Chapter 11
Removal of Shives

11.1 Introduction

For fully bleached pulps, good cleanness appears more important than high brightness. A lack of cleanliness can lead to a number of problems such as dark dots, fish eyes, gravure speckle, preparations, and uneven coating in the final product. The cleanliness level at a particular brightness is the result of the competition for bleaching chemicals between dissolved organic substances pulp fibers and wood particles. There are three main sources of dirt contamination: the wood, process problems, and external origins, for example plastics. More than half of the impurities found in pulp originate from wood (Robitaille 1991). The cleanliness of bleached pulp is affected by coarse particles derived from the cellular tissue of the tree and by extraneous particles. The former group consists of shives, knots, and bark specks. The latter group consists of pitch, fungus hyphae, rust strains, lime, and sand (Annergren and Lindblad 1996). Shive is a particle or fiber bundle large enough, or in enough quantity, to produce a paper and board quality or productivity problems. Normally, this particle has a thickness, or third dimension, that separates if from being benign to being problematic. For example:

- Shives in bleached pulps show up as dirt in paper or board.
- Shives in unbleached pulps reduce print quality, reduce end strength, decrease runnability, and present visual defects.
- Shives in mechanical pulps cause paper machine breaks, offset printer linting, pick outs, coater scratches, visual defects and reduce print quality.

In short, the presence of shives in pulp is problematic to meeting customer expectations and maintaining optimum production costs. In any pulping operation, a practical balance is struck between theoretical desirability and economical feasibility.

The concentration of shives decreases significantly during most of the bleaching operation (Axegard 1980; Axegard and Teder 1976; Germgard and Sjogren 1985). Typically, bleaching to make market pulp removes 95–99% of the shives

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Table 11.1 Methods used for improving pulp cleanliness

Method 1. Increase brightness	
	Increase in chemical use and bleaching costs
Method 2. Decrease number of stages	
	Increase in chemical use and bleaching costs
Method 3. Decrease temperature	
	No effect on chemical use if retention time is sufficient; Increase In utility costs
Method 4. Increase (CD) chemicals/decrease D1 and D2	
	Small increase in chemical use; increase AOX
Method 5. Add (CD) chemicals together rather than sequentially	
	Increase in chemical use; increase AOX

Based on Annergren and Lindblad (1996) and Bruun et al. (1993)

(Axegard 1990). Shives themselves do not consume significant amount of bleaching chemicals. However, the difficulties in removing shives by bleaching can increase bleaching chemical use significantly. The shive count of bleached pulp depends on the shive count for the pulp as it enters the bleach plant and the efficiency of shive removal by the bleaching chemicals. The efficiency of shive bleaching depends on the concentration of bleaching chemical overtime, which depends on the initial chemical charge and the temperature. An improved degree of shive removal is obtained by maintaining a high concentration of bleaching chemical for as long as possible. This can be accomplished by, for example, increasing the retention time, which is often impractical, decreasing the rate of reaction, or increasing the concentration of the bleaching chemicals. The methods that are used to do this are listed in Table 11.1 (Annergren and Lindblad 1996; Bruun et al. 1993). Bleaching in short bleaching sequences provides much better cleanliness than bleaching in long sequences. Progress in mill techniques such as whole tree utilization and closing up of the screening department including recycling the screenings aggravate cleanliness problems. Improved bleaching techniques with more extensive use of chlorine dioxide allow prolonged cooking without too much carbohydrate degradation during cooking and bleaching. The resulting pulp has fewer and probably less shives (Annergren and Lindblad 1996).

One of the technologies for improving the bleachability of kraft pulp involves the use of hemicellulase enzymes (Bajpai 2004, 2009; Bajpai and Bajpai 1992, 1997; Grant 1994, 1995; Hancock and Esteghlalian 2007; Lavielle 1993; Senior and Hamilton 1992; Skerker et al. 1991; Tolan 1992a, b; Viikari et al. 1993, 1994). This process, sometimes termed bleach boosting, has been successfully used in pulp mills throughout the world (Lavielle 1993; Viikari et al. 1994). The main enzyme needed to enhance the delignification of kraft pulp is reported to be endo-β-xylanase but enrichment of xylanase with other hemicellulolytic enzymes has been shown to improve the effect of enzymatic treatment (Viikari et al. 1994). These enzymes modify the xylan portion of the hemicellulose in such a way as to increase the efficiency of the subsequent bleaching stages. The effects of enzyme treatment on pulp brightness and delignification have been reported widely (Pedersen et al. 1992; Senior and Hamilton 1992; Skerker et al. 1991; Tolan 1992a, b). Typically, enzyme-treated pulp can be bleached to a target brightness with 15% less oxidative bleaching chemicals than untreated pulp, with no difference in pulp strength (Bajpai and Bajpai 1997; Viikari et al. 1994). These benefits have propelled xylanase enzyme treatment into regular use in many mills. Xylanase enzymes have been also used to increase the efficiency of shive removal by bleaching and encouraging results have been obtained (Tolan et al. 1994).

