with restoration of the properties of structurally damaged PVC. It is exemplified most frequently by reactions that destroy polyene chromophores.

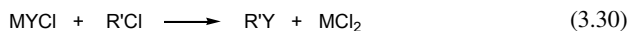
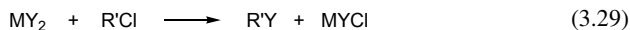
Additives that cause chemical stabilization generally can perform one or more of a number of major functions. The most important of these probably is the replacement of labile chlorine in unstable structural defects (including the chloroallylic end of a growing polyene) by groups that are less easily removed by heat. Perhaps first called the “Frye-Horst theory” in 1975 [55], in recognition of its proposers [56], this hypothesis was verified at that time [55, 57] and still is accepted by nearly all researchers. Another process that can lead to chemical stabilization is scavenging of the autocatalyst HCl. This result can be achieved with weakly basic additives whose strengths are insufficient to promote the dehydrohalogenation of the polymer. Deactivation of other prodegradant catalysts (Lewis acids) formed in the polymer (see below) is also a potential source of chemical stabilization phenomena.

3.4.2 Stabilizers Containing Metals

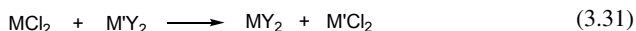
The most effective thermal stabilizers used commercially in PVC are salts of various metals. All of them are sufficiently basic to neutralize HCl, and this may be the only important function of some of these additives, e.g., hydrotalcites [16], zeolites [16], and various complex salts of divalent lead [9, 18]. Certain lead salts may react, however, with the lubricant, stearic acid, to form Pb(II) stearate [2, 20], a Frye-Horst stabilizer.

Many of the other stabilizers that replace labile halogen also are salts exemplified by the formula MY_2 , where M is a metallic cation such as R_2Sn^{+2} (R = alkyl), Ba^{+2} , Cd^{+2} , Zn^{+2} , or Pb^{+2} , and Y is an organic anion such as thiolate or carboxylate [2, 6, 7, 9, 10, 16, 22, 58].

Reactions 3.29 and 3.30, where R'Cl is an unstable defect, are simplified representations of the replacement steps.



A problem arises when the metal chloride formed in situ is a strong Lewis acid (e.g., CdCl₂ or ZnCl₂). Such a species may catalyze dehydrochlorination and thereby greatly reduce the stability of the formulation during long heating times. This difficulty can be alleviated by using mixtures of metal salts whose communal action is synergistic. Typical “mixed metal” stabilizers are the stearates or laurates of barium and zinc, calcium and zinc, or barium and cadmium [16]. Their synergism can be explained economically by a mechanism involving Reactions 3.29 and 3.30 (where M is the metal of higher Lewis acidity, i.e., Cd or Zn), accompanied by Reaction 3.31



(where M' is Ba or Ca) [2, 6, 7, 9, 10, 16, 18, 20, 22, 58]. The latter process has the twofold virtue of regenerating the Frye-Horst stabilizer, MY₂, while replacing a metal chloride that catalyzes degradation with a metal chloride that does not. This scheme is unduly simplistic, however, in that the stabilizing activity of metal carboxylate mixtures actually is affected considerably by complex formation and ligand exchange between the metal species [2, 6, 7, 9, 18, 20, 22, 58]. For example, a 1:1 bimetallic complex has been implicated as the substance that is responsible for barium-cadmium synergism [59]. Moreover, extensive studies have shown that when calcium and zinc stearates are used together in a molar ratio of 1:2, respectively, their effectiveness can be increased significantly by preheating either the mixture of stearates or the zinc stearate alone [60–63]. These interesting observations were rationalized in terms of complexation and the nature of the bonding between the metals and the ligands [60–63].

The Frye-Horst theory has been attacked occasionally [17, 19, 64–66] and defended vigorously [20]. Naqvi [17] has emphasized the stabilizing effects of organic groups that serve as nonpolar diluents. Iván et al. [19, 64–66] have described a “reversible blocking mechanism” that involves the detachment of stabilizer ligands from the polymer in reactions promoted by HCl. This mechanism actually is an integral part of the original Frye-Horst proposal [18, 20]. Frye-Horst chemistry seems to provide the only reasonable explanation [20] for the polyene lengths and initial rates of dehydrochlorination that were observed in several experiments carried out in dilute solution with PVC and metal stearates [65].

