Chapter 12

ENZYMATIC MODIFICATION OF FIBERS FOR TEXTILE AND FOREST PRODUCTS INDUSTRIES

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Abstract

A variety of enzymes are available for the surface modification of cellulosic fibers, both in the area of textile applications and for pulp and paper applications. Enzymatic treatment conditions are milder, less damaging for the fiber, and are environmentally friendly while producing effects comparable to chemical treatments. Surface modifications can be achieved by oxidative and/or hydrolytic enzymes. Some of the enzymatic processes have recently attained commercial importance and more systems are being developed. The following chapter will review current research in the application of oxidoreductases and hydrolases that are valuable for textile and forest products industries.

Keywords: surface modification; oxidoreductase; laccase; peroxidase; hydrolase; cellulose-binding domain.

12.1 Introduction

Fibers derived from plants have a surface chemistry that is inherent in the structure and the source of the material. These fibers will often have a set of properties, such as water-binding capability, flexibility, rigidity, hydrophilic and hydrophobic regions, and the ability to adhere to themselves and other materials, which is dependent on the structure and assembly of the major components of the fiber (hemicellulose, cellulose, and lignin). For economic or supply availability concerns, it is often desirable to modify these properties, thus altering

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the fiber or its surface, to suit the end-product. A variety of chemical techniques have been developed to achieve this goal.

One way of changing fiber surface properties is to remove components of the fiber. The first steps in both the textile and the pulp and paper industries are usually processes to separate the cellulosic material from non-cellulosic impurities. The well-known processes of kraft or sulfite pulping result in a cellulosic fiber with good paper strength and little lignin or hemicellulose content. The fiber is bludgeoned into the suitable form for the product. In the textile industry, scouring and bleaching processes remove oils, fats, pectin, hemicellulose, and coloring matter and render the fiber material clean, water absorbent, and prepared for further modification, such as dyeing.

Another possibility to alter a fiber is to add components. Pulps with high cellulosic content, for example, can be made into cellulose acetate films and carboxymethylcellulose derivatives depending on whether the carboxylic acid of the added acetyl group is involved in an ester or is free to react in an aqueous solution. The result of these additions is a more soluble fiber in the case of carboxymethylcellulose or a more insoluble fiber in the case of cellulose acetate. Acetyl esters of wood created with acetic anhydride can make the wood more dense and more hydrophobic [1]. Attachment of carboxylic acids also affects the strength of paper. The presence of carboxylic acids [2–4] and the effect of different cations [5–7] bound to the dissociated acid have been shown to have significant effects on the strength of paper. Cellulosic fibers for textile uses can be modified by addition of hydrophobic groups for water repellency, cross-linking agents for improved performance, or softeners for enhanced hand, for example [8].

A third method of fiber alteration is to change the nature of fiber functional groups; for instance, by oxidation reactions to increase the acidic groups available for better bonding in the case of pulp fibers [2]. A variety of bleaching techniques can be used to remove color from pulps used for writing papers by either oxidative or reductive methods [9–14]. As a result of bleaching, the chromophore is removed, altered, or destroyed, although in some cases brightness reversion may occur [10, 15, 16].

Chemical treatments of fiber involving harsh reaction conditions or highly reactive chemicals create problems with non-specific reactions, potential hazards to the user, and cost in yield of the products or loss of desirable components. Such conditions can cause a reduction in degree of polymerization, loss of hemicellulose, and oxidation reactions at end-groups so that the fiber negatively changes its properties and loses strength. It is of utmost importance to maintain mild conditions for modification of cellulosic surfaces when the fiber integrity is to be maintained [17]. As a consequence of these limitations of chemical systems and the nature of the fiber, the use of enzymes to perform some of these reactions has been investigated [18–21].

Enzymes, applied at mild conditions, have the advantage of being specific to their substrates and more easily controlled, and they are viewed as environmentally friendly and less damaging to the fiber [18, 20, 22]. The disadvantages with enzymes are that they are often not robust enough for the process [23]; they are expensive, especially when used in a single step without enzyme recycle, and frequently, they are not available in commercially useful quantities [18].

Enzymatic surface modifications of fibers can be created by oxidative and/or hydrolytic enzymes. Oxidoreductases, such as peroxidases, laccase, and cellobiose dehydrogenase, all have uses in the modification of fiber surfaces [10, 18–21]. Likewise hydrolases, such as cellulases, hemicellulases, pectinases, amylases, lipases, and proteases, are able to modify fiber surfaces [18–20, 22]. Attachment of various functional groups or enzymes by the use of cellulose-binding domains (CBDs) is also becoming more common [24, 25]. We will review recent research on enzymatic modifications of fibers for the textile and forest product industries, including results from experiments performed in our laboratories.

12.2 Oxidative enzymes and their applications

12.2.1 Laccases for pulp and paper modification

Laccases are enzymes that catalyze the oxidation of a variety of phenolic and similar compounds [26, 27] and are implicated in the degradation of lignin [28]. Laccases have been identified in both fungi and bacteria [29]. The enzymes abstract an electron from substrates containing phenolic or aromatic nitrogen, which produces a free radical, and reduce oxygen to water, as shown in Figure 12.1 for hydroquinone. Laccases can degrade model lignin compounds [30–32] and have been useful in the removal of lignin from pulps [33]. Removing lignin is important for the properties of chemical pulps (improved flexibility, better fiber to fiber bonding, increased sheet strength) and the brightness of the paper. In addition to delignification, laccases are able to bleach, oxidize, and graft materials onto the fiber surface [19, 28, 34].

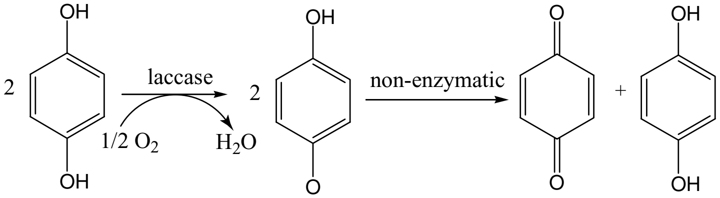


Figure 12.1. Enzymatic abstraction of electron from hydroquinone

Delignification of pulps and various mediator combinations with laccases have been studied by many authors [19, 28, 35–41]. Delignification is most prominent when the lignin content of the pulp is high [33]. For effective delignification, laccase requires the addition of a mediator [42]. The mediator oxidizes lignin at a distance from the enzyme and also reacts with compounds that are not substrates for laccase. As depicted for hydroquinone (Figure 12.1), laccase abstracts an electron from a suitable substrate with the reduction of molecular oxygen. The enzymatic free radical products may undergo further oxidative and non-enzymatic reactions, including polymerization and dismutation [41, 43].

The reaction and decay of the free radicals generated in a complex substrate such as lignin are difficult to foresee, and the products of the reaction are complex. The complexity of the products of the laccase reaction depends in part on the resonance structures of the free radical, the solubility of the product, other compounds available to react with the radical, and the longevity of the radical [41, 44]. Despite this complexity, carefully designed reactions can predict the reactions taking place and obtain product in reasonable yield [45].

Mediators are substrates of laccase able to react with structures that the laccase enzyme cannot oxidize [30, 46]. Mediators can be long-lived free radicals or transition metal complexes [38, 47]. They can be natural products of fungi or other chemicals [48]. The use of laccase in bleaching and delignification requires mediators, and commercial application is hampered by the lack of an inexpensive source [42, 49]. New mediators and laccase substrates are being sought and reported [27, 41].

