

Color and Color Reversion of Cellulosic and Lignocellulosic Fibers

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Abstract

Despite the increasing development of electronic devices, the use of paper made with cellulosic and lignocellulosic fibers is still a growing sector. The market of bleached fibers constitutes an important part of the pulp and paper industry. There are two main categories of fibers: the lignin-free cellulosic pulps are obtained from wood after chemical pulping, followed by various bleaching stages; the lignin-rich pulps or high-yield pulps (HYP) are obtained after mechanical defibration and lignin-retaining bleaching. The market of HYP is mainly newspapers and some magazines. The whiteness of bleached chemical pulps, measured by the reflectance at 457 nm by comparison to a white standard, is near 90 ISO, whereas the whiteness of bleached HYP is near 80 ISO. In this review, we consider first the cellulosic fibers with low lignin content and then lignocellulosic fibers with high lignin content. For each kind of fiber, first the bleaching of the fibers is detailed with a focus on the structure of the colored chromophores. The brightness reversion and the main mechanisms involved are approached in the second part of the chapter. The thermal brightness reversion is the main problem of bleached chemical pulps, whereas the brightness reversion under light exposure constitutes a serious drawback of bleached lignin-rich pulps for a more important development, especially to replace bleached chemical pulps in high quality magazine papers.

21.1 Introduction

In ancient Gaul, bleaching of vegetable fibers was accomplished by the action of sunlight on fibers moistened by alkaline solution made from wood ash. During the 18th century grass bleaching was performed in Holland mainly on materials made with linen fibers. Cotton was considered white enough, whereas hemp, jute and other vegetal fibers were considered too difficult to bleach [1]. Bleaching powder, made by reaction of chlorine on slaked lime, was the most dominant bleaching agent during the 19th century. The first large-scale chlorination of chemical pulp (i.e., lignin removed from the lignocellulosic fibers by a chemical treatment) was reported in Wisconsin (USA) in 1930–1931. Intermediate alkali extraction stages led to a further improvement of the pulp bleaching [1]. Chlorine dioxide, as pulp bleaching agent, was introduced after the Second World War; its popularity lies in its ability to react with lignin without attacking carbohydrates, conserving the mechanical strength of cellulosic fibers [1]. Due to stricter environmental regulations in the 1970s, new bleaching agents were considered such as oxygen, hydrogen peroxide, ozone

and peracids. Oxygen bleaching is nowadays widely implemented in pulp mills as the final stage of soda or kraft pulping processes or as the first bleaching stage of sulfite pulp. The use of totally chlorine-free (TCF) processes allows, by the absence of chlorides in the bleaching plants, counter-current washing all the way back to liquor recovery to be practiced, leading to the completely closed mill concept with all organic effluents to be burned for energy recovery. Actually, elemental chlorine-free (ECF) multistage bleaching sequences, involving one or more chlorine dioxide stages, are the worldwide technique used to bleach sulfite and kraft chemical pulps. The absence of lignin polymer in the bleached chemical pulps does not eliminate the susceptibility of the bleached products to yellow [2].

By contrast to chemical pulps, mechanical pulps and other high-yield pulps are defibrated by mechanical processes (stone grinding or refining) and retain most of the lignin present in the lignocellulosic material (wood and non-wood plants) used to make the pulp. Thus the pulps contain as much lignin as is expected for cellulose and hemicellulose in order to get the highest pulp yield. Therefore, the objective of bleaching high-yield pulps is to remove only the

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chromophores (i.e., units absorbing the visible light between 400 and 800 nm). This is possible because the structures responsible for color are polarizable groups (conjugated carbonyl groups, enones and quinones), able to react with hydrogen peroxide in alkaline medium by action of perhydroxyl anion (HOO^\cdot), leading to their selective oxidation in non-colored compounds. Sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$), also known as sodium hydrosulfite, by its ability to reduce selectively colored quinones into their corresponding non-colored hydroquinones, is the other main reagent used to bleach high-yield pulps. The brightness gains achieved in bleaching high-yield pulps are temporary, since almost all of the lignin present in the lignocellulosic material is still present in the pulp. Exposure to air and light produce new chromophores mainly from lignin, which is a phenolic polymer very prone to oxidation [3].

In this review, we will first consider cellulosic fibers produced by chemical pulping with low lignin content and then lignocellulosic fibers produced by high-yield pulping with high lignin content. In each section, first the bleaching of the fibers will be detailed with a focus on the structure of the colored chromophores. The brightness reversion and the main mechanisms involved will be approached in the second part.

21.2 Lignin-Free Cellulosic Fibers (Chemical Pulps)

21.2.1 Bleaching of Chemical Pulps

The principal goals of chemical pulp bleaching are to remove the residual lignin and chromophores inside the pulp without adversely affecting pulp strength. This was achieved through multistage processes whereby the first stages delignify and the later ones brighten the pulp [4].

21.2.1.1 Oxygen Delignification

The oxygen alkaline post-pulping delignification stage before bleaching largely implemented in the mills, allows a decrease of the residual lignin at least by one third. The main reactions are demethoxylation with intermediate formation of quinones, aromatic ring opening, cleavage of ether bonds and condensation of phenolic rings into biphenyl structures [5]. Oxygen bleaching introduces a large number of carboxylic acid groups into the residual lignin. They are in the form of muconic acids when aromatic rings of lignin are degraded and aliphatic acids when carbonyl groups in the side chains of lignin structure units are oxidized. The number of phenolic hydroxyl groups in residual lignin affects its reactivity towards oxidative bleaching agents and is therefore a very important parameter [6]. An important number of phenolic groups remain in the residual lignin after an alkaline oxygen stage [6, 7], due to the formation of new phenolic groups [8]. The mechanisms involve either radical processes initiated by

an electron transfer from the phenate group to oxygen giving a phenoxy radical and the superoxide anion (O_2^\cdot) or an ionic process between the phenate and the oxygen molecules in extreme conditions (high oxygen pressure and high temperature) [5, 9–11].

21.2.1.2 Elemental Chlorine-Free (ECF) Bleaching

In ECF bleaching, after the alkaline oxygen stage part of the pulping process, the first sequence usually starts with a chlorine dioxide (ClO_2) delignification stage D_0 [12]. Chlorine dioxide reacts with phenolic groups at about 10^6 faster than the non-phenolic entities [13, 14]. Most of the studies on lignin models indicate that phenolic structures in residual lignin react with chlorine dioxide by electron transfer from the phenol (or phenate anion) to ClO_2 , followed by addition of a second molecule of ClO_2 to the formed phenoxy radical. Elimination of different entities affords either muconic acid monomethyl esters (Figure 21.1, process I), or *o*- and *p*-quinones (Figure 21.1, processes II and III, if a benzylic alcohol structure is present on the side chain) [12, 15, 16]. Quinones appeared as the predominant oxidation products, and are generally formed in a $\approx 2:1$ ratio when compared with muconic structures [16]. Studies by Hamzeh *et al.* [17] showed that muconic derivatives also fully reacted with chlorine dioxide with reaction rates rather similar to non-phenolic aromatic structures.

Subsequently, in the delignifying stage D_0 , part of the oxidized lignin is solubilized and removed by an extraction stage (E) using sodium hydroxide alone or sodium hydroxide in the presence of oxygen (EO). The extraction stage (E) yields the saponification of muconic acid methyl ester structures, as well as that of their associated lactones methyl esters. Ionization of acidic groups (i.e., muconic acids) by alkali greatly enhances the solubility and dispersibility of the oxidized lignin fragments in water [18]. Lachenal *et al.* [19] showed that D_0 delignification could be greatly enhanced if the chlorine dioxide charge was experienced in “n” multiple mini stages and the oxidized lignin removed by extraction in $(\text{DE})_n$ sequences. Alkali treatment of the D_0 pulp in an E stage, in addition to removing solubilized lignin, converts quinones to polyphenols, somewhat analogous to that of hydrosulfite reduction [20]. The formation of polyphenols from the 1,4-reductive Michael addition of hydroxide ion to quinones in the E stage and the ease of oxidation of polyphenols by oxygen may provide an explanation of the reactivity of oxygen with D_0 lignin in a (EO) stage (Figure 21.2) [21]. The reinforced extraction of D_0 oxidized pulp by oxygen and hydrogen peroxide (EOP) leads to fragmentation of quinonic rings and muconic structures creating numerous acidic derivatives soluble in the bleaching liquor (Figure 21.2) [22].

Application of chlorine dioxide (D_1 bleaching stage) after alkaline extraction, oxidative-reinforced or not, oxidizes polyphenolic anions into hydroxyquinone anions, and further

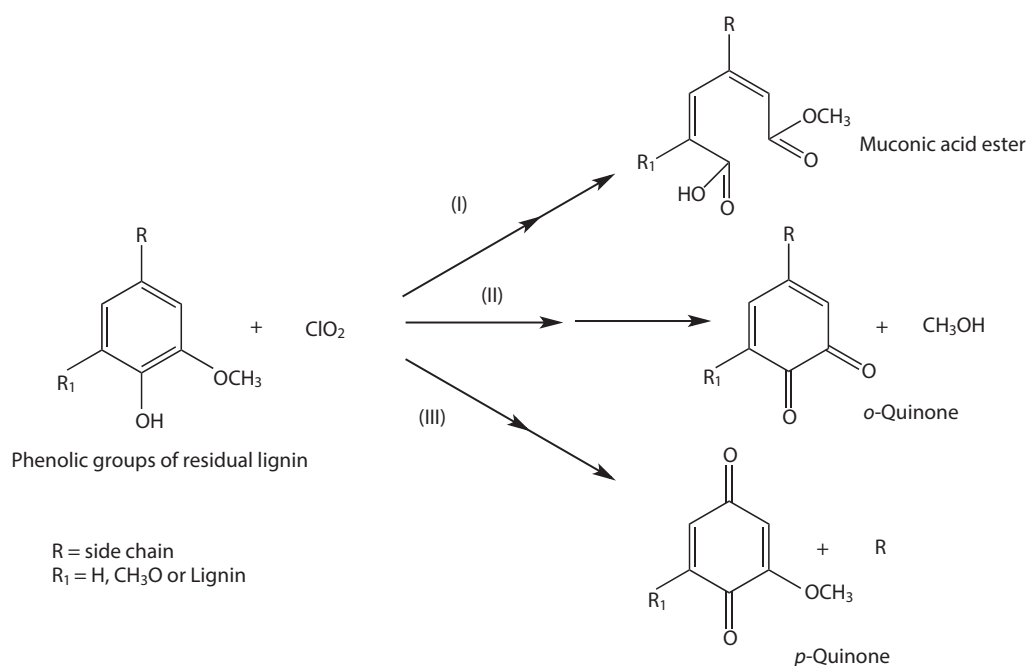


Figure 21.1 Reactions of chlorine dioxide with phenolic groups in residual lignin during a D_0 stage.