Organotin maleates are Frye-Horst stabilizers that also may have a curative function, namely, the destruction of polyene chromophores in Diels-Alder cycloadditions. These reactions could involve either the maleates themselves or maleic anhydride formed in situ [2, 6, 7, 9, 10, 16, 18, 22].

3.4.3 Organic Stabilizers

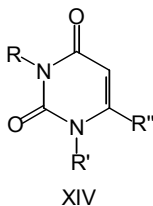
3.4.3.1 Costabilizers

In PVC, the thermal stabilizing effectiveness of organic compounds containing no metals generally is too low to allow these additives to be used alone. However, a number of them are able to function advantageously as costabilizers in some of the systems where metal-based additives are playing the major role. A variety of fully organic stabilizers has either been incorporated into commercial PVC products or considered for use in that way. Some of these additives are β -aminocrotonates, phosphites, epoxides, *N,N'*-diphenylthiourea, 2-phenylindole, β -diketones, β -ketocarboxylic esters, polyols, dihydropyridines, and dehydroacetic acid; original references to their usage and modes of action are cited in various reviews [2, 6, 9, 10, 16, 18, 22].

In certain cases, one of the functions of organic additives is to neutralize HCl. Moreover, in studies with model compounds, many of these costabilizers have been found to displace labile chloride through alkylation reactions. Also, a number of them may be able to deactivate acidic metal chlorides through complexation. Thus, generally speaking, the mechanisms of action of the organic additives resemble (qualitatively) those of the metal-containing stabilizers that were discussed above. Exceptions exist, however, one of which is the apparent ability of dihydropyridines to hydrogenate double bonds [67].

In recent years, an Egyptian research group has been especially active in the search for fully organic stabilizers of PVC. One of their reports [68] deals with the use of *N*-acryloyl-*N'*-*p*-substituted thioureas for this purpose and contains numerous references to their earlier work in this field. Interestingly, the literature also discloses an organonitrile stabilizer that may scavenge HCl by forming an imine hydrochloride [69].

Pyrimidinediones that are described by the general structure XIV are now receiving attention as thermal stabilizers [16, 70]. The packages that include them are being referred to as "organic-based" [70], though they also contain metal-based HCl scavengers such as hydrotalcites or metal carboxylates [16, 70]. The pyrimidinediones are stated to improve the initial color of formulations [16, 70] and to become bonded to the polymer during heating [70]. Such results imply the rapid displacement of labile chloride by these stabilizers. Nevertheless, the driving force for such a process is by no means apparent, since none of the sites in structure XIV is strongly nucleophilic.



10 Antistatic Additives

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10.1 Introduction

Electrostatic charges are commonly generated by frictional contact between two materials with different susceptibilities to electron loss. One material loses electrons and becomes positively charged; the other gains electrons and becomes negatively charged.

The presence of charged polymer surfaces can have serious consequences during production, forming operations, and service life. The magnitude of charge depends on:

- the degree of contact
- the frictional properties
- the surrounding medium: with increase of humidity, the surface conductivity increases, resulting in faster flow of the charges

the electrical properties, such as:

- dielectric constant: the constant of proportionality between the surface charge density and the field voltage. Materials of low dielectric constant undergo charge build-up quite easily,
- resistivity: materials of low resistivity lose charges more easily

A major factor affecting the surface resistivity value is the surrounding medium, especially the relative humidity present in air, as shown in Fig. 10.1.