The laccase mediator for bleaching may have different effects depending on the material being bleached or delignified [50–53], the enzyme used [27], and the mediator employed [46]. The mechanism of laccase mediator reactions has been investigated—some proceed by a radical hydrogen atom transfer (using mediators, 1-hydroxybenzotriazole, violuric acid, or hydroxyphthalimide) while the most often reported mediator, 2,2′-azino-*bis*(3-ethlybenzthiazoline-6-sulfonic acid), can proceed via an electron transfer mechanism [43].

The reaction of laccase on fiber can create a variety of effects. Wood-based products can be oxidized, providing better strength in composites [54], papers and fiberboards [55–57], and reducing energy costs [58]. For example, reactions of laccase with radiata pine chips resulted in energy savings during mechanical refining and a stronger handsheet from the pulp [58]. Laccase treatment was shown to increase the strength of various fiberboards [59, 60] and paper [55].

A relatively new area for laccase application is the grafting of materials to lignocellulose [61, 62]. The laccase reaction with lignin builds up a phenoxy-radical charge in the material [62]. The radicals in these polymers appear to be either long-lived or are rapidly regenerated by the enzyme. These radicals have been used to graft various materials onto the fiber, including carbohydrates [62], acrylates [63, 64], and acrylamides [65, 66]. Other polymeric materials [54, 62] can also be attached, thus modifying the fiber surface. The addition of polymers changes the material properties of the cellulosic material, increasing its strength or water-holding capacity.

Exploration of the vast substrate range of laccase and the effects of different substrates on a lignocellulose product are in its infancy [67]. Phenolic acids can be attached to pulps using laccase and various substrates such as gallic acid [68], 4-hydroxybenzoic acid [69], and 4-hydroxyphenylacetic acid [67, 70]. The attachment of the phenolic acids increases the burst and tensile strength of test handsheets, presumably by the presence of the organic acid. However, the attachment of phenolic materials that alter the surface characteristics of fiber, such as resorcinol, phloroglucinol, and catechol, does not increase the strength of handsheets [67]. The effect of laccase treatment of substrates must be empirically derived because of reactions with oxygen and other radicals generated in the reaction, polymerization of the substrate, and condensation onto lignocellulose. The nature of the laccase substrate can only suggest that a particular effect on the surface chemistry may be obtained.

12.2.2 Textile fiber applications of laccases

Laccases have also found applications in textile processes. The introduction of a more user-friendly laccase formulation to the textile-finishing market spurred an interest in its use for treatment of indigo-dyed cotton denim. Several reports of laccase bleaching appeared in the literature by the turn of the last century [71]. Laccase was applied together with a suitable mediator to create a bleached-out look to jeans, which was fashionable at that time. In this process, the indigo chromophore was transformed into isatin [71], and backstaining was reduced or avoided. This process worked especially well for indigo while laccase was found to be ineffective for bleaching undyed cotton. Tzanov et al. [72] developed a laccase pre-treatment that, when followed by a traditional hydrogen peroxide bleach, resulted in a whiter cotton fabric than possible without the pretreatment.

Lignin probably plays an important role in the reaction mechanism of laccase bleaching. Raw cotton probably could not be satisfactorily bleached using only laccases because cotton has little lignin. Ossala and Galante [73] published a comparative study on scouring of flax rove with a variety of enzymes. They found, however, that laccase performed the least effective of all investigated enzymes. Hydrolases, such as pectinase, gave superior results.

Similar to the case with the pulp and paper industry, laccases have been tested in reactions to both bleach and graft materials to textiles. Shin and

Cavaco-Paulo [74] made use of the laccase reaction by *in situ* dyeing of wool fibers with laccase and small phenols as substrates. Similar reactions were patented by Aaslyng et al. [75] for human hair.

12.2.3 Peroxidase applications for pulp

Manganese peroxidase, lignin peroxides, and other peroxidases have also been used for pulp-bleaching reactions [18]. The use of peroxidases requires the addition of hydrogen peroxide, which at high concentrations also inhibits the enzyme. One approach is to meter in the hydrogen peroxide at low concentrations, matching the consumption rate with the supply rate. Another is to use an enzyme like glucose oxidase or another hydrogen peroxide generating system at levels that produce the needed amount of substrate. The generation or metering of hydrogen peroxide alleviates the inhibition of the enzyme.

The requirement of an additional substrate such as manganese is a small problem for the marketable use of these enzymes compared to the lack of commercially available amounts of the enzymes. Laccases, even with the requirement for mediators, have been favored since they have been relatively easy to produce in heterologous expression systems. Peroxidases have long been available, but the use of manganese peroxidase and lignin peroxidase has been limited by the lack of commercial quantities of these enzymes.

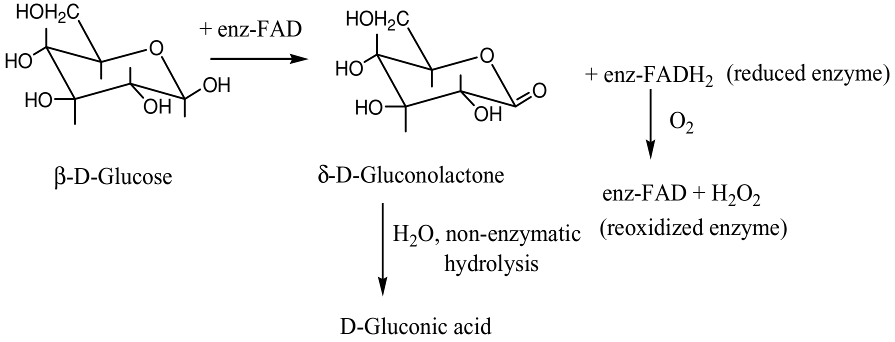
Research on the use of manganese peroxidase has indicated a variety of potential applications. Manganese peroxidase has been used for the bleaching of chemical pulps [76], delignification of pulps [77], and treatment of pulps to lessen electrical refiner energy and improve handsheet strength [78]. Lignin peroxidase is promising since it can react with non-phenolic components of lignin and does not require the addition of manganese. The commercialization of processes using lignin peroxidase has been hampered by the recalcitrant heterologous expression of the enzyme.

Textile applications of peroxidases for bleaching of cotton and of lignin-containing fibers, such as linen, are being explored, with limited success [79]. Possible options are combining compatible oxidoreductases or applying the enzymes in suitable sequences of optimum pH and temperature. For example, the application of manganese peroxidase in the first step followed by glucose oxidase results in slightly higher whiteness levels than the application of glucose oxidase alone. Such process modifications might have a greater potential than does treatment with only one peroxidase. However, the process costs are still high and might not be economically justified at present.

Cellobiose dehydrogenase has also been explored to modify the structure of lignocellulosic materials. While under certain conditions cellobiose dehydrogenase can catalyze lignin degradation [80], the cost and action of this enzyme will probably prohibit commercial application in pulp bleaching and delignification [81]. The modification of carbohydrate by creating carboxylic acids is a potential cost-effective application of cellobiose dehydrogenase [81].

12.2.4 Glucose oxidase bleaching of textile substrates

Flavo-enzymes, such as glucose oxidase, have long been regarded as uneconomical and ineffective for textile applications except for their incorporation in laundry formulations [82] for stain removal and as anti-redeposition agents [83].