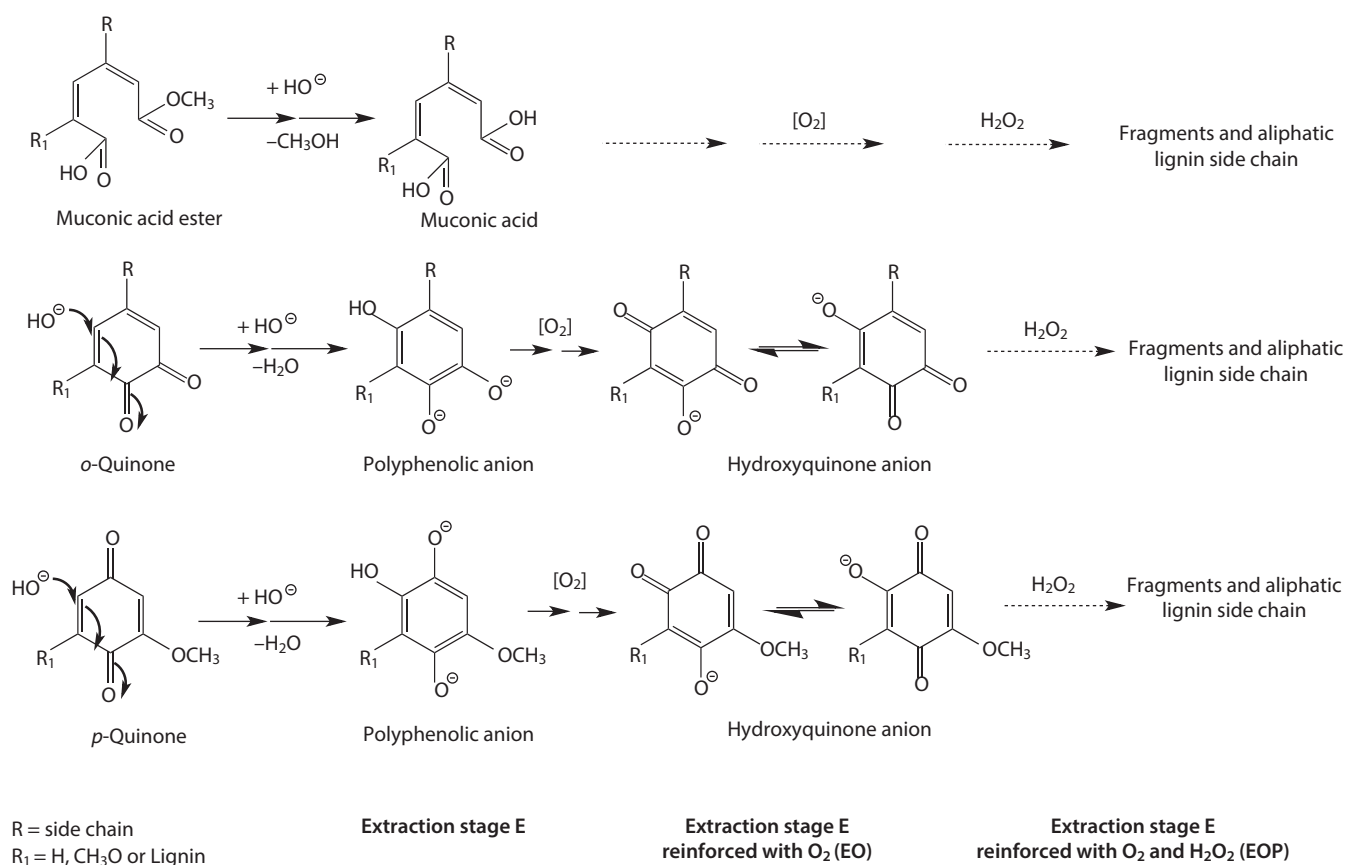


Figure 21.2 Reactions of muconic acid ester, o - and p -quinones with alkali to form polyphenolic structures during an E stage of D_0 oxidized pulp [20]. Hydroxyquinone anions are formed during a reinforced extraction stage with oxygen (EO) of D_0 oxidized pulp [21]. Reinforced extraction stage with oxygen and hydrogen peroxide (EOP) on D_0 oxidized pulp is also considered [22].

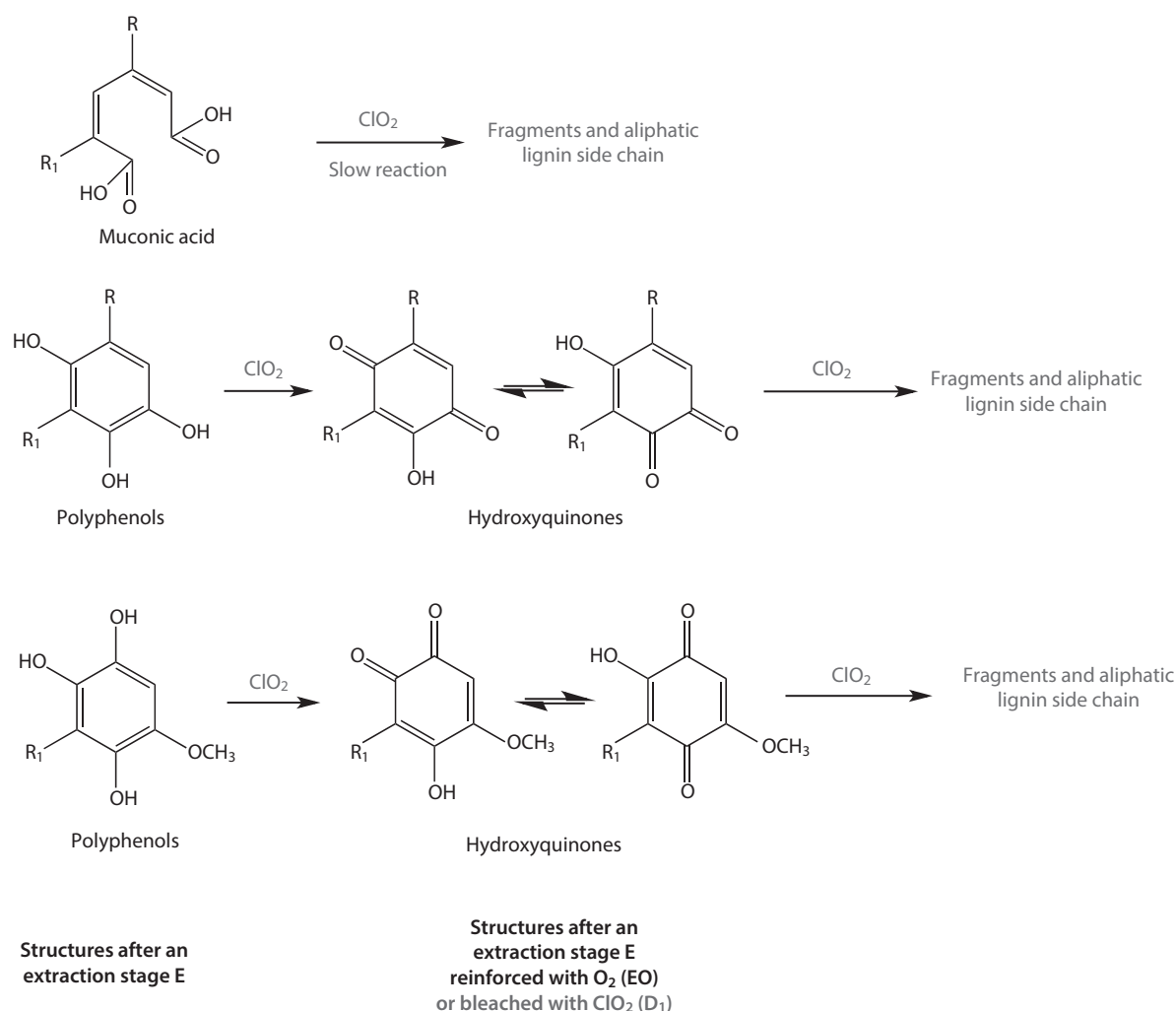


Figure 21.3 Reactions of muconic acids, polyphenols and hydroxyquinones during a ClO_2 bleaching stage D₁ [22].

quinone fragments and muconic structures in various acidic derivatives, soluble in the bleaching liquor (Figure 21.3) [22].

The oxidation of the polyphenolic groups in the oxidative-reinforced extraction stage, allowed in a D₁ stage chlorine dioxide to oxidize less reactive structures such as quinonoid, muconic and non-phenolic entities. It was observed [22] that bleaching kraft pulp with a D₀/alkaline extraction/D₁ sequence leads to a common brightness end value, regardless of the type of extraction employed, E or EO or EOP. The main difference among the pulps was how quickly the ceiling brightness was reached, indicating that the pulps have similar residual chromophores limiting their bleaching to higher level.

After pulping, and especially after oxygen delignification, kraft and other alkaline pulps contain not only residual lignin but also significant amounts of false lignin, consisting of hexenuronic acid (HexA) and other non-lignin structures, which are partly removed by a ClO_2 stage [23]. Some false lignin structures may be still present in fully bleached pulps

[23]. It was observed by Lachenal *et al.* [24–27] that the bleachability of alkaline pulps was very dependent on the quantity and the structure of residual quinonoid groups after pulping. Quinones linked to phenolic lignin fragments appeared possible structural elements for limiting the bleachability of some pulps.

21.2.1.3 Totally Chlorine-Free (TCF) Bleaching

Totally chlorine-free bleaching involves oxygen (O), hydrogen peroxide (P), ozone (Z) and sometimes peracetic acid (P_a). One of the most established bleaching stages is the OQP sequence: after the oxygen stage, the pulp is treated with a chelating agent (Q) prior to an alkaline hydrogen peroxide stage to remove transition metals, such as copper, manganese and iron, very detrimental to the bleaching [6]. With this sequence, brightness in the range of 70–75 ISO could be reached [6]. Several additional steps using, for example, ozone and/or peracetic acid, are necessary to reach high brightness near to 90 ISO [28]. The major lignin

degrading reaction in peroxide bleaching is a side-chain displacement reaction in phenolic phenylpropane units containing an alcoholic group on the C_α of the chain [29]. This Dakin-like reaction requires an initial formation of a quinone methide implying only phenolic structures, thus, the latter ones are preferentially degraded [29]. The strong bleaching action observed with alkaline hydrogen peroxide is due to the nucleophilic attack of perhydroxyl anion (HOO^-) on quinones, enones and quinone methides, introducing peroxidic groups in their structures, leading to their destruction in smaller fragments [9]. The different reactions are described in Figure 21.4.

Ozone is an electrophilic bleaching reagent having predominantly cationic properties [10]. Ozone reacts with aromatic and olefinic structures in 1,3-dipolar cycloadditions with the formation of a primary ozonide, which might undergo either rearrangement into a secondary ozonide or cleavage with the formation of carbonyl-containing fragmentation products, i.e., aldehydes, ketones and/or acids (Figure 21.5) [10].

Ozone is a chemical reagent both for ECF and ECF bleaching [30–32]. The ozone stage might be placed after the oxygen stage as a delignifying stage or later as a bleaching stage [30, 32]. The use of ozone as delignifying agent is more detrimental for the cellulose chain integrity than when used as bleaching agent. The pulp viscosity decrease is less when ozone is used in the final bleaching stages [30]. Chlorine dioxide degrades mainly phenols and is not very reactive against quinones, whereas ozone degrades both aromatic structures, phenolic or not, and quinones [31, 32]. This explains why for final bleaching, there is a pulp resistance to ClO_2 and a better efficiency of the ozone treatment [31].

21.2.1.4 Identification of Chromophores after Bleaching

Chemically pure glucans like bacterial cellulose are poor UV and visible light absorbers, whereas cellulosic pulps contain different chromophores formed from different polysaccharides because of chemical reactions during pulping and bleaching [33].

The chemical nature of the chromophores in cellulose has been assigned to glycosidic bonds [34]. Arndt and Stevens [35] demonstrated that mono- and disaccharides absorb only between 150 and 190 nm using UV-circular dichroism. Nevertheless, Bikova and Treimanis [36] observed absorption bands at 200–220 nm and 270–290 nm for oxidized xylans and monocarboxyl celluloses in alkaline solutions due to carbonyl and carboxyl groups respectively. In addition, these authors [36] assigned absorption bands at 230–250 and 290–320 nm to heteroaromatics of the furan and pyron type, and absorption above 300 nm with maxima at 350–370 and 430–450 nm to conjugated heteroaromatics.