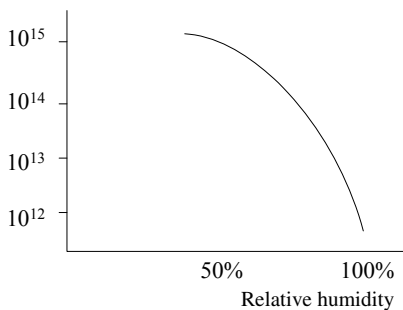


Fig. 10.1 The influence of atmospheric humidity on the surface resistivity of polyethylene

Plastics, as a class, combine high surface resistivity (10^{14} to 10^{16} Ohms, 20 °C, and 50% RH) with a low dielectric constant (2 to $3 \cdot 10^6$ Hertz). They readily undergo charge build-up and can reach the discharge potential in air of 15000 V/cm. The damage threshold of some

devices is as low as a few hundred V/cm. The maximum charge attainable by the polymer in terms of electric field intensity is a function of its conductivity or specific resistivity, as shown in Table 10.1.

Table 10.1 Electric field intensities attainable as a function of specific resistivity

Material Specific Resistivity (Ohm)	Electric Field Intensity (V/cm)
10^{15}	15,000
10^{11}	10,000
10^{10}	2,500
10^9	negligible

Following the data of Table 10.1, by reducing the resistivity of the material, we have available a convenient method to reduce the static electricity problem. Reducing the resistivity of a polymer can be done by using an antistatic additive. An antistatic additive can be applied externally or incorporated into a polymer in order to dissipate electrostatic charges.

By using an antistatic additive, problems caused by static electricity will be reduced or eliminated. Those problems are:

- dust pick up, which can ruin clarity and/or the sales appeal of items packages in plastics,
- handling problems, e.g. mutual repulsion of bodies of same charge in polymer bead packing,
- electrical discharges which may give electrical shocks to employees or start a fire or cause an explosion.

10.2 Basic Principles of Action of Antistatic Additives

Three materials can be used to increase the conductivity of plastics to prevent charge accumulation:

- external antistatic additives
- internal antistatic additives
- conductive fillers

10.2.1 External Antistatic Additives

External antistatic additives are dissolved in an appropriate solvent carrier. The plastic is coated with the additive by spraying or immersion. Then the carrier solvent is evaporated. The advantages of this method are relatively small amount of additive needed and the immediate effect. The main drawbacks of external additives are loss of antistatic properties resulting from surface abrasion and migration into the polymer and the difficulties involved

in producing a uniform coating. Printing and sealing problems can occur if the coating is not uniform.

10.2.2 Internal Antistatic Additives

Internal antistatic additives are incorporated into the polymer matrix. They migrate to the surface of the polymer and generally function by two mechanisms:

- as lubricants, in which case friction and therefore, static charge generation is reduced
- by providing a conductive path, which dissipates the static charge to the atmosphere. The conductive path consists of a thin water layer, which the antistatic additive absorbs from the atmosphere

Fig. 10.2 shows how antistatic additives, which are incorporated into the polymer matrix, have migrated to the surface of the polymer to form a uniform layer of molecules. The nonpolar part of the antistatic additive is anchored in the polymer while the polar part projects out of the polymer. It is this polar part which absorb the humidity in order to form a conductive path.

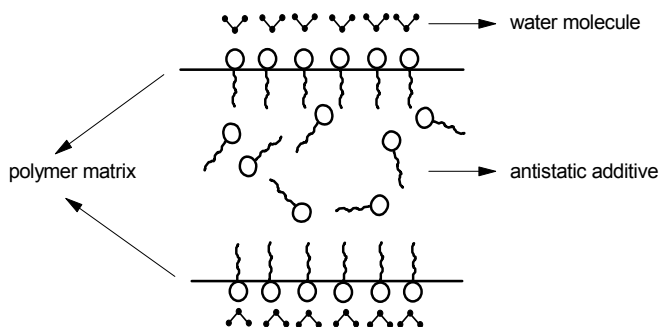


Fig. 10.2 Conductive path formed on polymer surface after migration of the antistatic additive

By carefully choosing the antistatic additive, the speed at which the antistatic effect develops and its duration may be optimized. These factors are mainly functions of the rate of migration of the additive to the polymer surface and its rate of removal from the surface.

The migration rate is mainly determined by:

- the relative compatibility of the antistat to the polymer: If an antistat is too compatible with the polymer, it does not migrate out and hence, does not impart the desired effect. If the product is not compatible enough, excessive migration occurs, resulting in greasy surface.
- the polymer crystallinity: The same antistatic additive performs better in PE than in PP because of PE's lower crystallinity. The antistatic additive migrates more easily through the amorphous phase of the polymer.