Glucose oxidase specifically oxidizes β-D-glucose to δ-D-gluconolactone, releasing hydrogen peroxide, which then can be used for bleaching of cellulosic materials. A closed-loop process using glucose-rich effluents from enzymatic desizing and scouring in conjunction with bleaching whitened cotton to a level close to that of chemically bleached material [84]. A similar bleaching process was established using glucose oxidase immobilized on alumina or glass support, which increased the stability of the enzymes and offers the possibility of enzyme recycling to reduce the cost of the process [85].

We performed bleaching studies involving the treatment of unbleached linen fabric with laccase alone and in combination with glucose oxidase. Laccase was first applied as the sole enzyme with minimal gain in whiteness. Adding glucose oxidase in a second step and finally, in the third step, raising the pH and temperature to 10.5 and 90 °C, respectively, resulted in whiteness levels nearly comparable to that of chemically bleached linen [79, 84].

12.3 Hydrolases

12.3.1 Xylanase for pulp and paper applications

Oxidative enzymes are not the only useful enzymes in the modification of pulp and paper. Perhaps the most successful enzymatic application in the pulp and paper industry has been the use of xylanase to assist in bleaching of kraft pulps. Xylanases have been shown to aid in the bleaching of many different softwoods and hardwoods [18, 86]. Both chemical and mechanical pulps have benefited by xylanase treatment [18]. Since the first description of the use of xylanase to boost the bleaching of pulps [87], there has been an acceleration in the identification of new xylanases and continuing research into developing xylanases that are more suitable for the elevated temperatures, alkaline pH, and other conditions (presence of proteases) in the stages where the enzyme is used [18, 86, 88–90].

In bleaching, xylanase acts by cleaving the xylan, producing shorter, easier to remove oligosaccharides, which aids in the removal of colored compounds [91–94] and bleach-consuming chemicals such as hexenuronic acid [95–98]. In addition, the removal of xylan enhances the removal of lignin, which is also a major contributor to color in the pulp. Synergistic action was noted when different xylanases were used [99] or a combination of xylanase and oxidative enzymes [100]. Xylanase treatment decreases the amount of bleaching chemicals required to attain the desired brightness. Again, as with laccase, several reviews have been published on the use of xylanases in enhancing pulp bleaching [18, 19, 101].

Other hydrolases have also been reported as suitable for the bleaching of paper pulps. Cellulases have been useful in the removing colored material from recycled yellow pages and print in recycled pulps [102]. Mannanases and xylanases can act synergistically to aid in bleaching some pulps [103–109]. These enzymes do not work on all pulps since there are considerable variations in the type of pulp (mechanical, thermomechanical, kraft, sulfite, or recycled fiber) as well as in the tree species used in the pulping process [18]. Different enzymes will often work better on a specific pulp, so the appropriate enzyme and dose are determined by empirical testing.

Xylanases have also been included in the enzymatic scouring formulation for raw cotton to reduce the amount of seed coat fragments. Immature cotton fibers and seed coat fragments are problems for the textile industry because they cannot be dyed, especially with dyes applied at neutral pH, and thus remain as small spots. Seed coat fragments and immature cotton fibers, which are low in cellulose, can be removed to a great extent by a harsh chemical scouring process under alkaline conditions. Enzymatic scouring with pectinases and cellulases, however, is specific for pectins and cellulose, respectively, thus ineffective on both seed coat fragments and immature cotton. The addition of xylanases has been helpful to some extent [79].

Lipases are used in both the pulp and paper and textile industries. Lipases remove pitch from pulps [20, 110]. Pitch deposits are imperfections in the paper caused by fats and resins. These deposits can accumulate and cause problems during the papermaking process and limit the value of the paper. Lipase treatment of the pulp cleaves the triglycerides and allows the fatty acids to be removed with other waste in the rinse water.

Cellulases have been applied in the pulp and paper industry with great caution [111]. The degradation of the cellulosic fibers must be avoided, but enzymes can be used to remove the cellulose that does not provide value to the product. Cellulases have been particularly effective in improving the drainage [102, 112–114] and deinking of recycled fiber [115–120] as well as cellulose fabrics [121]. Cellulases have also been used successfully followed by peroxide bleaching for low-quality recovered paper containing unbleached and mechanical fibers which are a major obstacle in recycling lower quality paper mixes [122]. Hemicellulases, lipases, and esterases have also been employed in deinking of recycled fiber [119].

Cellulase-assisted deinking can involve the use of other additives such as surfactants [123–125]. If floatation is the primary method of ink removal, the cellulase application must be tested to determine if removal of the amorphous cellulose on ink particles will be advantageous or detrimental to the removal of the specific type of ink used [126]. The removal of the amorphous regions can improve the drainage of the recycled fiber and has been used both before and after refining [19]. Removal of stickies contaminants with cellulase treatment during the recycling process not only enhanced flotation removal efficiency, but also allowed the process to be conducted at neutral pH. The enzyme process resulted in a substantially cleaner process overall [127].

Much research has been published on using enzymes to modify the properties of textiles. Lipases, amylases, and proteases have been included in a variety of detergent formulations to aid in removing stains [128–130]. Proteases have been used for shrink-proofing and softening wool fibers and for degumming silk [131, 132]. Cellulases are now commercially applied to biopolish and manually improve cotton [133–138] and to achieve the "peach-skin" effect on lyocell fibers by fibrillation [139, 140]. The macroscopic effect of cellulases is the removal of small protruding fibrils from the fiber surface with or without mechanical impact, thus enhancing softness and color brilliance by an "abrasive, bio-polishing" action.

Cotton is usually scoured in an alkaline solution. The process requires a considerable amount of water and generates waste that must be neutralized and disposed. Bioscouring using enzymes such as pectinases or a mixture of cellulases, pectinases, and xylanases can be done at neutral pH [141–146]. Because of the specificity of the enzymes, the fiber damage is minimal. Additionally, less waste water is generated. The end result is a stronger material with good absorbency.

12.3.2 CBDs as means of attachment

One new application is to establish the binding of various enzymes and other materials to cellulosic fibers using the CBDs of fungi and bacteria [147]. The fungal CBD is relatively short and can be added to the coding sequence of many enzymes (both carboxy- and amino-terminal extensions) to provide a functional domain able to fold properly and bind to cellulose [24, 25]. Bacterial CBDs are also used, and expression cassettes are available from molecular biology supply companies; the CBDs from both bacteria and fungi can be incorporated into the sequence of a protein to be expressed [148].

The simple binding of CBDs is sufficient to alter the dye affinity of cotton [149] and the properties of the pulps to which it is attached [150]. The addition of CBD increases the strength and drainability of secondary fibers [151]. As measured by atomic force microscopy, the binding of a CBD decreases repulsion between cellulose surfaces [152]. If the CBD is multimeric, there is also a greater adhesion between cellulose surfaces [152, 153]. CBD attachment alters the appearance of ramie cotton fibers, greatly smoothing their appearance.

The binding of different functional groups to cellulose has also been explored. Combining a CBD with a metal chelating peptide produces a product with the ability to remove metals [154]. Attaching an indicator enzyme to a CBD provides a solid-based device to detect the presence of a variety of components and is used in diagnostic and research materials [155]. Different CBDs bind to different regions of cellulose and with varying affinities. The presence of more than one cellulose-binding module per protein can influence the avidity with which the protein binds to cellulose.