11.2 Application of Enzymes for Shive Removal

Researchers from Iogen Corporation, Canada used a novel enzyme treatment to improve the efficiency of shive removal by bleaching. They used three xylanase enzymes from different microbial sources (Tolan et al. 1994). One of the enzymes was a product of Iogen Corporation, which was designed to enhance the removal of shives by bleaching and sold under the trade name "Shivex." Other two enzymes were commercial bleach boosting xylanase preparations. The ability of the xylanase enzymes to enhance the shive removal was found to vary greatly. Lack of correlation of shive removal with xylanase dosage was found showing that different shive removal factor (Sf) result from treatment with different enzymes all at the same xylanase dose (Table 11.2). Shivex had the highest degree of enhancement of Sf of

Table 11.2 Effect of different xylanase enzymes on shive removal factor and bleach boosting

Pulp treatment		Brightness (Elrepho)
Shive removal factor (Sf)		
Untreated	25.0	85.5
	35.3	86.6
	63.6	87.7
Xylanase 2	26.2	86.2
	32.3	87.0
	38.9	88.0
Xylanase 3	45.0	86.5
	62.5	87.1
Shivex	37.0	85.2
	46.6	86.3
	77.2	87.2
Kappa factor		
Untreated	0.20	83.5
	0.22	85.4
	0.24	86.5
	0.26	87.7
Xylanase 2	0.19	85.2
	0.21	86.3
	0.23	87.2
Xylanase 3	0.205	86.2
	0.225	87.0
	0.235	88.0
Shivex	0.20	86.4
	0.22	87.1

Based on Tolan et al. (1994)

Table 11.3 Effect of Shivex on shive counts and shive factor in different bleaching stages at varying kappa factor

Bleaching stage	Pulp treatment	D100 kappa factor	Shives	Log Sf (% of initial)
D100	Untreated	0.15	34.0	0.44
		0.17	34.0	0.44
		0.23	32.5	0.50
		0.26	27.5	0.56
	Shivex treated	0.15	35.0	0.44
		0.17	31.0	0.50
		0.23	27.5	0.56
		0.26	23.0	0.62
E	Untreated	0.15	16.7	0.76
		0.17	15.7	0.80
		0.23	10.0	1.00
		0.26	8.0	1.10
	Shivex treated	0.15	14.0	0.83
		0.17	13.3	0.86
		0.23	8.1	1.10
		0.26	6.0	1.13
D100E-D	Untreated	0.15	0.90	1.82
		0.22	0.86	1.91
		0.23	0.70	1.88
		0.24	0.60	2.00
		0.26	0.40	2.03
	Shivex treated	0.15	1.5	2.07
		0.17	1.1	2.07
		0.23	1.3	2.16
		0.24	1.0	2.25
		0.26	0.9	2.50

Based on Tolan et al. (1994)

the three enzymes. Xylanase 2 decreased Sf at a given brightness while xylanase 3 enhanced Sf less than Shivex. The ability of enzymes to enhance shive removal was not related to the degree of bleach boosting of the enzymes (Table 11.2). Shivex showed the highest enhancement of shive removal in spite of the fact that the bleach boosting performances of the three enzymes are similar. The best performance of the Shivex was found at pH 5.2–7.8, and temperature, 40–62°C and more than 1 h treatment. The conditions for shive removal by Shivex differed slightly from those for bleaching enhancement. Shivex did not have any measurable effect on the shive count or particle size in the enzyme treatment itself. The effects of Shivex became evident after subsequent bleaching. Treatment with Shivex decreased the shive count after each of the stages in D100-E-D bleaching sequence (Table 11.3). After the D100 stage for a given chemical dose, the shive count was 10% lower for enzyme-treated pulp than for untreated pulp. This enzyme effect was found to differ

Table 11.4 Effect of Shivex on shive removal factors (Sf)[a]