- the total additive formulation: Certain additives, such as fillers and pigments, tend to absorb antistatic additives. Other additives, such as slip, help the antistatic additive migrate towards the polymer's surface.
- the concentration of antistat used: Higher concentrations lead to higher migration rates.
- the temperature: Antistatic additives have higher mobility at higher temperature, resulting in increased migration

The difference between the ambient temperature and the glass transition temperature of the plastic is important: In a polymer with a low glass transition temperature, the movement of molecular segments can be observed microscopically (micro-Brownian motions). Assisted by this motion, antistatic additives migrate to the polymer surface. Polymers with glass transition temperatures above room temperature are in a frozen state at room temperature. The micro-Brownian motion that helped the antistatic additive migrate to the polymer surface is not expected. During processing, some of the antistatic additive concentrates at the surface, providing the antistatic effect. Recovery of this effect after surface cleaning is not possible unless the polymer is heated above its glass transition temperature. This heating activates the micro-Brownian motion and promotes the migration of the additive to the surface. Characteristics of external and internal antistatic agents are described in Table 10.2 [1].

An internal antistatic additive is required to:

- be sufficiently polar to perform antistatic functionality
- have a “balanced” affinity for the polymer
- be compatible with the polymer matrix across the entire range of processing conditions
- be compatible with other additives
- be thermally stable
- have no adverse effect on the resin properties
- conform to food contact regulations

10.2.3 Conductive Fillers

Conductive fillers, such as carbon black, are incorporated in the polymer matrix. They are used if the surface resistivity must be less than 10^8 Ohm. Conductive fillers are used for antistatic properties under the following conditions:

- in fields where the potential for explosion exists such as mining and the handling of solvents or finely dispersed goods, such as powdery polymers
- in physiologically sensitive workplaces or fields, such as operating rooms or precision engineering
- where sensitive electronic chips need to be protected against destruction by discharge sparks during transport and handling, as well as in use,
- in electronic switches
- to screen against electromagnetic radiation, such as in casings for electronic devices

Table 10.2 Comparison of internal and external antistatic additives

	Internal additive	External additive
Application technique	Dose of 0.1 to 3% is added either straightly or in masterbatch form	A dose of 0.1 to 10% water or solvent solution is sprayed or coated on product
	Added either singularly or together with other additives by resin producer, masterbatcher or processor	Coated by molder, secondary processor, or assembler
Characteristics	Antistat on surface may be removed by washing/abrasion, but reinforced by those migrating to surface to retain antistatic effects	Antistatic effects are lost if antistat on surface is removed
	As antistat inside the polymer migrates to the surface, it takes several hours to several days to achieve antistatic effect	Quick acting as antistatic effects are achieved immediately after coating
	Kind and dose are determined according to the type of plastic, processing technique and use of end product	Usable regardless of the type of plastics in most cases
	Not much handling work is necessary if added together with other additives	Coating equipment and process are necessary
Cautions	Because of possible processing at high temperature, pay attention to coloring and decomposition	Plastic is hard to wet, so antistat and solvent must be selected properly
	Property degradation and clarity degradation can occur	Pay attention to coat uniformly
	Pay attention to influences on pigment dispersion and synergistic effect with other additives	When organic solvent is used, be careful not to cause any fire
	Printing ink contact, heat sealing and label adhesion properties can be affected	Ventilator and protective equipment must be provided if irritating to skin or toxic substances are involved.
	Test processing is necessary as some antistats affect processability adversely	Some antistats are corrosive to metal

10.3 Description of Antistatic Additives

Antistatic additives can be divided in several classes:

- non-ionic
- anionic
- cationic
- amphoteric

10.3.1 Non-ionic Antistatic Additives

The non-ionic antistatic additives are the most commonly used class. The major groups in this class are:

- fatty acid esters
- ethoxylated alkylamines
- diethanolamides
- ethoxylated alcohol