The general processes of pulping and bleaching, which are required to obtain pure cellulose, without non-cellulosic wood components, induce the formation of minute amounts of chromophoric compounds (see aforementioned “bleaching of fibers”). The concentrations of these structures are generally extremely low, in ppb range. Due to their high molecular extinction coefficient, the chromophores are easily observable as a yellow coloration, because the human eye is very sensitive in the 400–500 nm yellow range. The chromophore content has so far been quantified as brightness, which is a percentage of diffuse reflectance (measured at 457 nm) of papers versus a white standard. The brightness is inversely related to yellowness. The chemical identification of the chromophores in bleached cellulosic fibers is rendered difficult by their low concentration and by the large number of different compounds contributing to the overall yellowness. The chromophores might be bound to the cellulosic matrix covalently or by adsorption, and located either on the surface or inside the fibers.

Recently, Rosenau and his group developed a novel analytical technique to isolate and identify well-defined chromophoric structures from bleached cellulosic fibers [37–39].

The technique comprises treatment of cellulosic material with boron trifluoride/acetic acid complex containing sulfite, chromatographic separation of the resulting chromophores-containing mixture, and structure determination of the main constituents by NMR and mass spectrometry and also comparison with authentic samples. Both adsorbed and covalently bound aromatic and quinonoid compounds are selectively released by the treatment. Covalent ester, ethers and carbon-carbon bonds extending from aromatic systems between chromophores and cellulose are broken [37–39]. Highly stabilized hydroxy-1,4-benzoquinone, hydroxy-5,8-naphthoquinones and 2-hydroxyacetophenones are the key compound classes found in bacterial cellulose, cotton and highly bleached pulps (Figure 21.6) [39].

Some of the compounds, called Theander products, arise from degradation of hemicellulosic and cellulosic polymers mainly upon acidic, alkaline and thermal treatments (Figure 21.7) [40–43].

21.2.2 Brightness Reversion

Brightness stability of bleached chemical pulps is an important characteristic for many paper grades. The interaction of environmental factors such as UV light, temperature and humidity with residual lignin, uronic acids and oxidized carbohydrates has been postulated as the main cause of color reversion [44]. Several factors have an effect on pulp brightness stability: wood origin [45], pulping process and bleaching sequences [46, 47], content and chemical structure of residual lignin [29, 48], resins [49], hemicellulose/uronic acid groups [50], oxidized carbohydrates [23], presence of metals

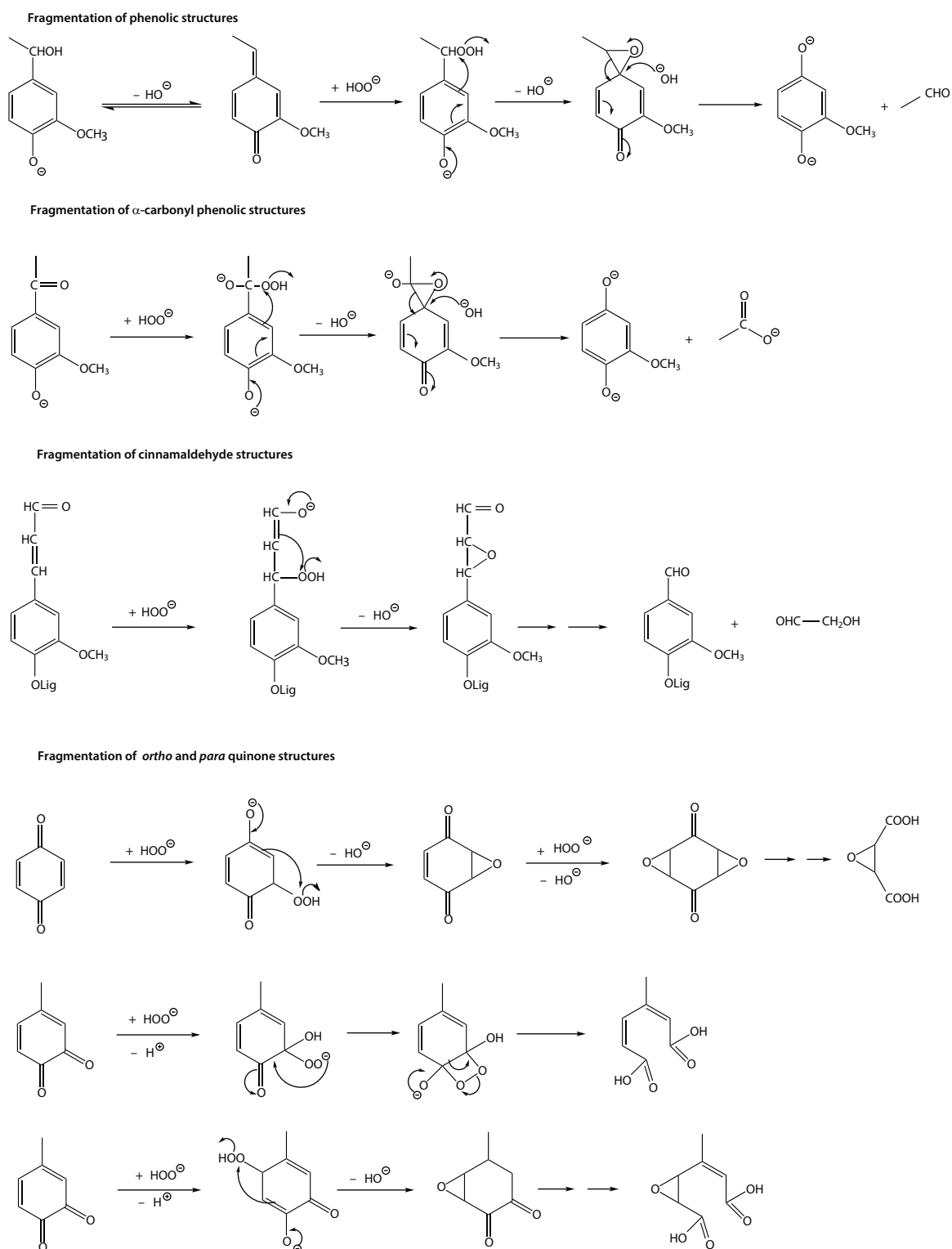


Figure 21.4 Reactions of hydrogen peroxide with various lignin structures during alkaline (P) bleaching stage [9].

[47, 51] and atmospheric pollution [52]. Exposure time, pulp pH, and dryness also have a significant effect on brightness instability caused by heat [53].

21.2.2.1 Photochemical Processes

The absorption of light by pulps or cellulosic fibers generally causes a decrease of the polymerization degree of cellulose

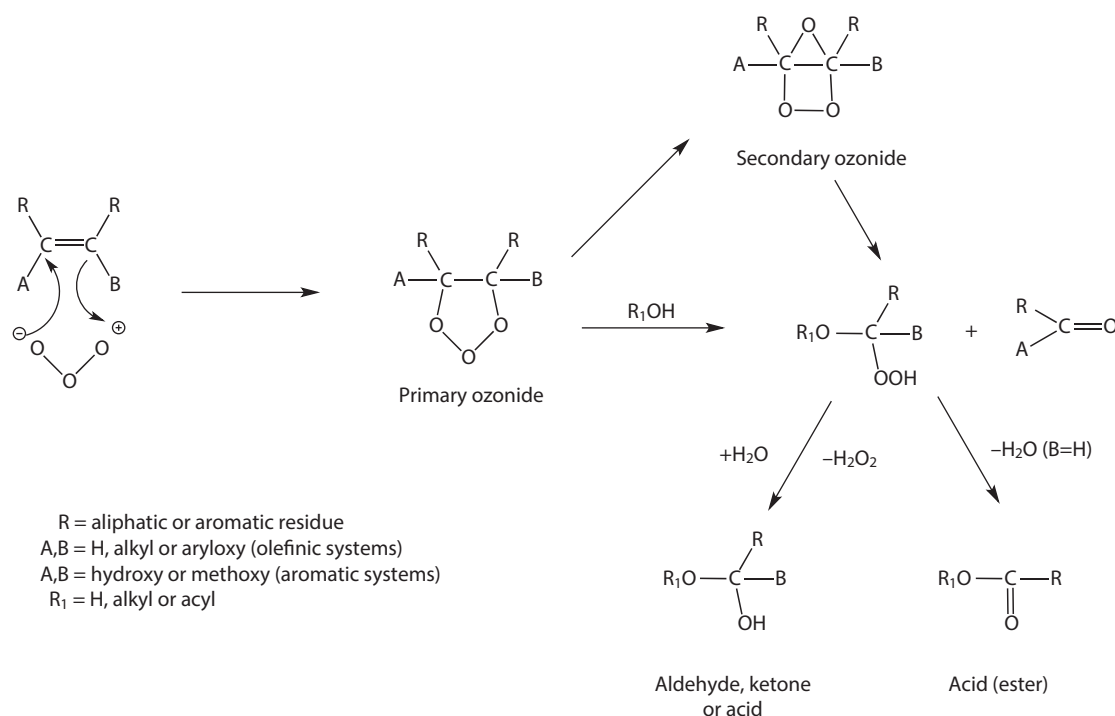


Figure 21.5 Reactions of ozone with various lignin structures during ozone bleaching stage [10].

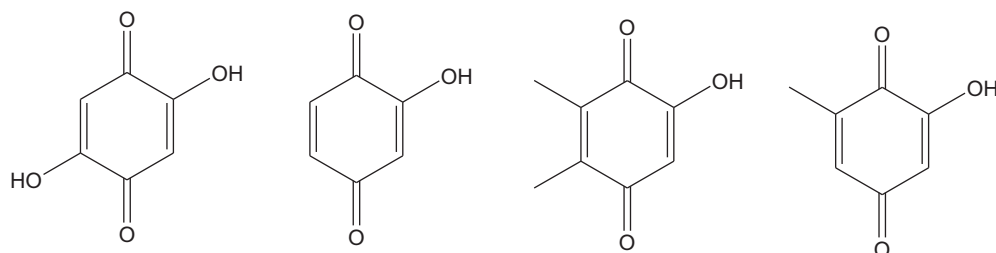
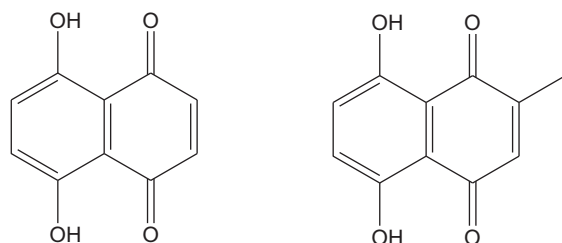
polymer and an increase of the copper number, i.e., the number of carbonyl functions, as well as an increase of alkali solubility [33]. Moreover, light-induced degradation induces yellowing and formation of carbonyl and carboxyl groups along the cellulosic chain. Carbon monoxide, carbon dioxide and hydrogen are the main gaseous products formed during photolysis of polysaccharides [33]. Photochemical brightness reversion of cellulosic fibers, in contrast to artificial irradiations, involves low intensity light in the visible and near UV regions (> 330 nm). Castellan *et al.* [54] studied the optical sensitivity of bleached bisulfite chemical pulps to UV light by UV-Visible diffuse reflectance spectrometry and fluorescence emission. They showed that the instability of peroxide bleached pulps was reminiscent of lignin-rich pulps (*vide supra*) and was due to residual lignin [54]. Incorporation of an ozone stage in the bleaching sequence improved the light stability of the pulp, whereas chlorine dioxide sequences brought some instability due to peroxide species in the cellulosic polymer [54]. Using the same type of techniques, Forskåhl *et al.* [55] concluded that heat and light induce different changes in the chromophore content of the pulps and a sequence Z/P/Z/P induced a good stability against both light and heat. Chirat and De La Chapelle [46] found that neither carbonyl nor carboxyl groups were detrimental to brightness reversion upon light exposure. For a given brightness reversion, light exposure leads to lower pulp degradation than heat exposure, supporting different mechanisms for the two processes [46]. Potthast *et al.* [56] studied the influence of UV irradiation on unbleached and TCF

bleached kraft eucalyptus and sulfite beech pulps. They analyzed the influence of irradiation on the polymer molecular weight distribution, the total number of carbonyl groups and carbonyl profile versus molecular weight [56]. UV irradiation influences the oxidation state (carbonyl content) of bleached and unbleached pulps. In unbleached pulps, the irradiation caused photobleaching, i.e., destruction of larger chromophores, whereas in bleached pulps no such effect was observed [56]. In bleached material, slightly more carbonyls were introduced into kraft pulps as compared to sulfite pulps. Cellulose degradation was relatively low in both types of pulps. The presence of hemicelluloses governed the photochemical behavior and the carbonyl profiles of the low-molecular-weight region of the cellulose matrix [56].