Natural polymers such as xyloglucan can also be used to bind to cellulose and provide new chemistries on the surface of cellulosic fibers. Modified xyloglucan oligosaccharides have been incorporated into xyloglucans using xyloglucan endoglycosylase [156]. The affinity of xyloglucans for cellulose fibrils has made them useful in both textiles [156] and papermaking [157]. The alteration of the chemistry present in the xyloglucan will further the use of the xyloglucans in modifying cellulosic materials.

12.4 Conclusions

Enzymes have provided new products and have improved the quality and economics of processes in both the textile and forest products industries. In a capital-intensive industry like pulp and paper, there is a reluctance to use new processes if they require additional capital investment. The process must be able to fit the existing equipment. The techniques of molecular biology and heterologous expression allow the adaptation of enzymes to the process used. Even with these possibilities, the cost of enzymes is often too high for the action of the enzyme. New enzymes are being identified by basic research and genomics studies. The application of new enzymes can be expected when applied research tests their suitability for given applications.

References

1. Rowell, R., Chemical modification of wood. *Forest Prod. Abstr.* **1983**, *6*(12), 363–382.
2. Barzyk, D.; Page, D. H.; Ragauskas, A. Acidic group topochemistry and fibre-to-fibre specific bond strength. *J. Pulp Paper Sci.* **1997**, *23*(2), J59–J61.
3. Scallan, A. M. The effect of acidic groups on the swelling of pulps: A review. *Tappi J.* **1983**, *66*, 73–75.
4. Katz, S.; Liebergott, N.; Scallan, A. M. A mechanism for the alkali strengthening of mechanical pulps. *Tappi J.* **1981**, *64*(7), 97–100.
5. Scallan, A. M.; Grignon, J. The effect of cations on pulp and paper properties. *Sven. Papperstidning* **1979**, *82*(2), 40–47.
6. Lindstrom, T.; Carlsson, G. The effect of chemical environment on fiber swelling. *Sven. Papperstidning* **1982**, *85*(3), R14–R20.
7. Salmen, L. Influence of ionic groups and their counterions on the softening properties of wood materials. *JPPS* **1995**, *21*, J310–J315.
8. Slate, P. E. *Handbook of Fiber Finish Technology* (ed.). Marcel Dekker, New York, **1998**, 319–447.
9. Bucher, W. Bleaching 101: The basics of bleaching. *Solutions!* **2004**, *87*(February), 36–37.
10. Wong, K. K. Y.; Mansfield, S. D. Enzymatic processing for pulp and paper manufacturing. *Appita J.* **1999**, *52*(6), 409–418.
11. Johnson, A. P. Fitting together the ecf–tcf jigsaw. *Appita J.* **1994**, *47*(3), 243–250.
12. McDonough, T. J. Recent advances in bleached chemical pulp manufacturing technology. *Tappi J.* **1995**, *78*(3), 55–62.
13. Suchy, M.; Argyropoulos, D. S. Catalysis and activation of oxygen and peroxide delignification of chemical pulps: A review. *Tappi J.* **2002**, *1*(2), 1–18.
14. Li, K.; Collins, R.; Eriksson, K. E. Removal of dyes from recycled paper. *Prog. Paper Recycling* **2000**, *10*(November), 37–43.
15. Buchert, J.; Bergnor, E.; Lindblad, G.; Viikari, L.; Ek, M. Significance of xylan and glucomannan in the brightness of kraft pulp. *Tappi J.* **1997**, *80*(6), 165–171.
16. Forsskahl, I.; Tylli, H.; Olkkonen, C. Participation of carbohydrate-derived chromophores in the yellowing of high-yield and tcf pulps. *J. Pulp Paper Sci.* **2000**, *26*(7), 245–249.
17. Baiardo, M.; Frisoni, G.; Scandola, M.; Licciardello, A. Surface chemical modification of natural cellulose fibers. *J. Appl. Polym. Sci.* **2002**, *83*, 38–45.
18. Kenealy, W. R.; Jeffries, T. W. Enzyme processes for pulp and paper: A review of recent developments. In: Goodell, B.; Nicholas, D.D.; Schultz, T. P. (Eds.) *Wood Deterioration and Preservation: Advances in Our Changing World.* American Chemical Society, Washington, **2003**, 210–239.
19. Bajpai, P. Application of enzymes in the pulp and paper industry. *Biotechnol. Prog.* **1999**, *15*(2), 147–157.
20. Kirk, T. K.; Jeffries, T. W. Roles for microbial enzyme in pulp and paper. In: Jeffries, T. W.; Viikari, L. (Eds.) *Enzymes for Pulp and Paper Processing*. American Chemical Society, Washington, **1996**; Symposium series 655, 1–14.
21. Eriksson, K. E. Biotechnology in the pulp and paper industry: An overview. In: Eriksson, K. E.; Cavaco-Paulo, A. (Eds.) *Enzyme Applications in Fiber Processing*. American Chemical Society, **1998**; Symposium Series 687, 2–14.
22. Daniels, M. J. Using biological enzymes in papermaking. *Paper Technol.* **1992** *33*(June), 14–17.
23. Klibanov, A. Improving enzymes by using them in organic solvents. *Nature Biotechnol.* **2001**, *409*, 241–246.

24. Tomme, P.; Warren, A. J.; Miller, R. C. J.; Kilburn, D. G.; Gilkes, N. R. Cellulose-binding domains: Classification and properties. In: Saddler, J. N.; Penner, M. H. (Eds.) *Enzymatic Degradation of Insoluble Carbohydrates*. American Chemical Society, Washington **1995**; ACS Symposium series 618, 142–163.
25. Tomme, P.; Boraston, A.; McLean, B. W.; Kormos, J.; Creagh, A. L.; Sturch, K.; Gilkes, N. R.; Haynes, C. A.; Warren, A. J.; Kilburn, D. G. Characterization and affinity applications of cellulose-binding domains. *J. Chromatogr. B* **1998**, *715*, 283–296.
26. Xu, F. Oxidation of phenols, anilines, and benzenethiols by fungal laccases: Correlation between activity and redox potentials as well as halide inhibition. *Biochemistry* **1996**, *35*, 7608–7614.
27. Xu, F.; Kulys, J. J.; Duke, K.; Li, K.; Krikstopaitis, K.; Deussen, H. J. W.; Abbate, E.; Galinyte, V.; Schneider, P. Redox chemistry in laccase-catalyzed oxidation of *n*-hydroxy compounds. *Appl. Environ. Microbiol.* **2000**, *66*(5), 2052–2056.
28. Yaropolov, A. I.; Skorobogat, K. O. V.; Vartanov, S. S.; Varfolomeyev, S. D. Laccase: Properties, catalytic mechanism, and applicability. *Appl. Biochem. Biotechnol.* **1994**, *49*(3), 257–280.
29. Martins, L. O.; Soares, C. M.; Pereira, M. M.; Teixeira, M.; Costa, T.; Jones, G. H.; Henriques, A. O. Molecular and biochemical characterization of a highly stable bacterial laccase that occurs as a structural component of the *Bacillus subtilis* endospore coat. *J. Biol. Chem.* **2002**, *277*(21), 18849–18859.
30. Li, K.; Xu, F.; Eriksson, K. E. L. Comparison of fungal laccases and redox mediators in oxidation of a nonphenolic lignin model compound. *Appl. Environ. Microbiol.* **1999**, *65*, 2654–2660.
31. Bourbonnais, R.; Paice, M. G.; Freiermuth, B.; Bodie, E.; Borneman, S. Reactivities of various mediators and laccases with kraft pulp and lignin model compounds. *Appl. Environ. Microbiol.* **1997**, *63*, 4627–4632.
32. Srebotnik, E.; Hammel, K. E. Degradation of nonphenolic lignin by the laccase/1-hydroxybenzotriazole system. *J. Biotechnol.* **2000**, *81*(2–3), 179–188.
33. Bourbonnais, R.; Paice, M. G. Enzymatic delignification of kraft pulp using laccase and a mediator. *Tappi J.* **1996**, *79*, 199–204.
34. Balakshin, M.; Chen, C.; Gratzl, J. S.; Kirkman, A. G.; Jakob, H.; Chen, C. L. Biobleaching of pulp with dioxygen in the laccase-mediator system. Part 1. Kinetics of delignification. *Holzforschung* **1999**, *54*(4), 390–396.
35. Muheim, A.; Fiechter, A.; Harvey, P. J.; Schoemaker, H. E. On the mechanism of oxidation of non-phenolic lignin model compounds by the laccase-abts couple. *Holzforschung* **1992**, *46*(2), 121–126.
36. Johannnes, C.; Majcherczyk, A. Natural mediators in the oxidation of polycyclic aromatic hydrocarbons by laccase mediator systems. *Appl. Environ. Microbiol.* **2000**, *66*, 524–528.
37. Call, H. P.; Mucke, I. History, overview and applications of mediated lignolytic systems, especially laccase-mediator-systems (Lignozym® process). *J. Biotechnol.* **1997**, 53(2–3), 163–202.
38. Li, K.; Prabhu, G. N.; Cooper, D. A.; Xu, F.; Elder, T.; Eriksson, K.-E. L. Development of new laccase-mediators for pulp bleaching. In: Argyropoulos, D. S. (Ed.) *Oxidative Delignification Chemistry*. American Chemical Society, Washington, **2001**, 400–412.
39. Call, H. P.; Mucke, I. Enzymatic bleaching of pulps with the laccase-mediator-system (lms). In: *Advances in Pulp and Papermaking* (ed.); American Institute of Chemical Engineers, New York, Symposium series #307, **1995**; 91, 38–52.