Bleaching stage	Untreated	Enzyme-treated	Shive benefits
D100	3.1	3.5	1.13
E	3.2	3.5	1.09
D	10	12.5	1.25
Total	100	155	1.55

Based on Tolan et al. (1994)
[a]Kappa factor 0.24

from that observed in bleach boosting by xylanase enzymes, in which there was a little change in the brightness or kappa number of chlorinated pulp. After the extraction stage, the enzyme-treated pulp had 20% fewer shives than the untreated pulp. The benefit of enzyme treatment was greatest after the D1 stage to the extent that the shive count for treated pulp was 50% lower than for untreated pulp. Sf for the bleaching sequence increased from 100 to 155, showing about 55% increase in shive reduction (Tables 11.3 and 11.4). At a given bleached brightness, Shivex treatment was found to result in lower shive count. Enzyme treatment, therefore, helps to remove shives from the pulp beyond the associated gain in the brightness.

11.3 Mechanism of Shive Removal with Xylanase Enzymes

Enzymatic shive removal and bleach boosting are affected through different mechanisms (Tolan et al. 1994). It appears that shive removal is accomplished by an enzyme other than xylanase or that some property of xylanase other than its ability to hydrolyze xylan is important in shive removal. Most bleach boosting enzymes are the mixtures of 6–20 different proteins many of which have not been identified and only one or two of which are xylanase. Preliminary investigation of several enzymes that digest various portions of pulp including α-arabinosidase, mannanase and cellulase failed to identify a single enzyme that is responsible for enhanced shive bleaching. In terms of properties of the xylanase protein, the ability to bind on to shives or to penetrate in to shives could conceivably vary among the enzymes and cause different efficiencies of shive removal. However, there has been no direct evidence of this. The enzymes used for shive removal had molecular weights of 20–22,000 and showed similar binding tendencies on the substrate. Axegard (1990) has identified two mechanisms for shive removal by chlorine dioxide: peeling of fibers from the surface and fragmentation of the particles. The rate controlling step of both these reactions is the diffusion of chemical within the particles. Tolan et al. (1994) have suggested that enzyme acts on the surface of the shives to remove diffusion barriers and thereby increasing the efficiency of shive bleaching.

11.4 Benefits with Enzymes

Mills have following options for using enzyme treatment to decrease shives (Tolan et al. 1994).

Option 1: Maintain the same brightness, decrease shives and bleaching chemicals.
Option 2: Increase brightness and decrease shives.
Option 3: Maintain the same shive factor, decrease brightness and bleaching chemicals.

The choice at a given mill will depend on the mills operating objectives and constraints.

Option 1 is accomplished by running enzyme treatment and adjusting the control of the bleach plant to maintain the same bleached brightness as without enzyme treatment. This option saves bleaching chemicals and increases the shive factor.

Option 2 is accomplished by running enzyme treatment with no changes in the beaching chemical use. The result is higher brightness and the increase in shive factor. This option gives the maximum increase in shive factor.

Option 3 would be of interest to mills that are bleaching to a higher than necessary target brightness to maintain a low shive count. In this case, the shive factor is unchanged but the brightness target is decreased which allows a decrease in kappa factor.

Benefits of shive reduction would often be difficult to observe directly in the short term in an operating mill because mills necessarily run with Sf that allows a large margin of safety and, therefore, usually have few shives in the bleached pulp. On the contrary, treatment with Shivex would allow a mill to take benefits in chemical savings without undue risk of increasing shive counts. Shivex can be used in conjunction with other oxidizing chemicals to decrease the use of chlorine compounds without increasing the tendency to form shives. Most effective means to decrease kappa factor while increasing Sf is to combine Shivex treatment with peroxide reinforcement of the extraction stage (Table 11.5).

Table 11.5 Shive removal in different bleaching sequences

Bleaching sequence	Kappa factor	Shive removal factor
Control (D100ED)	0.26	115
3 kg/tons peroxide (D100(EP)D)	0.235	100
Shivex (SD100ED)	0.235	155
6 kg/tons peroxide [D100(EP)D]	0.20	90
Shivex plus 3 kg/tons peroxide [SD100(EP)D]	0.20	145

Based on Tolan et al. (1994)

11.5 Conclusions

Enzymes can be efficiently used to increase the efficiency of shive removal by bleaching. By treating brownstock with enzymes, mills can increase the degree of shive removal in the subsequent bleaching. Depending upon the shive level in the incoming brownstock and the desired shive level of the bleached pulp, this allows a mill to decrease its actual shive counts or to increase its margin of safety against shives. The increase in shive removal is accompanied by an increased efficiency in the bleaching of pulp. Therefore, mills can decrease chlorine use in bleach plant without compromising on shive counts. The enzyme activity responsible for the enhanced shive removal is not known. The degree of shive removal by the enzyme is not directly related to the enzyme's xylanase activity or bleach boosting effectiveness.