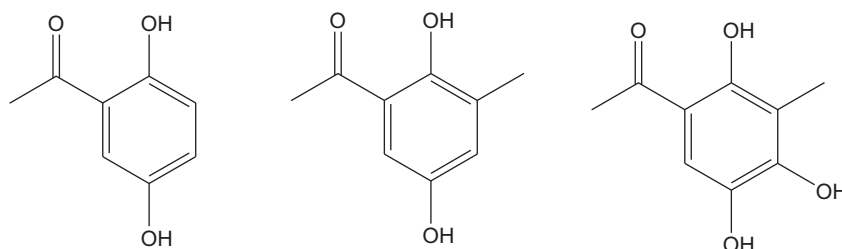
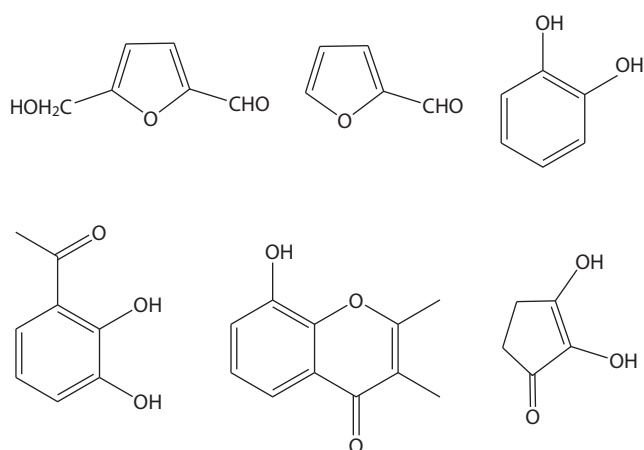
In conclusion, for bleached chemical pulps, the influence of UV/Visible irradiation on brightness reversion appeared to be of much less importance than heat reversion.

21.2.2.2 Heat Processes

The brightness and brightness stability of commercial pulps are quality parameters of great importance, and they strongly affect the pulp price. After transportation and storage, it is important that the pulp has the brightness that the customer ordered. To increase the drying capacity, shorter drying times and higher temperatures are selected, leading to the more serious problem of thermal yellowing. Heat induces thermal processes in cellulosic materials such as bleached chemical wood pulp or paper when they are in contact with

Hydroxy *p*-quinonesHydroxy *p*-naphtoquinones

Hydroxy acetophenones

**Figure 21.6** Residual chromophores in bacterial cellulose, cotton and highly bleached pulps [39].**Figure 21.7** Some of the Theander compounds formed by degradation of polysaccharide fragments [40–43].

hot surfaces or high temperatures (above 100 °C) during their processing for various usages. The material might discolor, yellow or release unpleasant odor.

Many parameters were reported to potentially affect brightness stability of bleached chemical pulps and papers on heat exposure: pulp type, wood species, residual lignin content and hemicellulose, oxidized groups in cellulose, and metal ions [46]. The changes that occurred in the bleaching technology of chemical pulps with the use of new chemical reagents, oxygen, hydrogen peroxide, ozone and chlorine dioxide, in ECF and TCF sequences led to the formation of additional oxidized groups in cellulose (carbonyl and carboxyl groups). The use of hydrogen peroxide, which is a powerful whitening agent, may produce pulps with high brightness but still containing non-negligible residual lignin [46]. Chirat and De La Chapelle [46] showed, by creating selectively oxidized groups on cellulose, that ketone groups impaired heat reversion significantly, whereas aldehyde groups at C₂ and C₃ had only a minor effect. By contrast, carboxyl groups at C₂ and C₃ affect brightness stability to heat.

The yellowing process includes thermal decay of polysaccharide chains to give short-chain products or sugar monomers; this process is facilitated by low pH [50]. High temperature leads to oxidation of the cellulose surface with

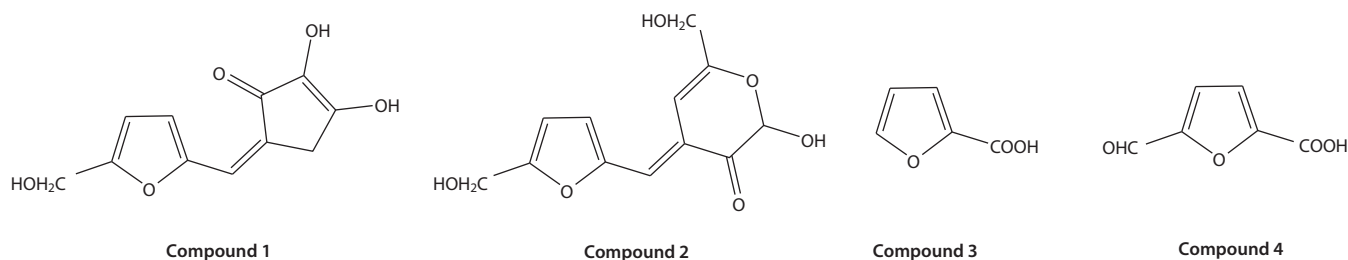


Figure 21.8 Some key compounds formed by heat aging of polysaccharides (see text, [23, 50]).

the participation of oxygen radical [57]. Beyer *et al.* [50] found that the yellowing tendency of pulps upon heating is associated with the presence of thermally less stable polysaccharide components. They are principally represented by hemicelluloses, undergoing partial oxidation and degradation. These substances contain the major part of oxidized groups, such as carboxyl entities, with respect to the whole pulp. They are considered to be the main source of low molecular precursors, which gives rise first to the formation of dehydration products, such as 5-hydroxymethylfurfural or 2,3-dihoxypent-2-enone (reductic acid) (Figure 21.7), and then to colored condensation products [50]. Compounds 1 and 2 (Figure 21.8), identified after their extraction from colored heated pulps, are formed by condensation of 5-hydroxymethylfurfural with reductic acid and a dehydration product of glucose, respectively [50].

Gellerstedt and collaborators [23, 51, 53] studied in detail the thermal reversion of TCF bleached pulps, which are generally less stable than ECF bleached pulps. Hexenuronic acid content, dry level, temperature, time and pH influence the process of color reversion. The color formation reaches a maximum at pH 4.5, but requires long aging time and high temperature [53]. Low molecular weight substances and new aromatic structures are formed during thermal aging [23, 51]. The hexenuronic acid structures are good chelating agents in pulps and are hydrolyzed during thermal aging, lowering the chelating properties of pulp significantly, implying that metal ions were liberated. The metal ions (mainly iron) together with small organic molecules constitute a large part of the colored material soluble in water [51]. Selective removal of oxidizable structures of carbohydrate origin improved the brightness stability and the thermal yellowing was found proportional to the content of hexenuronic acid groups [23]. The mechanism of color formation involves several stages, including an acid-induced degradation of hexenuronic acid with the formation of reactive compounds such as furoic acid (compound 3), 5-formylfuroic acid (compound 4) (Figure 21.8) and reductic acid (Figure 21.7). One or more of these compounds takes part in further reactions, leading to the formation of colored pulps [23]. An enzymatic post-treatment of bleached hardwood kraft pulp by xylanases resulted in a significant improvement of heat yellowing by selective removal

of hexenuronic acid structures, rather than affecting the lignin-polysaccharide networks [58].

Rosenau *et al.* applied their novel analytical technique previously described [37–39] to study the chromophores created in bleached chemical pulps by heat aging [39]. They also found that the highly stabilized hydroxy-1,4-benzoquinones, hydroxy-5,8-naphthoquinones and 2-hydroxyacetophenones are key compound classes as recondensed chromophores formed upon aging and brightness reversion. Aging and chromophore formation in cellulose is highly dependent on the content of carbonyl groups (“CO effect”). Carboxyl groups, by contrast, are not chromogenic by themselves, but they exert a strong catalytic effect if carbonyl structures are present (“COOH effect”). By means of model compounds, Rosenau *et al.* [39] described a complete pathway from a single keto group in an oxidized anhydroglucose unit (3-keto-glucopyranose) to the final 2,5-dihydroxy-1,4-benzoquinone chromophore, as key intermediate [39]. The whole pathway was identified and supported by X-ray structure analysis and ^{13}C isotopic labeling [39]. Thus, carbonyls in cellulose are the most basic chromophore precursor.

21.3 Lignin-Rich Cellulosic Fibers (High-Yield Pulps)

Mechanical pulping (MP) is the other process with chemical pulping (CP) to produce pulp from wood. MP retains about 80 to 95% of the lignocellulosic fibers; thus, from the same weight of wood a double quantity of pulp is produced for MP when compared to CP, but higher yield induces certain unfavorable properties such as lower mechanical strength, brightness and an important brightness reversion to light. However the high opacity of MP fibers is well suited for printing papers. The defibration of wood is carried out either by grinding or refining [59]. The processes might be pressurized, giving thermomechanical pulp (TMP) or pressurized groundwood pulp (PGWP). Generally the temperature for TMP is set near 130°C, where the lignin polymer becomes softened and the fiber requires less energy to be liberated from the woody material [59]. Combination of a soft chemical treatment and refining allows the preparation of chemithermomechanical pulps (CTMP) displaying higher strength quality fibers. The dominant chemical process for CTMP is

the sodium sulfite treatment for softwoods and hardwoods, whereas sodium hydroxide and hydrogen peroxide treatment were developed for hardwoods [59].

21.3.1 Bleaching of High-Yield Pulps

High-yield pulping to prepare TMP or CTMP leaves most of the lignin in the fibers, so the bleaching process should be adapted to these pulps. The bleaching technology used for chemical pulps is not available for high-yield pulps because the extraction of carbohydrates and lignin should be as low as possible. For newsprint production, the initial brightness of unbleached mechanical pulp, between 55 ISO and 65 ISO, is sufficient, but for higher quality grade paper, such as newsprint, magazines, supercalendered or lightweight coated papers, a bleaching step is required [59].

21.3.1.1 Chromophores and Leucochromophores in High-Yield Pulps before Bleaching

Unbleached mechanical pulps have a yellowish color. This is due to the presence of native wood chromophores and leucochromophores and also to new ones created by the fiber separation process, refining or grinding [60].

Together with α,β -unsaturated aldehydes, quinonoid structures are believed to constitute the major chromophoric systems in mechanical pulp lignins. In contrast with α,β -unsaturated carbonyl chromophores, which are formed exclusively during lignification, *ortho*- and *para*-quinones belong to the lignin of native wood during lignification, but they are also created in mechanical pulps during pulping, bleaching and storage [61].

Coniferaldehyde structures (Figure 21.9) are essentially present in lignin as end groups [62]; their content in native spruce lignin has been estimated to be 3%. This structure is the main contributor to the absorption in the near UV and violet-blue region of the visible spectrum, the maximum absorption being around 350 nm [62]. Coniferyl alcohol structures (Figure 21.9) constitute another important end group in softwood lignin. They absorb around 320 nm and constitute leucochromophores in lignin when they are transformed into colored coniferaldehyde structures by oxidation [62].