10.3.1.1 Fatty Acid Esters

Very often used in polyolefins is glycerol monostearate (GMS). GMS meets most food contact regulations and can therefore be used in all types of food packaging applications. In polyolefins, this antistat migrates fast to the surface, as it is not very compatible with the polymer. The antistatic effect is noticed very quickly. Because of its high level of incompatibility, the additive does not stay very long in the bulk of the polymer, which means its performance is limited in terms of time. Glycerol monostearate is therefore known in the industry as providing immediate performance, but only for a short period. How long the product performs depends on the polymer, the total additive formulation, and the thickness of the end-article. The thicker the article is, the larger the “reservoir” of antistat remaining in the bulk of the polymer, and therefore, the longer the antistatic effect.

Glycerol monostearate is very often used in combination with an ethoxylated amine. A synergistic effect occurs, resulting in both short term and long term performance.

Several grades of glycerol monostearate are available, each are specified by its monoester content. The higher the monoester content, the better the antistatic performance is. This can be easily understood through Figs. 10.3, 10.4, and 10.5. Glycerol monostearate has two –OH groups available for absorbing moisture out of the environment. When a GMS contains a lot of glycerol distearate, only one –OH group is available. A glycerol tristearate has no –OH groups available. Fig. 10.6 shows the antistatic performance of the different GMS types [3].

A glycerol monostearate with a low monoester content is not as good an antistatic additive but provides good lubricating properties. A low monoester content GMS is very often used for this reason in PVC. Available on the market are:

- GMS90: contains a minimum 90% monoester, often more than 95%
- GMS60: contains a minimum 60% monoester
- GMS40: contains a minimum 40% monoester

16 Fluorescent Whitening Agents

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16.1 Introduction

The use of fluorescent whitening agents in plastics has extensively been covered in the literature [1]. This chapter is an extension of this previously published material, including technical performance data on fluorescent whitening agents in various substrates.

For a long time, fluorescent whitening agents (FWAs) have been used to improve the appearance of finished articles in the paper, soap, detergent, and textile industries. As thermoplastics markets have grown, fluorescent whitening agents have penetrated this field, too.

The objectives of using FWAs in plastics are the same as in paper and textiles:

- Improvement or masking of the initial color of plastics, which is often slightly yellowish
- Production of brilliant white end use articles, such as fashion goods of imitation leather, packaging materials, etc.
- Increase of the brilliancy of colored and black pigmented articles

In principle, FWAs can be used in all plastics; however, not all FWAs can be used in all plastics because of possible restrictions on their suitability in a given application. Therefore, great care has to be taken to select the right chemistry and concentration. A technically suitable FWA shows high whitening effectiveness at low concentrations. In practice, concentrations of 50 to 500 ppm are used in thermoplastics. Only special applications, including processing recycled thermoplastics, may require concentrations exceeding 1,000 ppm.

16.2 Basic Principles of Whitening Mechanisms

Many thermoplastics absorb light in the blue spectral range of natural daylight (“blue defect”), causing a more or less pronounced yellow appearance (Fig. 16.1A). There are three basic principles on compensating for this deficiency, i.e., increasing the degree of whiteness:

- Bleaching
- Compensating for the blue deficit
- Increase in reflection

A traditional way to reduce the initial discoloration of plastics and fibers, especially cotton but also synthetic fibers, such as polyester, polyamide, and acrylics, is to bleach them. While the yellowish cast diminishes significantly with bleaching, care has to be taken not to damage the fabric, reducing its strength and worsening its appearance.

Decades ago, textiles were brightened by adding very small amounts of a blue pigment, a technique known as “bluing”. In this way, the yellowish cast of the substrate was offset by

increasing the reflected blue portion. The substrate appears whiter, but the total amount of reflected light is reduced (Fig. 16.1B), so consequently, it appears duller [2].

In contrast, fluorescent whitening agents absorb invisible UV radiation in the wavelength range of about 360 to 380 nm, converting it to longer wavelength light and re-emitting it as a visible blue or violet light. As a result, the unwanted yellowish appearance of the substrate is offset and, in addition, more visible light in the range of 400 to 600 nm is reflected than was originally incident. The article now appears whiter, brighter, and more brilliant (Fig. 16.1C). Such optical brightening was discovered early in the 20th century, when natural substances were used to whiten fibers [3]. Additional information concerning the historical development of FWAs is found in Anliker [4].