---

40. Bourbonnais, R.; Paice, M. G. Demethylation and delignification of kraft pulp by *Trametes versicolor* laccase in the presence of 2,2′-azino*bis*-(3-ethylbenzthiazoline-6-sulphonate). *Appl. Microbiol. Biotechnol.* **1992**, *36*(6), 823–827.
41. Shleev, S. V.; Khan, I. G.; Gazaryan, I. G.; Morozova, O. V.; Yaropolov, A. I. Novel laccase redox mediators. *Appl. Biochem. Biotechnol.* **2003**, *111*, 167–183.
42. Paice, M. G.; Bourbonnais, R.; Reid, I. D.; Archibald, F.; Jurasek, L. Oxidative bleaching enzymes: A review. *J. Pulp Paper Sci.* **1995**, *21*(8), J280–J284.
43. Baiocco, P.; Barreca, A. M.; Fabbrini, M.; Galli, C.; Gentili, P. Promoting laccase activity towards non-phenolic substrates: A mechanistic investigation with some laccase-mediator systems. *Org. Biomol. Chem.* **2003**, *1*, 191–197.
44. d'Acunzo, F.; Galli, C.; Masci, B. Oxidation of phenols by laccase and laccase-mediator systems. *Eur. J. Biochem.* **2002**, *269*, 5330–5335.
45. Pilz, R.; Hammer, E.; Schauer, F.; Kragl, U. Laccase-catalysed synthesis of coupling products of phenolic substrates in different reactors. *Appl. Microbiol. Biotechnol.* **2003**, *60*, 708–712.
46. Knutson, K.; Ragauskas, A. Laccase-mediator biobleaching applied to a direct yellow dyed paper. *Biotechnol. Prog.* **2004**, *20*, 1893–1896.
47. Bourbonnais, R.; Rochefort, D.; Paice, M. G.; Renaud, S.; Leech, D. Transition metal complexes: A new class of laccase mediators for pulp bleaching. *Tappi J.* **2000** (October), 68.
48. Eggert, C.; Temp, U.; Dean, J. F. D.; Eriksson, K. E. L. A fungal metabolite mediates degradation of non-phenolic lignin structures and synthetic lignin by laccase. *FEBS Lett.* **1996**, *391*(1–2), 144–148.
49. Wong, K. K. Y.; Anderson, K. B.; Kibblewhite, R. P. Effects of the laccase-mediator system on the handsheet properties of two high kappa kraft pulps. *Enzyme Microb. Technol.* **1999**, *25*, 125–131.
50. Gronqvist, S.; Buchert, J.; Rantanen, K.; Viikari, L.; Suurnakki, A. Activity of laccase on unbleached and bleached thermomechanical pulp. *Enzyme Microb. Technol.* **2003**, *32*, 439–445.
51. Sealey, J.; Ragauskas, A. J. Residual lignin studies of laccase-delignified kraft pulps. *Enzyme Microb. Technol.* **1998**, *23*(7–8), 422–426.
52. Sealey, J.; Ragauskas, A. J.; Elder, T. J. Investigations into laccase-mediator delignification of kraft pulps. *Holzforschung* **1999**, *53*(5), 498–502.
53. Camarero, S.; Garcia, O.; Vidal, T.; Colom, J.; del Rio, J. C.; Gutierrez, A.; Gras, J. M.; Monje, R.; Martinez, M. J.; Martinez, A. T. Efficient bleaching of non-wood high-quality paper pulp using laccase-mediator system. *Enzyme Microb. Technol.* **2004**, *35*, 113–120.
54. Huttermann, A.; Mai, C.; Kharazipour, A. Modification of lignin for the production of new compounded materials. *Appl. Microbiol. Biotechnol.* **2001**, *55*, 387–394.
55. Wong, K. K. Y.; Richardson, J. D.; Mansfield, S. D. Enzymatic treatment of mechanical pulp fibers for improving papermaking properties. *Biotechnol. Prog.* **2000**, *16*(6), 1025–1029.
56. Lund, M.; Felby, C. Wet strength improvement of unbleached kraft pulp through laccase catalyzed oxidation. *Enzyme Microb. Technol.* **2001**, *28*, 760–765.
57. Felby, C.; Pedersen, L. S.; Nielsen, B. R. Enhanced auto adhesion of wood fibers using phenol oxidases. *Holzforschung* **1997**, *51*(3), 281–286.
58. Mansfield, S. D. Laccase impregnation during mechanical pulp processing-improved refining efficiency and sheet strength. *Appita J.* **2002**, *55*, 49–53.
59. Felby, C.; Hassingboe, J.; Lund, M. Pilot-scale production of fiberboards made by laccase oxidized wood fibers: Board properties and evidence for cross-linking of lignin. *Enzyme Microb. Technol.* **2002**, *31*, 736–741.