Biphenyl structures, mainly included in dibenzodioxocin elements (Figure 21.9) [63], and α -carbonyl- β -aryl ether structures (Figure 21.9), are considered as important leucochromophores in lignins, which are not present as end groups but more likely in the bulk lignin biopolymer [62]. Among chromophoric structures, a dienone structural element (Figure 21.9) was found [60] and proved to be the precursor of β -1 diaryl propane elements, mainly as end groups [62]. Phenylcoumaran structures (Figure 21.9) were found to be quite resistant towards all kinds of high-yield pulping [60, 62] in contrast to studies with molecular models, which indicated their transformation in phenylcoumarone and stilbene

structures [64]. The natural content of stilbenes in spruce wood is considered to be very low [62] and very little, or not at all, seems to be formed during refining [60]. In addition, metal ion complexes play an important role in the color of pulps [60]. In that respect, colored metal ion complexes, absorbing light throughout the entire visible region, are formed during the refining [60].

Vanillin structures can be considered as minor lignin end groups in wood and unbleached TMP, but they are important chromophores because they absorb above 300 nm and they can be transformed in hydroquinone in peroxide bleaching [62].

It was found by near infrared-FT-Raman spectroscopy that *para*-quinone structures (Figure 21.9) are largely responsible for determining the pulp brightness of spruce TMP [65]. *Para*-quinones were clearly detected in softwood but not in hardwood [65]. Confocal laser scanning microscopy [66] was used to detect *ortho*-quinones (Figure 21.9) in softwood after specific fluorescent labeling with orthophenylenediamine, giving fluorescent phenazines. The highest concentration of *o*-quinones was found in the torus middle lamella, cell corner, ray cells, and in lesser concentration in the cell wall [66]. After defibration, these *o*-quinones will survive in thermomechanical pulps.

Due to limits on harvest, and/or public pressure to supply virgin wood fibers for high-yield pulps, some attempts have been made to use other wood species containing highly colored extractive [67]. Also, straw from annual plants was not found appropriate to produce bleached high-yield pulps, because they have a strong residual yellowness due to their important content of cinnamic acid derivatives (Figure 21.9) [68].

21.3.1.2 Chromophores and Leucochromophores in High-Yield Pulps after Bleaching

The current industrial technologies for the bleaching of high-yield pulps use the oxidative alkaline hydrogen peroxide process [69] and/or the reductive sodium hydrosulfite process [70]. Alkaline hydrogen peroxide, in the presence of peroxide stabilizers such as sodium silicate [71] and magnesium sulfate [72], is able to bleach spruce TMP to brightness near 70–80 ISO. However this process reduces the pulp yield and produces effluents with high chemical oxygen demand and pulp with high anionic trash [73]. Sodium hydrosulfite bleaching is more selective but less effective in terms of maximum brightness gain and needs to be carried out in a relatively oxygen-free environment. It also generates byproducts such as thiosulfate, corrosive for paper machines [74]. More recently Hu *et al.* [75] described the use of water-soluble phosphorus compounds, as a new class of very efficient reducing bleaching agents usable over a wide range of consistency, pH and temperature.

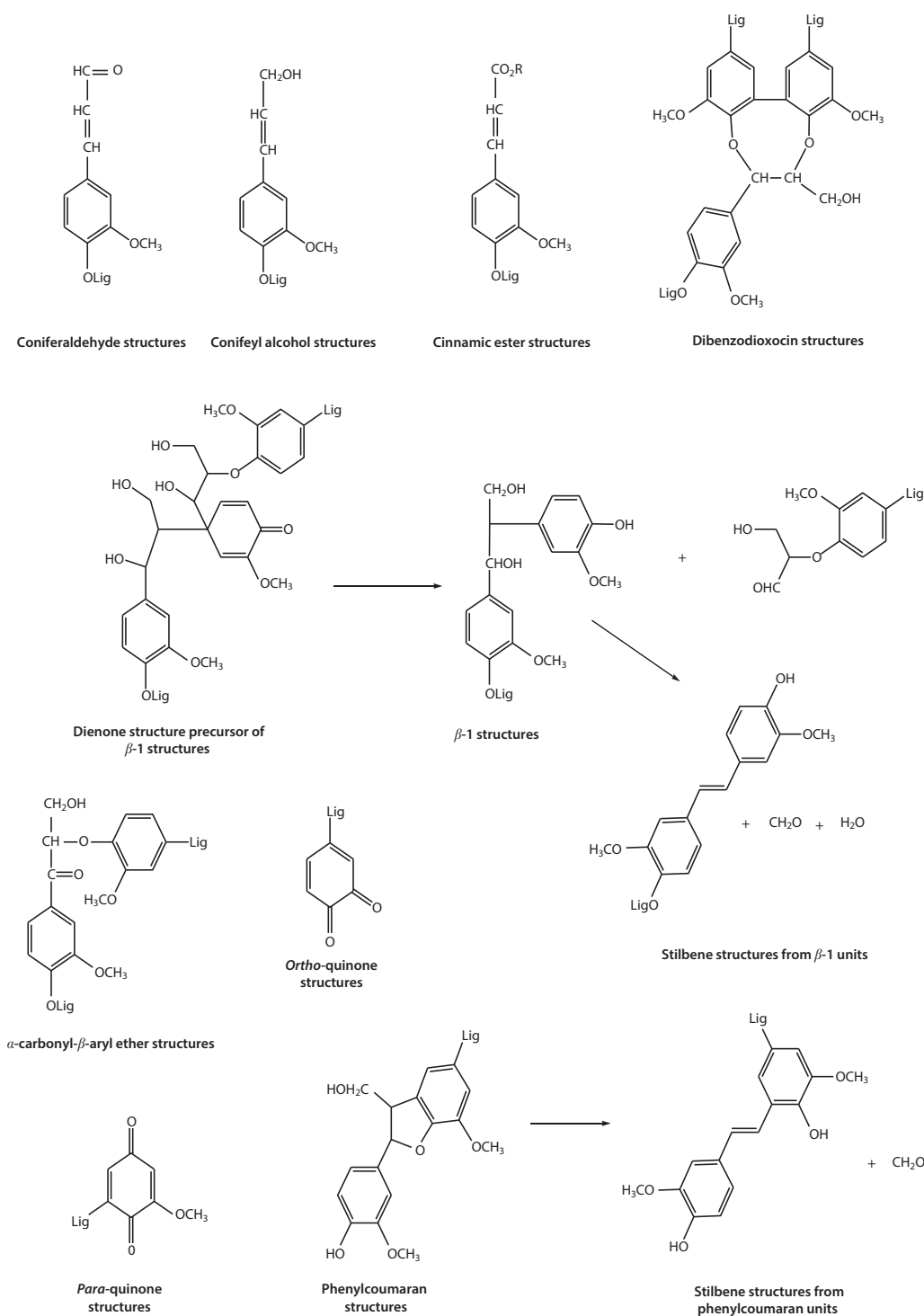


Figure 21.9 Some key chromophores and leucochromophores in unbleached high-yield pulps (see text).

The major native chromophoric structures present in wood, coniferaldehyde and quinone structures, have been shown to react rapidly with alkaline hydrogen peroxide with the formation of colorless degradation products such as organic acids, hydroquinone and vanillin structures (see Figure 21.4) [76]. Pan *et al.* [77] revisited the reaction of

hydrogen peroxide in alkaline medium on coniferaldehyde structures by comparison of the action of peracetic acid in neutral medium. The mechanism of hydrogen peroxide bleaching involves nucleophilic attack by perhydroxyl anion (HOO^-), and its pKa at 25 °C being equal to 11.6 sufficient alkali is needed to generate sufficient anion concentration

[77]. By contrast, the pKa of peracetic acid is equal to 8.2, and the generation of sufficient concentration of peracetate anion can be obtained at neutral or moderate alkaline conditions. Peracetate anion is also a strong nucleophile, leading to selective removal of chromophores in high-yield pulps [77]. The degradation of coniferaldehyde-type structures occurs primarily by oxidation of the double bond of the side chain to an epoxide function followed by breaking the α,β -bond and by splitting off the γ -carbon. The α,β -bond cleavage products are mainly substituted benzaldehydes and benzoic acids. The p -hydroxybenzaldehyde derivative (substituted vanillin) subsequently undergoes the Dakin reaction to produce substituted methoxyhydroquinone. On the other hand, the β,γ -bond rupture predominantly produces phenylacetic acid-type compounds, especially when peracetic acid is the reagent. Hydrogen peroxide gives more products resulting from α,β -double bond cleavage, with possible formation of methoxyhydroquinones, very light sensitive leucochromophores [77]. By contrast, peracetic acid gives more products resulting from β,γ -bond cleavage with formation of phenylacetic acid derivatives [77], less sensitive to UV-light. The reactions are summarized in Figure 21.10.

Gellerstedt and Zhang showed that during alkaline bleaching of spruce groundwood and chemithermomechanical pulps with hydrogen peroxide, diarylpropane structures generate guaiacyl stilbene structures (Figure 21.9) [62]. These structures are moderately reactive against hydrogen peroxy anion, whereas they are degraded into the corresponding aromatic aldehydes and carboxylic acid under peracetic acid treatment [78]. Combining peracid and hydrogen peroxide

treatments appeared more effective in reaching high brightness for ground pulps [79]. Agarwal and Landucci [65] investigated the structural modification of spruce TMP under bleaching by NIR FT-Raman spectroscopy and ^{13}C NMR spectrometry and they showed that coniferaldehyde elements are removed first by H_2O_2 treatment; then an additional degree of brightening is obtained, and correlated to the removal of p -quinones either by oxidative or reductive treatments [65]. Using milled pulp lignin extracted from softwood mechanical pulp, Rundlöf *et al.* [76] investigated by NMR spectrometry (^1H , ^2D , and ^{31}P) the behavior of chromophoric structures under alkaline hydrogen peroxide bleaching. The authors confirmed the breakdown of coniferaldehyde structures and showed that the concentration increase of vanillin units was only marginal despite the fact that vanillin was formed from coniferaldehyde [76]. Vanillin structural elements were transformed into hydroquinone, the latter being oxidized into p -quinones by residual decomposed products from hydrogen peroxide.

A phenomenon called "alkali darkening" is a concern during peroxide bleaching, as it affects the bleaching efficiency and the brightness ceiling of high-yield pulps. Giust *et al.* [80] showed that the alkaline darkening of high-yield sulfite and stone ground pulps is caused by formation of o -quinones and coniferaldehydes. The alkali darkening can be eliminated by treatment with borohydride that eliminates quinones from TMP or prevents them from forming [81]. Also, under mild alkaline conditions (low temperature, low alkalinity, short time), the newly formed chromophores can be destroyed by a subsequent peroxide stage [82], whereas