The physical process undergone in the FWA molecule in the whitening process follows the pattern shown in Fig. 16.2: By absorption (A) of photons (energy) from ultraviolet light, the whitener molecule raises its energy from the singlet ground state S_0 to the electronically excited singlet state S_1 and S_2 . Because of non-radiating deactivation, brightener molecules from the S_2 state relax to the vibrational ground state S_1 . Direct deactivation from the S_1 state to the singlet ground state S_0 leads to the emittance of fluorescent radiation. Because a certain portion of the energy received is remitted as non-radiating energy, the emitted photons are at a lower energy level, i. e., the radiation is of a longer wavelength. Small amounts of foreign matter (such as catalysts and impurities) are able to partially or completely quench the fluorescence because of their absorption of excitation energy [5].

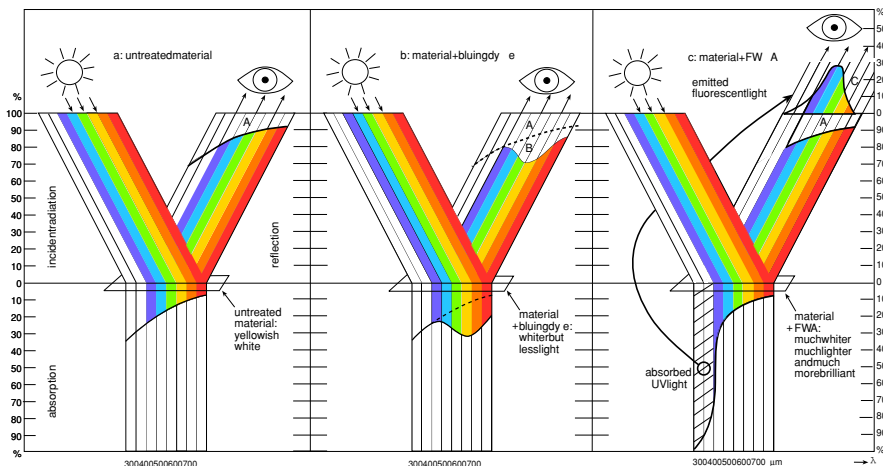


Fig. 16.1 Absorption and reflection of daylight on white surfaces

- a) Untreated substrate absorbs mainly blue light (A) → yellow cast (blue deficit)
- b) Blued substrate: compensation of yellow cast (A) by additional absorption of green-yellow light (B) → luminosity loss
- c) Whitened substrate: remission + fluorescence → yellow cast compensated + excess of blue light (C).

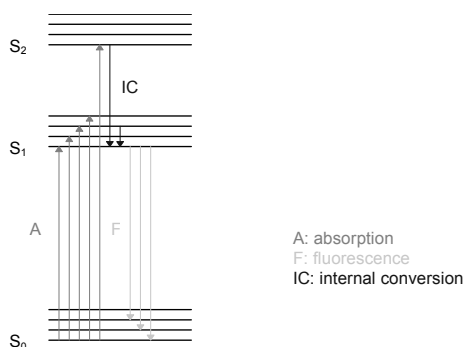


Fig. 16.2 Simplified functional diagram of physical processes in an excited whitener molecule. A) Excitation through incident light, I C) Radiationless transition, F) Fluorescence, emitting light

16.3 Selection and Technical Requirements of Optical Brighteners

The determining factors for the selection of the most suitable FWAs for a given plastic material are:

- Achievable whitening effect
- Compatibility
- Light-fastness

The selection of the whitener is also affected to a certain extent by its hue. In general, neutral and neutral blue to blue-greenish hues are preferred. However, especially in Asia, sometimes a reddish hue is preferred.

The achievable degree of whiteness of a given FWA depends on the substrate (Fig. 16.3). In addition, the whiteness degree may be affected by processing conditions as well as possible interactions with other components in the formulation, such as pigments and UV absorbers.