---

60. Felby, C.; Olesen, P. O.; Hansen, T. T. Laccase catalyzed bonding of wood fibers. In: Eriksson, K. E.; Cavaco-Paulo, A. (Eds.) *Enzyme Applications in Fiber Processing.* American Chemical Society, Washington, **1998**, Symposium Series 687, 88–98.
61. Mai, C.; Schormann, W.; Huettermann, A. The effect of ions on the enzymatically induced synthesis of lignin graft copolymers. *Enzyme Microb. Technol.* **2001**, *28*(4–5), 460–466.
62. Huttermann, A.; Majcherczyk, A.; Braun, L. A.; Mai, C.; Fastenrath, M.; Kharazipour, A.; Huttermann, J.; Huttermann, A. H. Enzymatic activation of lignin leads to an unexpected copolymerization with carbohydrates. *Naturwissenschaften* **2000**, *87*, 539–541.
63. Mai, C.; Majcherczyk, A.; Huttermann, A. Chemo-enzymatic synthesis and characterization of graft copolymers from lignin and acrylic compounds. *Enzyme Microb. Technol.* **2000**, *27*(1–2), 167–175.
64. Mai, C.; Schormann, W.; Huttermann, A. Chemo-enzymatically induced copolymerization of phenolics with acrylate compounds. *Appl. Microbiol. Biotechnol.* **2001**, *55*(2), 177–186.
65. Mai, C.; Milstein, O.; Huttermann, A. Fungal laccase grafts acrylamide onto lignin in presence of peroxides. *Appl. Microbiol. Biotechnol.* **1999**, *51*, 527–531.
66. Mai, C.; Milstein, O.; Hutterman, A. Chemoenzymatical grafting of acrylamide onto lignin. *J. Biotechnol.* **2000**, *79*, 173–183.
67. Kenealy, W.; Klungness, J.; Tshabalala, M. A.; Horn, E.; Akhtar, M.; Gleisner, R.; Buschle-Diller, G. Modification of lignocellulosic materials by laccase. TAPPI Fall Technical Conference, Chicago, IL, Oct 26–30, **2003**; Abstract 3381.
68. Chandra, R. P.; Lehtonen, L. K.; Ragauskas, A. J. Modification of high lignin content kraft pulps with laccase to improve paper strength properties. 1. Laccase treatment in the presence of gallic acid. *Biotechnol. Prog.* **2004**, *20*, 255–261.
69. Chandra, R. P.; Ragauskas, A. J. Evaluating laccase-facilitated coupling of phenolic acids to high-yield kraft pulps. *Enzyme Microb. Technol.* **2002**, *30*(7), 855–861.
70. Chandra, R. P.; Ragauskas, A. J. Laccase: The renegade of fiber modification. Tappi Pulping Conference, Tappi press, Atlanta, GA, **2001**.
71. Mueller, M.; Shi, C. Laccase for denim processing. *AATCC Rev.* **2001**, *1*(7), 4–5.
72. Tzanov, T.; Basto, C.; Guebitz, G. M.; Cavaco-Paulo, A. Laccases to improve the whiteness in a conventional bleaching of cotton. *Macromol. Mater. Eng.* **2003**, *288*, 807–810.
73. Ossala, M.; Galante, Y. M. Scouring of flax rove with the aid of enzymes. *Enzyme Microb. Technol.* **2004**, *34*, 177–186.
74. Shin, H.; Cavaco-Paulo, A., In-situ enzymatically prepared polymers for wool coloration. *Macromol. Mater. Eng.* **2001**, *286*, 691–694.
75. Aaslyng, D., Sorensen, N. H., Rorbaek, K. Laccases with improved dyeing properties. US 5948121, **1998**.
76. Paice, M. G.; Bourbonnais, R. Non-chlorine bleaching of kraft pulp. US Patent 691193, **1997**.
77. Paice, M. G.; Bourbonnais, R.; Reid, I. D. Bleaching kraft pulps with oxidative enzymes and alkaline hydrogen peroxide. *Tappi J.* **1995**, *78*(9), 161–169.
78. Sigoillot, J. C.; Petit, C. M.; Herpoel, I.; Joseleau, J. P.; Ruel, K.; Kurek, B.; de Choudens C.; Asther, M. Energy saving with fungal enzymatic treatment of industrial poplar alkaline peroxide pulps. *Enzyme Microb. Technol.* **2001**, *29*(2–3), 160–165.
79. Buschle-Diller, G. Oxidoreductases for textile applications. INTB Intern. Network Text. Biotechnol., Graz, Austria, Jun 13–16, **2004**.
80. Mansfield, S. D.; De, J. E.; Saddler, J. N. Cellobiose dehydrogenase, an active agent in cellulose depolymerization. *Appl. Environ. Microbiol.* **1997**, *63*(10), 3804–3809.

81. Henriksson, G.; Johansson, G.; Pettersson, G. A critical review of cellobiose dehydrogenases. *J. Biotechnol.* **2000**, *78*, 93–113.
82. Pramod, K. Liquid laundry detergents containing stabilized glucose–glucose oxidase system for hydrogen peroxide generation. US 5288746, **1994**.
83. Thoen, C. A. J.; Fredj, A.; Labeque, R. Detergent compositions inhibiting dye transfer in washing. EP 596186, **1994**.
84. Buschle-Diller, G.; Yang, X. D.; Yamamoto, R. Enzymatic bleaching of cotton fabric with glucose oxidase. *Text. Res. J.* **2001**, *71*(5), 388–394.
85. Tzanov, T.; Costa, S. A.; Guebitz, G. M.; Cavaco-Paulo, A. Hydrogen peroxide generation with immobilized glucose oxidase for textile bleaching. *J. Biotechnol.* **2002**, *93*, 87–94.
86. Clarke, J. H.; Rixon, J. E.; Ciruela, A.; Gilbert, H. J.; Hazlewood, G. P. Family-10 and family-11 xylanases differ in their capacity to enhance the bleachability of hardwood and softwood paper pulps. *Appl. Microbiol. Biotechnol.* **1997**, *48*(2), 177–183.
87. Viikari, L.; Ranva, M.; Kantelinen, A.; Sanquist, J.; Linko, M. Bleaching with enzymes. Third International Conference in Biotechnology in the Pulp and Paper Industry, Stockholm, Sweden, **1986**, 67–69.
88. Rizzatti, A. C. S.; Sandrim, V. C.; Jorge, J. A.; Terenzi, H. F.; de Lourdes, M.; Polizeli, M. L. T. M. Influence of temperature on the properties of the xylanolytic enzymes of the thermotolerant fungus *Aspergillus phoenicis*. *J. Ind. Microbiol. Biotechnol.* **2004**, *31*, 88–93.
89. Bocchini, D. A.; Damiano, V. B.; Gomes, E.; Da, S. R. Effect of *Bacillus circulans* d1 thermostable xylanase on biobleaching of eucalyptus kraft pulp. *Appl. Biochem. Biotechnol.* **2003**, *106*, 393–401.
90. Kumar, B. K.; Balakrishnan, H.; Rele, M. V. Compatibility of alkaline xylanases from and alkaliphilic *Bacillus* ncl (87-6-10) with commercial detergents and proteases. *J. Ind. Microbiol. Biotechnol.* **2004**, *31*, 83–87.
91. Wong, K. K. Y.; de Jong, E.; Saddler, J. N.; Allison, R. W. Mechanisms of xylanase aided bleaching of kraft pulp. *Appita J.* **1997**, *50*(6), 509–518.
92. Kantelinen, A.; Hortling, B.; Sundquist, J.; Linko, M.; Viikari, L. Proposed mechanism of the enzymatic bleaching of kraft pulp with xylanases. *Holzforschung* **1993**, *47*, 318–324.
93. Hortling, B.; Korhonen, M.; Buchert, J.; Sundquist, J.; Viikari, L. The leachability of lignin from kraft pulps after xylanase treatment. *Holzforschung* **1994**, *48*, 441–446.
94. de Jong, E.; Wong, K. K. Y.; Saddler, J. N. The mechanism of xylanase prebleaching of kraft pulp: An examination of using model pulps prepared by depositing lignin and xylan on cellulose fibers. *Holzforschung* **1997**, *51*, 19–26.
95. Chakar, F. S.; Allison, L.; Ragauskas, A.; McDonough, T. J.; Sezgi, U. Influence of hexenuronic acids on U.S. bleaching operations. *Tappi J.* **2000** *83*(November), 62.
96. Dence, C. W.; Reeve, D. W. In: *Pulp Bleaching—Principles and Practice*. Tappi Press, Atlanta, **1996**, 365–377.
97. Viikari, L.; Kantelinen, A.; Sundquist, J.; Linko, M. Xylanases in bleaching: from an idea to the industry. *FEMS Microbiol. Rev.* **1994**, *13*, 335–350.
98. Jiang, Z. H.; Lierop, B. V.; Berry, R. Hexenuronic acid groups in pulping and bleaching chemistry. *Tappi J.* **2000**, *83*(1), 167–175.
99. Elegir, G.; Sykes, M.; Jeffries, T. W. Differential and synergistic action of *Streptomyces* endoxylanases in prebleaching of kraft pulps. *Enzyme Microb. Technol.* **1995**, *17*(10), 954–959.
100. Bermek, H.; Li, K.; Eriksson, K. E. L. Pulp bleaching with manganese peroxidase and xylanase: A synergistic effect. *Tappi J.* **2000**, *83*(10), 69.