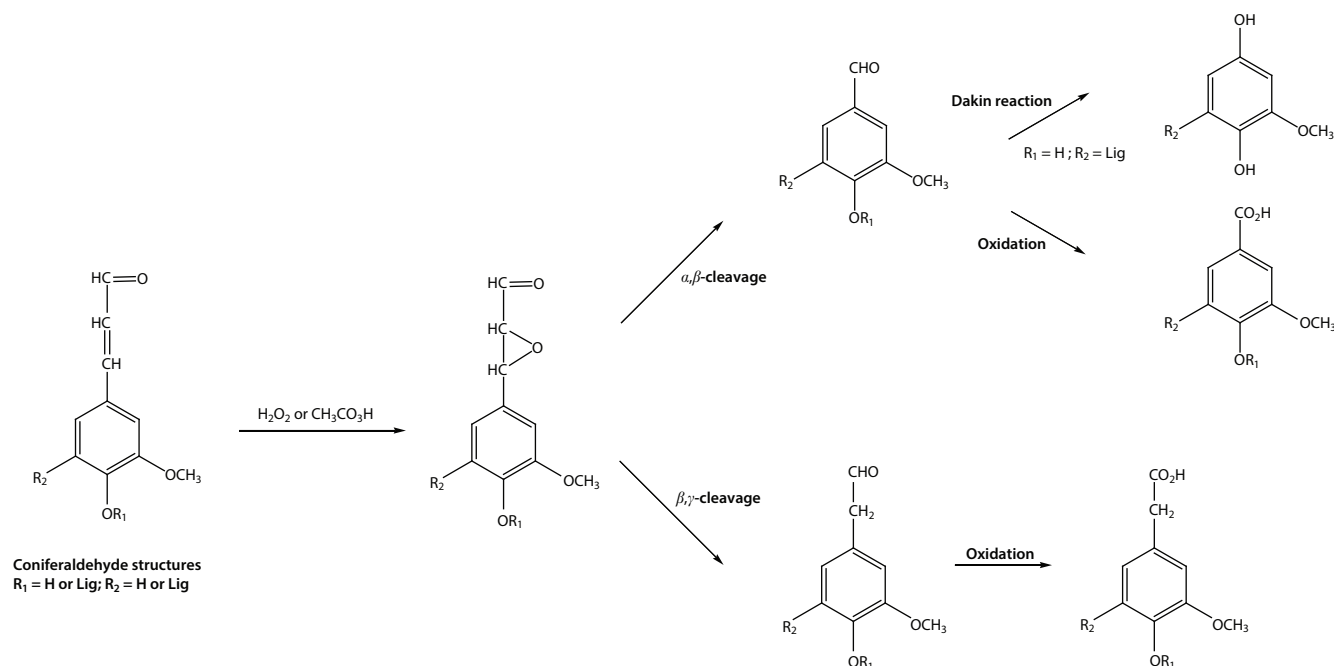


Figure 21.10 Reactivity of coniferaldehyde structures in the presence of hydrogen peroxide or peracetic acid in alkaline or neutral aqueous media during bleaching of high-yield pulps [77].

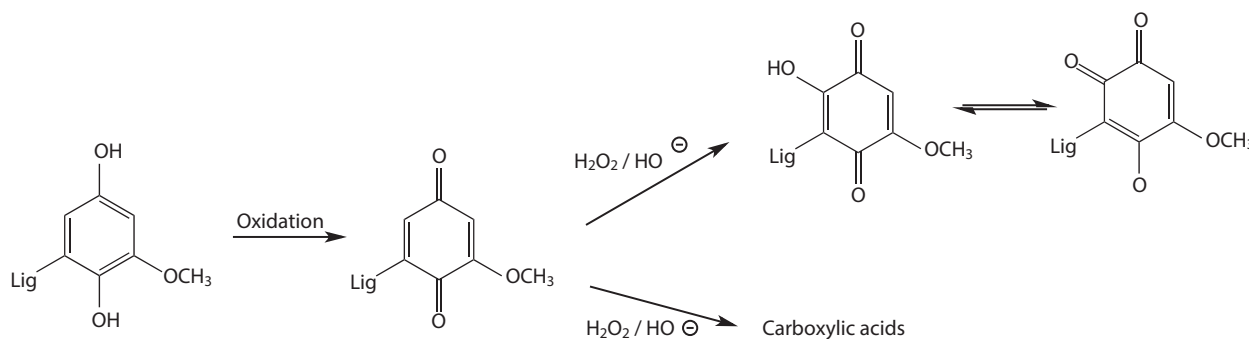


Figure 21.11 Formation of hydroxyquinones in an alkaline hydrogen peroxide oxidation system [76].

harsh alkaline conditions result in the formation of peroxide-resistant chromophores [82].

Rundlöf *et al.* [76], showed that elimination of phenolic hydroxyl groups in lignin does not suppress the brightness ceiling observed in bleaching mechanical pulp, due to alkali darkening. The latter is likely due to the action of alkaline hydrogen peroxide to quinones giving hydroxyquinones [76], which are very stable structures, as already mentioned in the aging of chemical pulps. These reactions are described in Figure 21.11.

Hydrosulfite, the main reagent used in reductive brightening, is able to reduce many types of aldehydes and ketones [70], however it reacts sluggishly in water with ketones. The brightening of lignin by sodium hydrosulfite is based on the reduction of *ortho*- and *para*-quinones to hydroquinones and catechols, but also on the sulfonation of enones and carbonyl structures including or not a reductive step. Some reactions are reported in Figure 21.12 as an adaptation of reference [70].

21.3.2 Brightness Reversion and Stabilization Attempts

21.3.2.1 Brightness Reversion

The photoyellowing is the major problem in using bleached high-yield pulps for high quality papers. It is generally accepted that the photoyellowing is mainly due to photooxidation of lignin via a series of radical reactions [3]. Numerous research efforts have been carried out in an attempt to elucidate the exact mechanism by which mechanical pulps photoyellow, and some articles giving important mechanistic aspects have been published [3, 83–93]. A tentative rationalization of the complex mechanism of photochemical brightness reversion of bleached high-yield pulps (HYP) will be presented and some of the solutions to limit the process will be indicated.

The effect of oxygen atmosphere on HYP photoyellowing has been a subject of debate for a long time. Careful experiments made on thorough vacuum degassed CTMP paper sealed in Pyrex container showed that photoyellowing

remained without the presence of oxygen, but the rate of discoloration was less [94], in contrast to Leary's results [95, 96] and Lin and Kringstad's experiments [97]. Paulsson *et al.* [98] came to a similar conclusion on bleached CTMP comparatively irradiated in the presence of air atmosphere or in the presence of oxygen-free argon. The photoyellowing decreased only moderately [98], indicating that oxygen is not the only cause of light-induced discoloration or that only a trace amount of oxygen strongly adsorbed on the fiber material is necessary to cause discoloration.

The numerous reactions proposed for color formation during the light-induced yellowing of HYP can be divided into three steps.

Absorption of UV light: Yellowing reactions are initiated by UV-light [99] in the 290–400 nm wavelength range that is absorbed by the lignin chromophores as discussed in the “chromophores and leucochromophores” section. By contrast, visible light induces a photobleaching effect [99].

Formation of radicals: The key radicals formed as important intermediates in the photoyellowing of HYP are phenoxy and ketyl radicals [100] (Figure 21.13).

The first and older statement for the formation of phenoxy radicals was the abstraction of phenolic hydroxyl hydrogen either by a carbonyl group in the triplet state [101], or by singlet oxygen [102], or by hydroxyl radical and/or peroxy radicals [103] (Figure 21.13, path A).

Gierer and Lin [104] and Castellan *et al.* [105] showed that cleavage of β -O-4 bond in 2-aryloxy-1-arylpropanones structures efficiently generates phenoxy radicals from phenolic and non-phenolic units (Figure 21.13, path B).

Scaiano *et al.* [106] and then Schmidt and Heitner [107] described the light-induced intramolecular cleavage of β -O-4 bond in arylglycerol- β -aryl ether structures and proposed this process as the main photodegradative pathway for lignocellulosics (Figure 21.13, path C).

Castellan *et al.* [108] noticed that direct photolysis of phenols in lignin, absorbing above 300 nm, was an important source of colored chromophores in bleached HYP (Figure 21.13, path C). Gellerstedt and Zhang [62] showed that phenolic stilbene structures were formed in HYP by hydrogen peroxide bleaching from diarylpropane structures

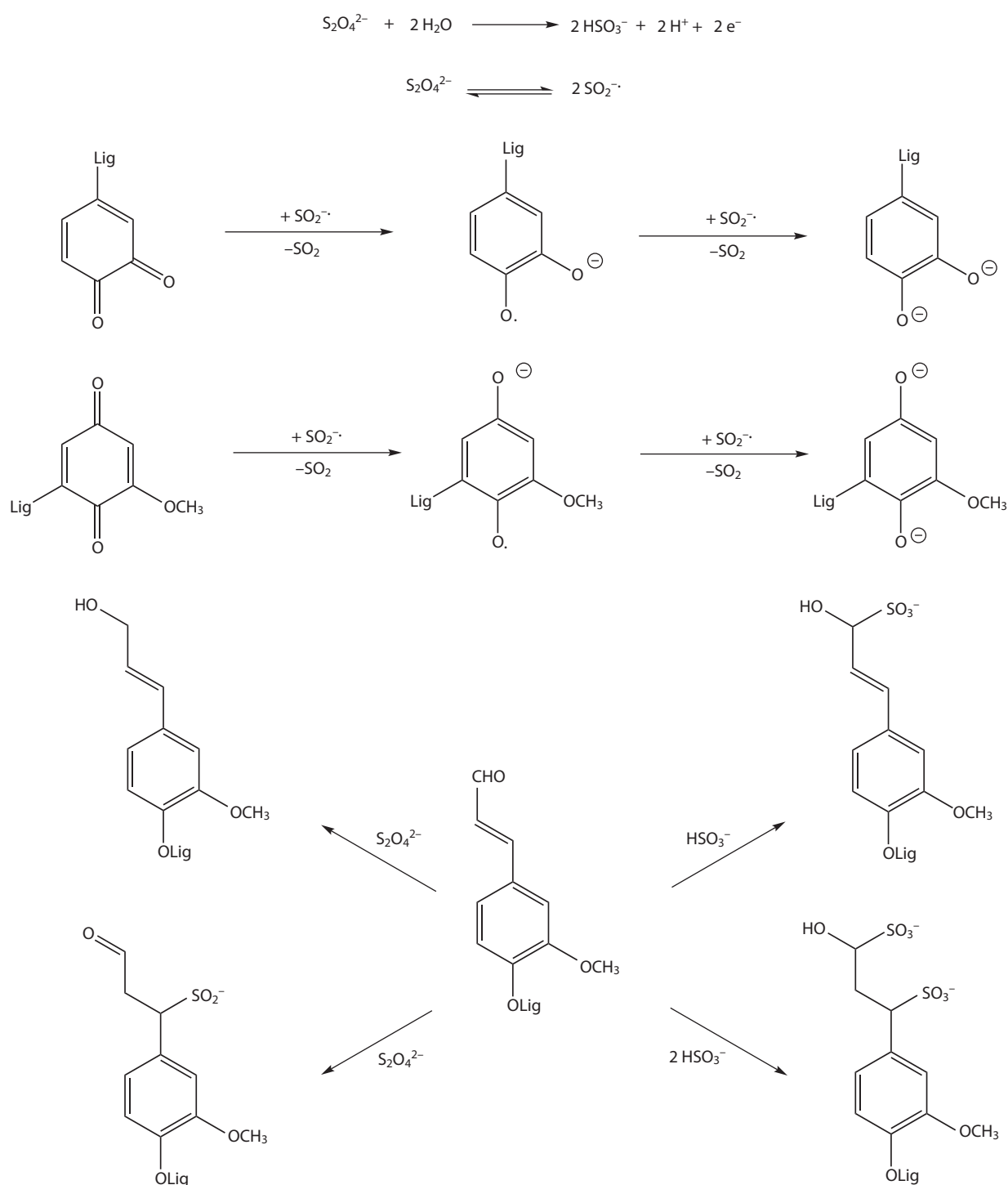


Figure 21.12 Action of sodium hydrosulfite on quinones and coniferaldehyde-type structures (adapted from [70]).

(β -1 units, *vide infra*). These units are very prone to photooxidation and might be the main source of photoyellowing of bleached HYP [62, 109] (Figure 21.13, path D). Ruffin *et al.* [110] did not confirm their involvement in the photoyellowing process, according to the low quantity of phenolic stilbenes found in bleached HYP and the inefficiency of the

hydrogenation process to stabilize HYP, in contrast to styrene polymeric models [109].

Formation of chromophores: The formation of phenoxy radicals is the first step in going to colored units. Phenoxy radicals are further oxidized by molecular oxygen or peroxidic species into *ortho*- and *para*-quinones [86, 92].