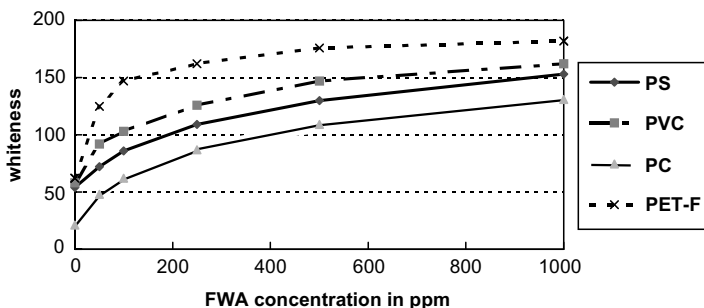


Fig. 16.3 Whitening effectiveness (Ganz formula) of a bis-benzoxazole whitener in various substrates (with rutile type TiO₂) as a function of whitener concentration

Titanium dioxide pigments absorb in the long-wavelength UV range, which is essential for exciting FWAs, thus generating lower whiteness degrees. Anatase pigments absorb at 380 nm about 40%; rutile pigments, on the other hand, absorb about 90% of the incident radiation (Fig 16.4).

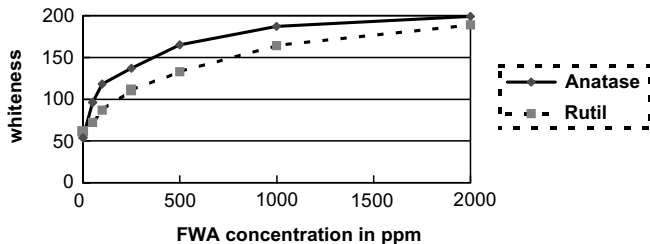


Fig. 16.4 Whitening effectiveness [W] of a bis-(styryl)biphenyl whitener in plasticized PVC as a function of whitener concentration in presence of 5% titanium dioxide as anatase type (a) and rutile type (b)

UV absorbers also absorb radiation in the FWA exciting range of the spectrum, and may therefore lead to reduced whiteness. However, this whiteness decrease is small because the FWA on the surface of the polymer receives sufficient energy to become excited.

An essential requirement for the technical suitability of a FWA is its light-fastness in the substrate under consideration. FWAs are usually more or less light sensitive in the wavelength range needed to excite the molecule. Consequently, the light-fastness of whiteners is limited, and is considerably lower than the light-fastness of pigments and the light stability of most plastics. Colored structures, which may lead to additional yellowing, must not be generated at the end of the photochemical degradation of a FWA. The light-fastness of a FWA is considerably affected by the substrate (Fig. 16.5).

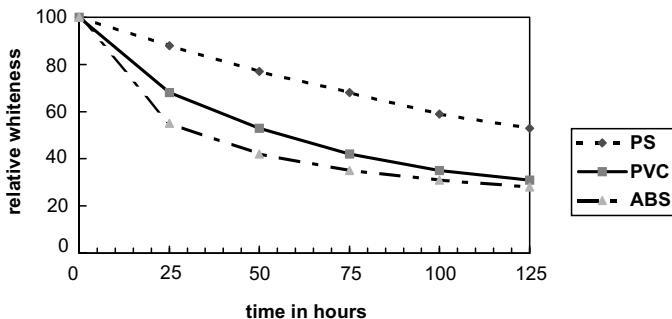


Fig. 16.5 Lightfastness of a bis-benzoxazole type FWA in various substrates; Relative whiteness (Ganz formula) as a function of weathering time in a xenotest 150 with filtered xenon radiation corresponding to daylight behind window glass.

To achieve maximum effectiveness with a FWA, it is imperative that the whitener is fully dissolved and homogeneously distributed in the finished article, i.e., the distribution must be monomolecular. Sufficient compatibility is necessary to avoid exudation. The requirements regarding thermal stability and low volatility of FWAs for thermoplastics are higher than those of for textile whitening. In textiles, FWAs are usually applied topically from solution.