101. Beg, Q. K.; Kapoor, M.; Mahajan, L.; Hoondal, G. S. Microbial xylanases and their industrial applications: A review. *Appl. Microbiol. Biotechnol.* **2001**, *56*(3–4), 326–338.
102. Bajpai, P.; Bajpai, P. K. Deinking with enzymes: A review. *Tappi J.* **1998**, *81*(12), 111–117.
103. Clarke, J. H.; Davidson, K.; Rixon, J. E.; Halstead, J. R.; Fransen, M. P.; Gilbert, H. J.; Hazlewood, G. P. A comparison of enzyme-aided bleaching of softwood paper pulp using combinations of xylanase, mannanase and α-galactosidase. *Appl. Microbiol. Biotechnol.* **2000**, *53*(6), 661–667.
104. Buchert, J.; Salminen, J.; Siika, A. M.; Ranua, M.; Viikari, L. The role of *Trichoderma reesei* xylanase and mannanase in the treatment of softwood kraft pulp prior to bleaching. *Holzforschung* **1993**, *47*, 473–478.
105. Suurnakki, A.; Clark, T.; Allison, D.; Viikari, L.; Buchert, J. Xylanase and mannanase-aided ecf and tcf bleaching. *Tappi J.* **1996**, *79*(7), 111–117.
106. Suurnakki, A.; Heijnesson, A.; Buchert, J.; Tenkanen, M.; Viikari, L.; Westermark, U. Location of xylanase and mannanase action in kraft fibers. *J. Pulp Paper Sci.* **1996**, *22*(3), J78–J83.
107. Saake, B.; Clark, T.; Puls, J. Investigations on the reaction mechanism of xylanases and mannanases on sprucewood chemical pulps. *Holzforschung* **1995**, *49*, 60–68.
108. Sunna, A.; Gibbs, M. D.; Chin, C. W.; Nelson, P. J.; Bergquist, P. L. A gene encoding a novel multidomain β-1,4-mannanase from *Caldibacillus cellulovorans* and action of the recombinant enzyme on kraft pulp. *Appl. Environ. Microbiol.* **2000**, *66*(2), 664–670.
109. Kansoh, A. L.; Nagieb, Z. A. Xylanase and mannanase enzymes from *Streptomyces galbus* nr and their use in biobleaching of softwood kraft pulp. *Antonie van Leeuwenhoek* **2004**, *85*, 103–114.
110. Gutierrez, A.; del Rio, J. C.; Martinez, M. J.; Martinez, A. T. The biotechnological control of pitch in paper pulp manufacturing. *Trends Biotechnol.* **2001**, *19*(9), 340–348.
111. Pere, J.; Siika, A. M.; Buchert, J.; Viikari, L. Effects of purified *Trichoderma reesei* cellulases on the fiber properties of kraft pulp. *Tappi J.* **1995**, *78*(6), 71–78.
112. Pommier, J. C.; Fuentes, J. L.; Goma, G. Using enzymes to improve the process and the product quality in the recycled paper industry. *Tappi J.* **1989**, *72*(6), 187–191.
113. Jackson, L. S.; Heitmann, J. A.; Joyce, T. W. Enzymatic modifications of secondary fiber. *Tappi J.* **1993**, *76*(3), 147–154.
114. Heise, O. U.; Fineran, W. G.; Unwin, J. P.; Sykes, M. S.; Klungness, J. H.; Abubakr, S. Industrial scale-up of enzyme enhanced deinking of non-impact printed toners. Tappi Pulping Conference, Tappi Press, Altanta, **1995**, 349–354.
115. Jeffries, T. W.; Klungness, J. H.; Sykes, M. S.; Rutledge-Cropsey, K. Comparison of enzyme-enhanced with conventional deinking of xerographic and laser-printed paper. *Tappi J.* **1994** *77*(April), 173–179.
116. Klungness, J. H.; Sykes, M. S.; Jeffries, T. W.; Abubakr, S. Enzyme enhanced deinking of toners. In: Doshi, D. (Ed.) *Paper Recycling Challenge Vol II—Deinking.* Doshi and Associates, Appleton, WI, **1997**, 155–160.
117. Rutledge-Cropsey, K.; Klungness, J. H.; Abubakr, S. Performance of enzymatically deinked wastepaper on papermachine runnability. Tappi Pulping Conference, Tappi Press, Atlanta, **1995**, 639–643.
118. Welt, T.; Dinus, R. J. Enzymatic deinking: Effectiveness and mechanisms. *Wochenb. Papierfabrik.* **1998**, *126*(9), 396–407.
119. Welt, T.; Dinus, R. J. Enzymatic deinking—A review. *Prog. Paper Recycling* **1995** *4*(February), 36–45.