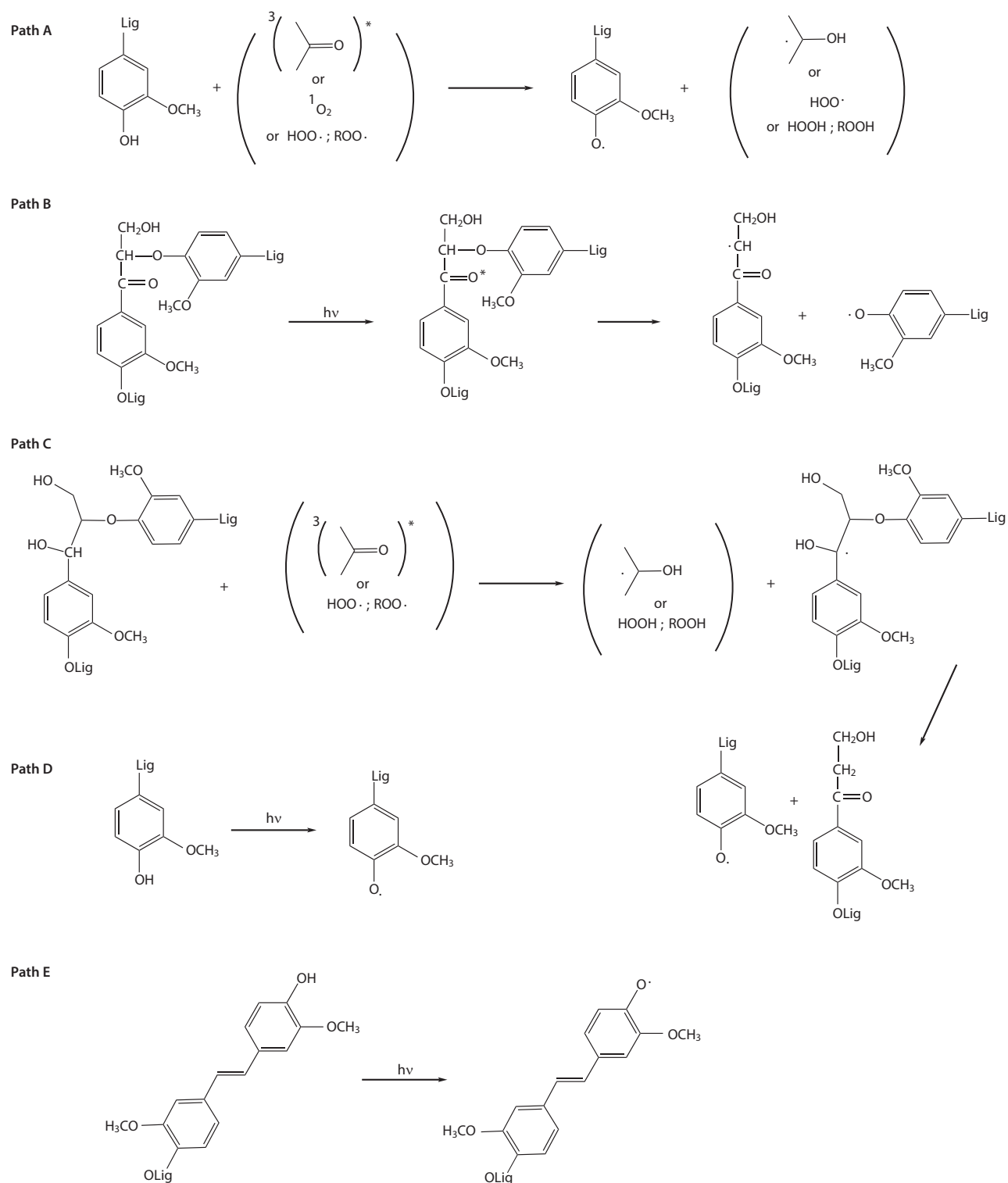


Figure 21.13 Reaction mechanisms for the formation of phenoxy radicals on irradiation of peroxide bleached HYP (adapted from [3, 83-93]).

Figure 21.14 describes some simplified schematic routes to quinones from phenoxy radicals.

The *o*-quinones formation under UV-irradiation in alkaline peroxide bleached stone ground spruce pulp was clearly

shown by Argyropoulos [89] using ^{31}P NMR spectrometry after selective derivatization with trimethylphosphite of the irradiated pulps. The formation of *o*-quinones is observed in the early irradiation, followed by a content reduction of these

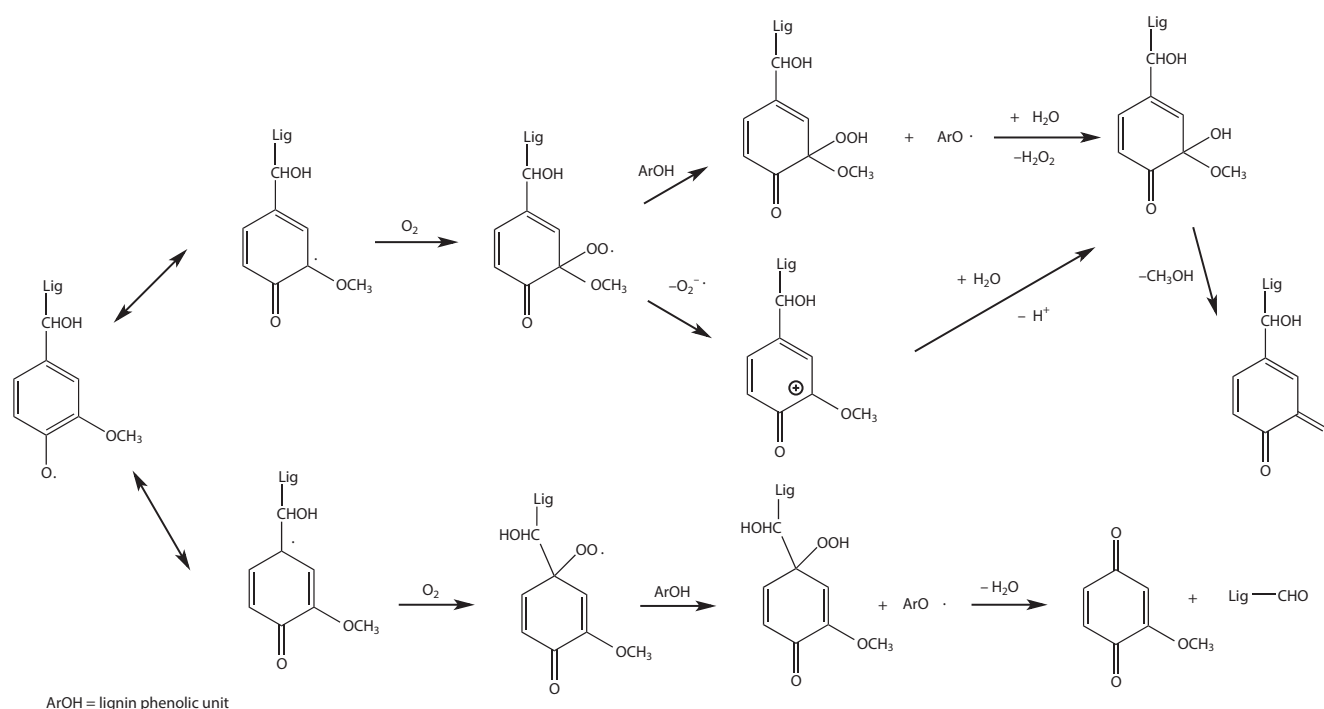


Figure 21.14 Formation of *ortho*- and *para*-quinones from phenoxy radicals on irradiation of peroxide bleached HYP (adapted from [3, 83–93]).

species at later phases due to secondary condensation reactions [89]. Agarwal [88], using FT-Raman spectroscopy studies on peroxide bleached HYP, concluded that coniferaldehyde and coniferyl alcohol structural units are degraded in non-yellowed photoproducts, mainly vanillic acid elements, whereas hydroquinone units are oxidized into colored *p*-quinonoid structures. Later, Jäskeläinen *et al.* [91], using resonance Raman spectroscopy, confirmed these conclusions.

The couple hydroquinone/*p*-quinone also appeared to be another important element in the photoyellowing process of bleached HYP [93, 111–113]. 2-Methoxyhydroquinone, presenting a significant absorption above 300 nm, where the sunlight is efficient, undergoes a more severe yellowing than 4-methylcatechol [113]. 2-Methoxy-*p*-benzoquinone is very rapidly photoreduced and then behaves as 2-methoxyhydroquinone. Mechanistic studies [93] using laser flash photolysis and continuous irradiation indicated that the photochemical behavior of hydroquinone was likely a combination of oxidation by ground state oxygen and photohydration of the formed quinone from its triplet state, giving, *inter alia*, more colored *o*-quinonoid type molecules (Figure 21.15).

Parkas *et al.* [114, 115] studied the photoreactivity of lignin on filter paper by quantitative solution ^{13}C NMR spectrometry using ^{13}C -enriched dehydrogenation polymer (DHP), mimicking lignin. The DHPs were selectively ^{13}C -enriched successively at position α , or β , or γ of the phenylpropane lignin unit side chain, or at position 1, or 3, or 4, or 5 of the lignin aromatic rings. They showed that coniferyl alcohol end groups

were almost completely removed upon irradiation, while the amount of coniferaldehyde end groups appeared to increase somewhat with the subsequent formation of α -carbonyl structures, e.g., vanillin end groups. A small amount of vanillic acid end groups were also detected [114]. Although a drastic photoyellowing of the papers was observed, no signals assignable to quinoid carbons were detected in the spectra [115], likely due to non-extractable compounds for the solution NMR analysis. Castellan *et al.* [112] described a similar observation in studies of the photochemistry of methoxyhydroquinone incorporated in hydroxypropylcellulose.

The important photostabilization effect on peroxide bleached HYP noticed after a short treatment of acetylation [85, 90, 116, 117] is in accordance with the importance of phenolic functions of lignin during the photoyellowing process. The phenolic groups might be of different structural origin such as absorbing stilbenes and/or hydroquinones. It was shown by Paulsson [85] that esterification occurred mainly on phenols and γ -hydroxyl groups of the side chains; the benzylic hydroxyl groups being almost unaffected. The remaining residual *p*-quinones after bleaching, which are not eliminated by the Winter-Thiele reaction upon acetylation, are photoreduced by irradiation and also contribute to the photoyellowing process. The β -O-4 bond cleavage in arylpropanone units (Figure 21.13, path B), and the ketyl pathway (Figure 21.13, path C), which operate on phenolic and non-phenolic units, are likely involved in the long-term degradation of lignocellulosics. Nevertheless, the contribution of