Migration stability must also be considered, particularly with FWAs used in flexible PVC and polyurethane coatings. An insufficiently compatible whitener may be transported to the surface (for example, resulting from plasticizer migration). Consequently, partial loss of whitener results; furthermore, the surface may become discolored either uniformly or in spots.

16.4 Structure of Optical Brighteners

Only few of the known chemical classes of fluorescent whitening agents (Fig. 16.6) possess the properties required for mass whitening of plastics and fibers [5 to 9].

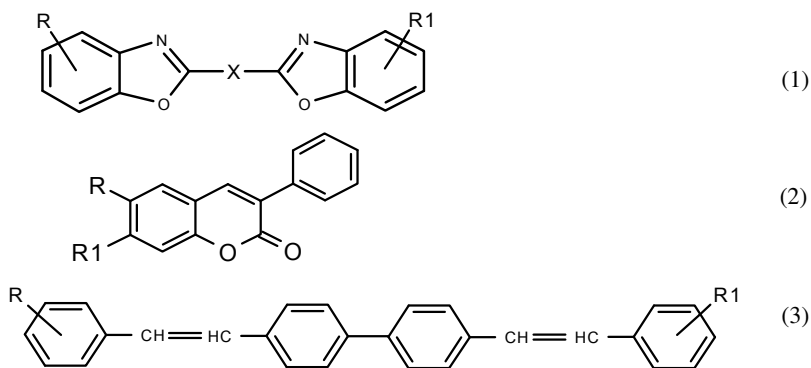


Fig. 16.6 Chemical classes for the mass whitening of plastics and fibers

- 1) bis-benzoxazoles
- 2) phenylcoumarins
- 3) bis-(styryl)biphenyls

16.5 Incorporation of Optical Brighteners into Polymers

Fluorescent whiteners are incorporated exclusively into the thermoplastics' mass before the forming process; i.e., the whitener is not applied subsequently by means of solutions, hence the term "mass-whitening."

Usually, fluorescent whiteners are introduced by dry-blending with the plastic material (powder or pellets). If necessary, an adhesion promoter such as butyl stearate is added. In flexible PVC, fluorescent whiteners are frequently applied as a solution or dispersion in a plasticizer. To achieve distribution of improved homogeneity at low concentrations, fluorescent whiteners are often added as a concentrate or as a master blend, e.g., 10% active whitener blended with chalk or a plasticizer.

In the case of PET fibers, some types of FWA can be applied during polymerization. In this case, the FWA is added with the monomers; extremely good thermal stability and low volatility are especially important requirements for FWAs incorporated in this manner.

16.6 Testing of Optical Brighteners in Polymers

16.6.1 Migration and Exudation

Examination for migration and exudation effects is carried out best in the light of a UV lamp. Migration and exudation effects result in random yellow and greenish spots, which fluoresce distinctly brighter than the surrounding area.

16.6.2 Whitening Effect

The evaluation of the whitening effect of an FWA may be carried out visually (preferably under daylight) or by means of colorimetric measurements.

For visual evaluation, so-called “white scales” are used for comparison, e.g., the plastic white scale developed by Ciba Inc. This consists of a melamine molding resin which is graded with yellow pigments or fluorescent whiteners into 12 different whiteness degrees. The calibration point is physically ideal white, approximately represented by magnesium oxide or barium sulfate. This calibration point represents by definition the whiteness degree 100.

The result of any visual evaluation depends considerably on luminosity and spectral energy distribution of incident light, as well as on physiological influences and the color sensitivity of the observer. The assessment should be carried out in daylight (behind window glass, or even better, outdoors) with adequate brightness between 10 am and 3 pm (1000 to 1500 hours), facing north in the northern hemisphere and south in the southern hemisphere.

Visual evaluation, however, is not completely satisfactory because of numerous variables which are difficult to control. For that reason, in recent years, instrument assessment of whiteness has been increasingly adopted [10].

Whiteness, as a physiological impression, is not directly measurable; for that reason, it has to be calculated from colorimetric data. On the basis of physical measurements, objective characteristic values are obtained, free of subjective influences. A specified light source in the color measuring device is a prerequisite for reproducible results, independent of time, location, or operator.