120. Moran, B. R. Enzyme treatment improves refining efficiency, recycled fiber freeness. *Pulp Paper* **1996** *70*(September), 119–121.
121. Zeyer, C.; Joyce, T. W.; Rucker, J. W.; Heitmann, J. A. Enzymatic deinking of cellulose fabric: A model study for enzymatic paper deinking. *Prog. Paper Recycling* **1993** *3*(November), 36–44.
122. Sykes, M. S.; Klungness, J. H.; Abubakr, S.; Tan, F. Upgrading recovered paper with enzyme pre-treatment and pressurized peroxide bleaching. *Prog. Paper Recycling* **1996**, *5*(August), 39–45.
123. Elegir, G.; Panizza, E.; Canetti, M. Neutral-enzyme-assisted deinking of xerographic office waste with a cellulase–amylase mixture. *Tappi J.* **2000**, *83*(11), 71.
124. Park, J. W.; Park, K. N. Biological de-inking of waste paper using modified cellulase with polyoxyethylene. *Biotechnol. Tech.* **1999**, *13*, 49–53.
125. Morkbak, A. L.; Zimmermann, W. Deinking of mixed office paper, old newspaper and vegetable oil-based ink printed paper using cellulases, xylanases and lipases. *Prog. Paper Recycling* **1998** *7*(February), 14–21.
126. Sanciolo, P.; Warnock, H.; Harding, I.; Forbes, L.; Lonergan, G. Microscopy study: Liberation of ink from fibers during enzymatic deinking of mixed office papers. *Prog. Paper Recycling* **2000** *9*(May), 22–30.
127. Sykes, M. S.; Klungness, J. H.; Geisner, R.; Abubakr, S. Stickie removal using neutral enzymatic pulping and pressure screening. Tappi Recycling Symposium, Tappi Press, Atlanta, **1998**, 291–296.
128. Schulein, M.; Outtrup, H.; Jorgensen, P. L.; Bjornvad, M. E. Alkaline xyloglucanases from *Bacillus* suitable for fabric detergents. US 9902663, **1999**.
129. Nickel, D.; Bianconi, P.; Voelkel, T.; Speckmann, H.-D.; Jekel, M. Textile care agent containing cellulase and a color-fixing agent. IntPA 2001074982, **2001**.
130. Galante, Y. M.; Formantici, C. Enzyme applications in detergency and in manufacturing industries. *Curr. Org. Chem.* **2003**, *7*(13), 1399–1422.
131. Levene, R.; Shakkour, G. Wool fibers of enhanced luster obtained by enzymic descaling.*J. Soc. Dyers Colour* **1995**, *111*(11), 352–359.
132. Guo, W.; Zhang, J.; Cheng, L. Silk cold padding and whitening method. *Faming Zhuanli Shenqing Gongkai Shuomingshu* **2001**, CNXXEV CN1284574 A 20010221.
133. Pedersen, G. L.; Screws, G. A.; Cedroni, D. M. Biopolishing of cellulosic textiles. *Tinctoria* **1993**, *90*(8), 59–63.
134. Cortez, J. M.; Ellis, J.; Bishop, D. P. Cellulase finishing of woven, cotton fabrics in jet and winch machines. *J. Biotechnol.* **2001**, *89*(2, 3), 239–245.
135. Ramkumar, S. S.; Abdalah, G. Surface characterization of enzyme treated fabrics. *Colourage* **2001**, *48*(4), 15–16, 24.
136. Auterinen, A.; Carreras, D.; Navarro, M. Developments in enzyme technology for textile application. *Rev. Quim. Text.* **2000**, *148*(34), 36–37, 40–42, 44.
137. Heikinheimo, L.; Cavaco-Paulo, A.; Nousiainen, P.; Siika-aho, M.; Buchert, J. Treatment of cotton fabrics with purified *Trichoderma reesei* cellulases. *J. Soc. Dyers Colour.* **1998**, *114*(7/8), 216–220.
138. Cavaco-Paulo, A.; Guebitz, G. M. (Eds.) *Textile Processing with Enzymes*. Woodhead Publ., Cambridge, U.K., **2000**, 86–119.
139. Taylor, J.; Fairbrother, A., Tencel—it's more than just peachskin. *J. Soc.Dyers Colour.* **2000**, *116*(12), 381–384.
140. Gandhi, K.; Burkinshaw, S. M.; Taylor, J. M.; Collins, G. W. A novel route for obtaining a "peach skin effect" on lyocell and its blends. *AATCC Rev.* **2002**, *2*(4), 48–52.

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141. Ibrahim, N. A.; El-Hossamy, M.; Morsy, M. S.; Eid, B. M. Development of new eco-friendly options for cotton wet processing. *J. Appl. Polym. Sci.* **2004**, *93*(4), 1825–1836.
142. Losonczi, A.; Csiszar, E.; Szakacs, G.; Kaarela, O. Bleachability and dyeing properties of biopretreated and conventionally scoured cotton fabrics. *Text. Res. J.* **2004**, *74*(6), 501–508.
143. Calafell, M.; Garriga, P. Effect of some process parameters in the enzymatic scouring of cotton using an acid pectinase. *Enzyme Microb. Technol.* **2004**, *34*(3–4), 326–331.
144. Traore, M. K.; Buschle-Diller, G. Environmentally friendly scouring processes. *Text. Chem. Color. Am. Dyestuff Rep.* **2000**, *32*(12), 40–43.
145. Waddell, R. B. Bioscouring of cotton: Commercial applications of alkaline stable pectinase. *AATCC Rev.* **2002**, *2*(4), 28–30.
146. Takagishi, T.; Yamamoto, R.; Kikuyama, K.; Arakawa, H. Design and application of continuous bio-scouring machine. *AATCC Rev.* **2001**, *1*(8), 32–34.
147. Terpe, K. Overview of tag protein fusions: From molecular and biochemical fundamentals to commercial systems. *Appl. Microbiol. Biotechnol.* **2003**, *60*(5), 523–533.
148. Shoseyov, O.; Warren, R. A. J. Cellulose binding domains—a novel fusion technology for efficient, low cost purification and immobilization of recombinant proteins. *Innovations* **1997**, *7*, 1–3.
149. Cavaco, P. A.; Morgado, J.; Andreaus, J.; Kilburn, D. Interactions of cotton with cbd peptides. *Enzyme Microb. Technol.* **1999**, *25*(8–9), 639–643.
150. Xiao, Z.; Gao, P.; Qu, Y.; Wang, T. Cellulose-binding domain of endoglucanase III from *Trichoderma reesei* disrupting the structure of cellulose. *Biotechnol. Lett.* **2001**, *23*(9), 711–715.
151. Pala, H.; Lemos, M. A.; Mota, M.; Gama, F. M. Enzymatic upgrade of old paperboard containers. *Enzyme Microb. Technol.* **2001**, *29*, 274–279.
152. Nigmatullin, R.; Lovitt, R.; Wright, C.; Linder, M.; Nakari-Setala, T.; Gama, M. Atomic force microscopy study of cellulose surface interaction controlled by cellulose binding domains. *Colloids Surfaces B: Biointerfaces* **2004**, *35*, 125–135.
153. Boraston, A. B.; McLean, B. W.; Chen, G.; Li, A.; Warren, R. A. J.; Kilburn, D. G. Cooperative binding of triplicate carbohydrate-binding modules from a thermophilic xylanase. *Mol. Microbiol.* **2002**, *43*(1), 187–194.
154. Xu, Z.; Bae, W.; Mulchandani, A.; Mehra, R. K.; Chen, W. Heavy metal removal by novel cbd-ec20 sorbents immobilized on cellulose. *Biomacromolecules* **2002**, *3*(3), 462–465.
155. Degani, O.; Gepstein, S.; Dosoretz, C. G. A new method for measuring scouring efficiency of natural fibers based on the cellulose-binding domain-β-glucuronidase fused protein. *J. Biotechnol.* **2004**, *107*, 265–273.
156. Brumer III, H.; Zhou, Q.; Baumann, M. J.; Carlsson, K.; Teeri, T. Activation of crystaline cellulose surfaces through chemoenzymatic modification of xyloglucan. *J. Am. Chem. Soc.* **2004**, *126*, 5715–5721.
157. Lima, D. U.; Oliveira, R. C.; Buckeridge, M. S. Seed storage hemicelluloses as wet end additives in papermaking. *Carbohydr. Polym.* **2003**, *52*, 367–373.