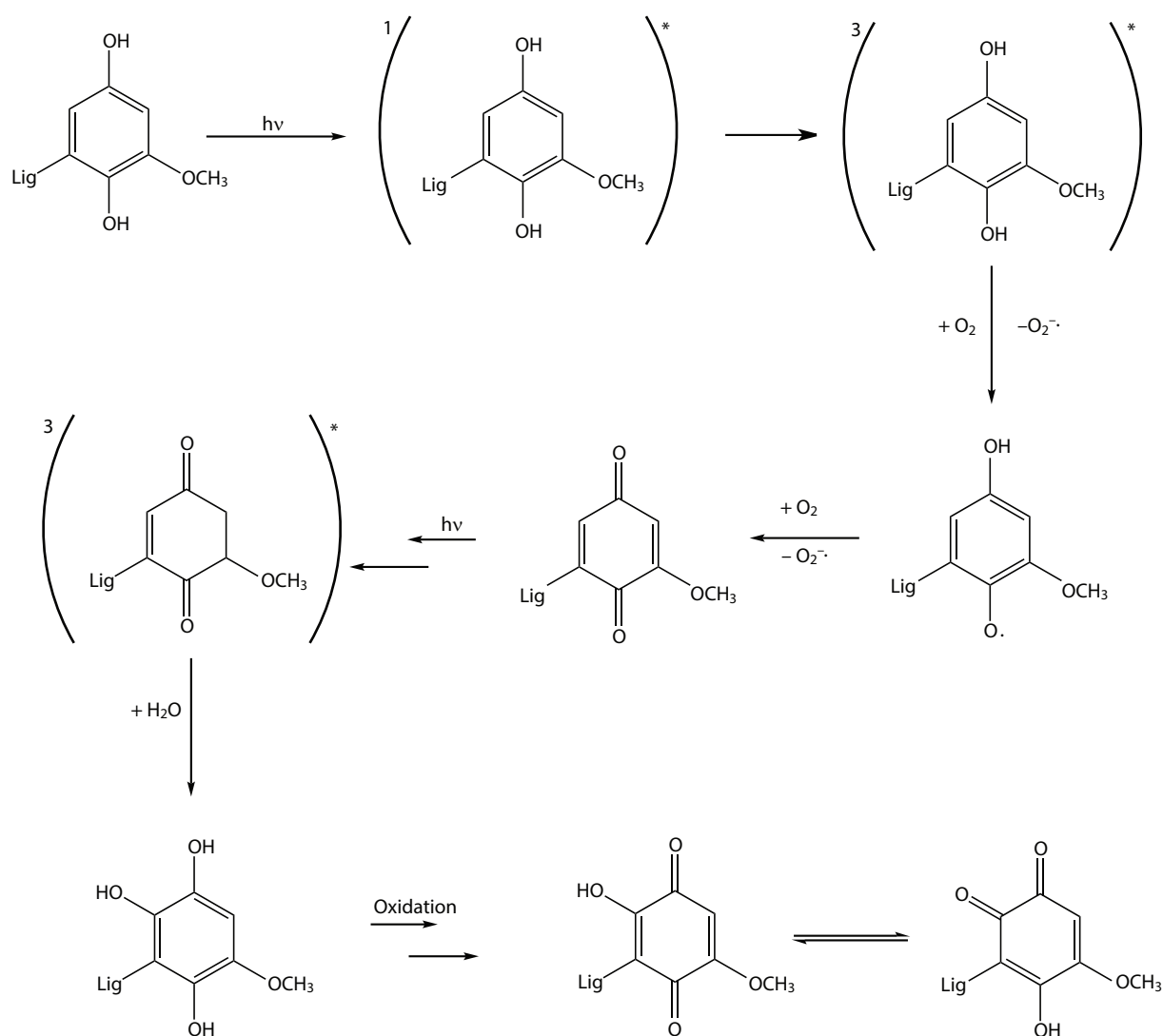


Figure 21.15 Speculative hypotheses on the photoreactivity of hydroquinones in bleached HYP (adapted from [93, 111–113]).

arylpropanone units (Figure 21.13, path B) might be important in the rapid phase of photoyellowing, when they are formed during strong alkaline peroxide bleaching [118].

21.3.2.2 Stabilization Attempts

Methods of inhibiting yellowing can be divided into two main categories. The first one involves the chemical modification of the chromophores or leucochromophores at the origin of the photoyellowing in order to stop or limit their photoreactivity. Proposals have included reduction of lignin α -carbonyls [118–120], alkylation or esterification of lignin phenolic groups [85, 86, 116–121], and catalytic hydrogenation [120, 122]. None of these methods is fully effective, except acetylation of HYP, which chemically targets both phenolic hydroxyl groups and quinones (Figure 21.15) [123], industrially applicable for wood but not for pulps.

The second category of limiting photo-brightness reversion involves the use of chemical additives applied to papers to retard or eliminate the formation of colored compounds [84, 124]. During the last decade, a great number of substances and substance combinations have been tested to inhibit the photoyellowing [84, 124–135]. Among the additives, there are different classes: UV-absorbers, radical scavengers, fluorescent whitening agents, and mineral pigments.

UV-absorbers of 2,4-dihydroxybenzophenone (DHB) and 2-(2'-hydroxyphenyl)benzotriazole (HBT) types (Figure 21.17) tend to be very efficient in limiting the photo-brightness reversion of high-yield pulps [130]. Organic polymers, such as polyethylene glycols [127], polyvinylpyrrolidone [128] and polytetrahydrofurans [129] (Figure 21.17), were effective against the photoyellowing of HYP; often they increased the initial brightness, but too large amounts are needed for an economical industrial application. Sulfur-containing compounds,

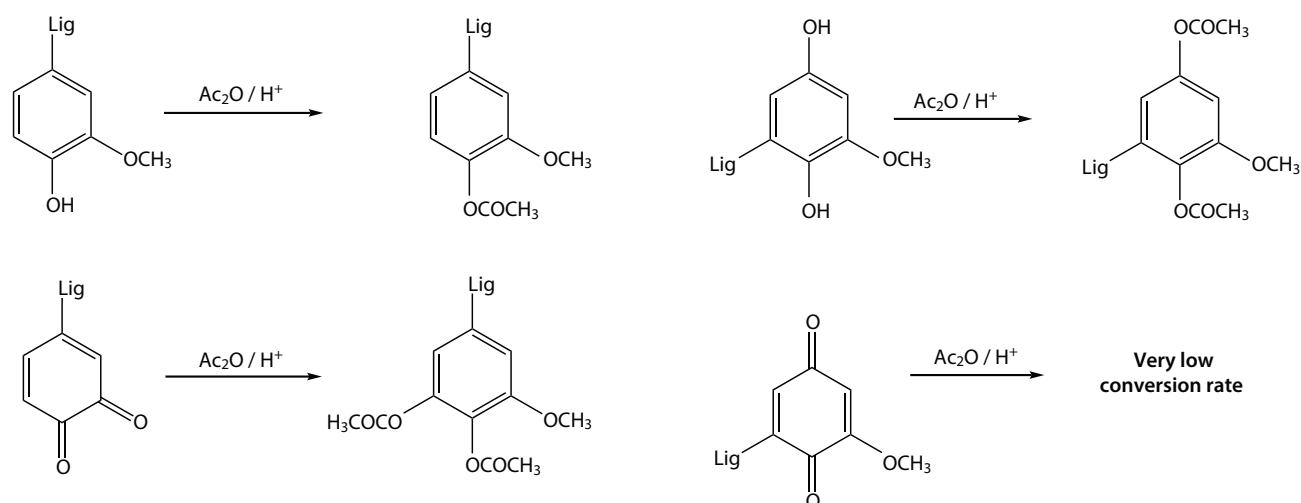


Figure 21.16 Acetylation of phenols and quinones (adapted from [123]).

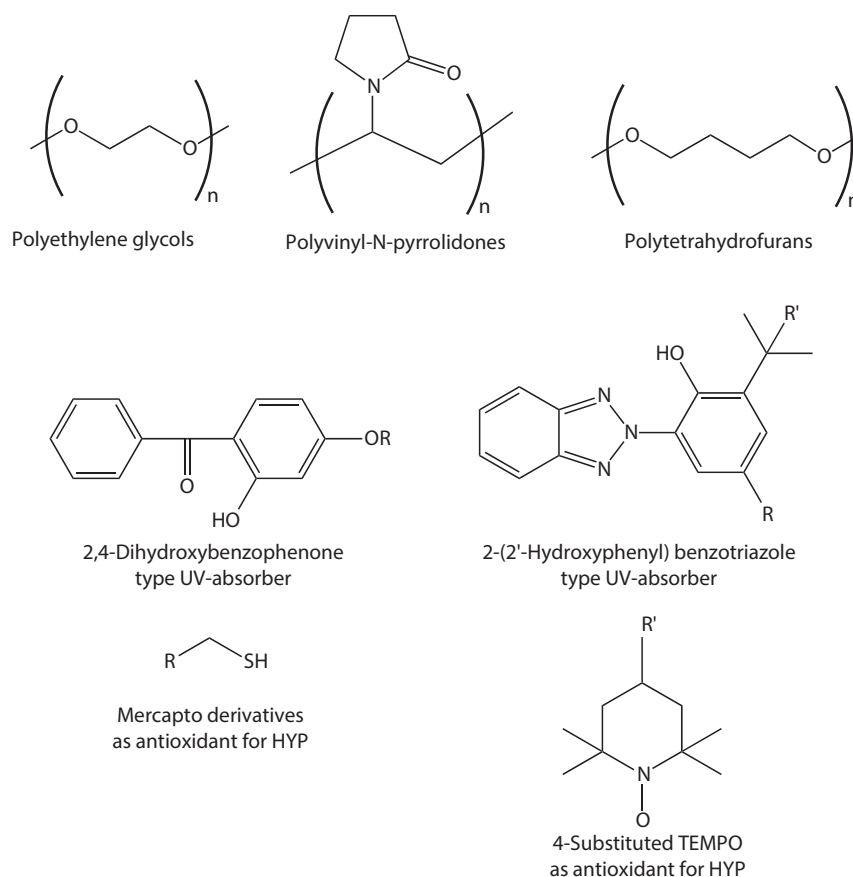


Figure 21.17 Different types of additives to limit the brightness reversion of high-yield pulps.

such as thioalcohols, mercapto acids and esters (Figure 21.17), sulfonates constitute another class of interesting compounds to limit the brightness reversion of HYP [125, 126]. The majority of them present an unpleasant smell, but some display lack of odor [126]. Hindered amine light stabilizers of TEMPO type (Figure 21.17) constitute the most effective class of compounds

to prevent and limit the photoyellowing of HYP [131–133]. They are very often used in combination with DHB or HBT UV-absorbers [130–133]. Another way to inhibit photoyellowing is to use fluorescent whitening agents [134], absorbing light in the UV-A region and reemitting light in the visible region. They act as UV absorbers and induce some photobleaching of

the formed chromophores under UV-irradiation. Another way to limit the photoyellowing is to coat the bleached fibers with mineral pigments such as kaolin, calcium carbonate or titanium dioxide [135].

Despite many attempts to develop an industrial application of additives to limit the brightness reversion of bleached high-yield pulps [136], no economical solution appears to be presently developed in the paper industry for bleached high-yield pulps.

21.3.2.3 Thermal Brightness Reversion of High-Yield Pulp

The brightness reversion of high-yield pulp is very often neglected, because the phenomenon is far less intense than light reversion [137]. Nevertheless, due to the presence of lignin in which various phenolic structures are present, lignin-rich pulps and papers undergo a more important thermal yellowing than chemical pulps.

21.4 Conclusion

During the recent decade, strict environmental regulation has led to the large implementation of elemental chlorine-free and totally chlorine-free processes worldwide for bleaching chemical pulps. The tendency to develop pulping without sulfur for biorefinery usages will still modify the bleaching procedures. Nevertheless, the basic knowledge gained in recent years will be very profitable for a more sustainable usage of chemicals necessary to bleach and conserve the whiteness of the cellulose fibers. In that respect, the use of ozone in final stages of elemental chlorine-free, and more specifically, in totally chlorine-free bleaching, [30] is very interesting, because this reagent is able to eliminate any unsaturated carbon-carbon bonds present in numerous residual colored chromophores of bleached chemical pulps.

Bleached lignin-rich pulps constitute an eco-friendly material, because they can be made without sophisticated and expensive chemicals, as is the case for alkaline peroxide mechanical pulps (APMP) bleached to more than 80 ISO. The origin of their rapid yellowing remains uncertain; however, the role of phenolic structures and α -carbonyl in β -aryl ether structures appears of utmost importance. By contrast, the phenacyl pathway found by Scaiano *et al.* [106], appears to dominate in the long-term photodegradative steps of lignocellulosics: lignin-rich pulps, wood and non-wood plants. Further new breakthroughs are needed for the development of an industrially acceptable process limiting the brightness reversion of bleached high-yield pulps under light exposure.

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