References

Annergren GE, Lindblad PO (1996) Shives/brightness: a problem of bleaching optimization. Tappi J 59(11):95–98

Axegard P (1980) Effect of prebleaching with chlorine and chlorine dioxide on the cleanliness of softwood kraft pulp. Svensk Papperstidn 83(10):284

Axegard P (1990) Bleaching shives and dirt – an overview. In: Paper presented at 1990 bleach plant operations short course held 17–22 June 1990, Hilton Head, SC, pp 27–34

Axegard P, Teder A (1976) Model experiments in bleaching of shives and bark particles. In: 1976 International pulp bleaching conference, 2–6 May 1976, pp 35–43

Bajpai P (2004) Biological bleaching of chemical pulps. In: Stewart GG, Russell I (eds) Critical reviews in biotechnology, vol 24. CRC Press, Boca Raton, pp 1–58

Bajpai P (2009) Xylanases. In: Schaechter M, Lederberg J (eds) Encyclopedia of microbiology, vol 4, 3rd edn. Academic, San Diego, pp 600–612

Bajpai P, Bajpai PK (1992) Biobleaching of kraft pulp. Process Biochem 27:319–325

Bajpai P, Bajpai PK (1997) Realities and trends in enzymatic prebleaching of kraft pulp. Adv Biochem Eng/Biotechnol 57:1–31

Bruun H, Henricson K, Kronlof T (1993) Particles in bleached softwood sulphate pulp and their reduction. Pap Puu 10(3):126

Germgard U, Sjogren B (1985) Ozone prebleaching of a modified cooked and oxygen bleached softwood kraft pulp. Svensk Papp 88(15):R127

Grant R (1994) Enzymes' future looks bright, as range improves and expands. Pulp Paper Int 36(8):20

Grant R (1995) Enzymes help to increase pulp and paper production. Pulp Paper Int 37(8):26

Hancock B, Esteghlalian AR (2007) New technology tools discover enzyme products to enhance pulp bleaching. In: 2007 Engineering, pulping and environmental conference, Jacksonville, FL, 21–24 Oct 2007, 4pp

Lavielle P (1993) Xylanase prebleaching. Asia Pac Papermaker 3(5):29

Pedersen LS, Choma PP, Holm HC, Kihlgren P, Munk N, Nissen AM (1992) Enzymatic bleach boosting of kraft pulp: laboratory and mill scale experiences. In: Paper presented at 1992 pulping conference, Boston, MA, Book 1, 1–5 Nov 1992, pp 31–37

Robitaille MA (1991) Policing dirt and plastic contamination Bleach plant operations short course notes. Tappi Press, Atlanta, p 39

Senior DJ, Hamilton J (1992) Use of xylanases to decrease the formation of AOX in kraft pulp bleaching. J Pulp Paper Sci 18(5):J165–J169

Skerker PS, Farrell RL, Chang HM (1991) Chlorine free bleaching with Cartazyme HS treatment. In: Proceedings of the international pulp bleaching conference, Stockholm, vol 2, pp 93–105

Tolan JS (1992a) The use of enzymes to decrease the chlorine requirements in pulp bleaching. In: 78th CPPA annual meeting, preprints, Montreal, pp A163–A168

Tolan JS (1992b) The use of enzymes to enhance pulp bleaching. In: Proceedings of Tappi pulping conference, Boston, MA, 6–10 Nov 1992, pp 13–17

Tolan JS, Guenette M, Thebault L, Winstanley C (1994) The use of a novel enzyme treatment to improve the efficiency of shive removal by bleaching. Pulp Pap Canada 95(12):T488

Viikari L, Tenkanen M, Buchert J, Ratto M, Bailey M, Siika-aho M, Linko M (1993) Hemicellulases for industrial applications. In: Saddler JN (ed) Bioconversion of forest and agricultural plant residues. CAB International, Wallingford

Viikari L, Kantelinen A, Sundquist J, Linko M (1994) Xylanases in bleaching: from an idea to the industry. FEMS Microbiol Rev 13:335–351