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ABSTRACT

The authors studied the effect of concentration, reaction time, and addition of flotation aid for bacterial a-amylase hydrolytic enzyme to enhance flotation deinking of copy papers by analyzing pulp properties, optical properties, and strength of handsheets. Brightness values obtained after the enzymatic deinking process were in the same range as the original copy papers. After one flotation deinking cycle, the number of toner particles could be reduced up to 70%. The deinking process did not adversely affect the pulp properties and sheet strength properties.

Application:

Using an enzyme-assisted deinking process provides higher efficiency with an increase in toner particle removal from approximately 50% to 70–85%

Enzymatic deinking of nonimpact printed white office paper with α-amylase

HELGA K. ZOLLNER AND LELAND R. SCHROEDER

NONIMPACT PRINTED WHITE office papers that include xerographic and laser printed papers are difficult to deink with conventional deinking methods *(1)*. Because offices use more laser printers and copy machines every year, the volume of nonimpact printed papers entering the recycled paper stream is increasing. Ink removal from these papers remains a major challenge. Deinking processes are also substantial sources of solid and liquid waste. Disposal of this waste can present a problem. Deinking plants would benefit from processes that are more effective and generate less waste.

Conventional chemical deinking is not an effective means for deinking nonimpact printed papers *(2)*. The reduced efficiency is due primarily to the strong adherence of the toner particles to the paper surface. Enzymatic deinking methods represent a new approach to convert these recycled papers into quality products. Investigators have examined hydrolytic enzymes such as cellulase and various hemicellulases to improve the deinking performance of nonimpact printed white office papers *(3–5)*. Residual ink areas are less than those after chemical deinking treatment. Yield reduction could result from losses in fines due to cellulase and hemicelluase activity. Little information is available concerning the total yield loss in enzyme-assisted flotation deinking compared with chemical flotation deinking alone. Potential benefits of these enzyme-assisted processes include higher freeness and reduced water retention values, greater paper strength, reduced chemical usage, lower bleaching costs, and reduced liquid and solid waste *(6)*.

The role of surface sizing applications on white office papers is becoming increasingly important. Surface sizing improves surface strength, controls penetration by water and ink, and prevents linting and dusting *(7)*. The higher demands on the surface properties of the finished product must be met. Earlier work has suggested that internal and surface sizing and the coating of papers will influence the deinking performance of recycled papers *(8, 9)*.

The objective of this work was to develop a novel deinking process for surface-sized white copy papers. Alpha-amylases pretreated the copy paper in the first stage of recycling. The enzyme influenced the degradation of the starch layer on the surface of the papers. The toner particles adhering to the paper surface released by the enzymatic treatment underwent subsequent separation from the pulp suspension via flotation.

EXPERIMENTAL

Enzyme activity

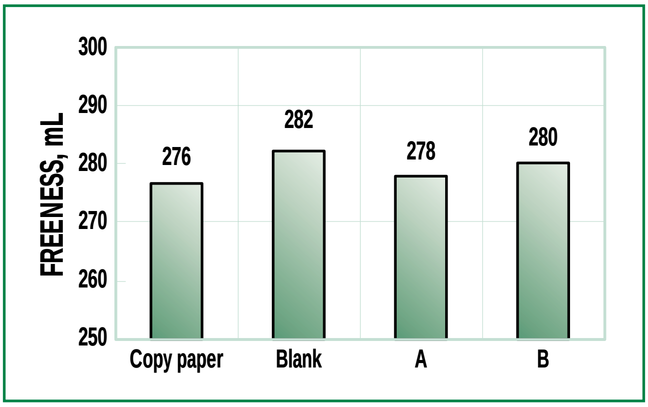
The amylase activity (bacterial alpha-amylase, BAN 120L from Novo Nordisk; optimum pH, 7.0; and optimum temperature, 50°C) was measured by the iodine staining method *(10)* and the Nelson-Somogyi method *(11)* of measuring the increase in the number of saccharide reducing ends. One Kilo-Novo-α-amylase-Unit (KNU) is the enzyme amount that will dextrinize 5.26 g dry starch (Merck Amylum soluble, Erg. B 6 Batch No. 9947275) per h under standard conditions. One International Unit (IU) is the amount of enzyme necessary to produce one micromole of starch reducing ends per min under specified conditions of starch concentration, pH, and temperature.

Paper furnish

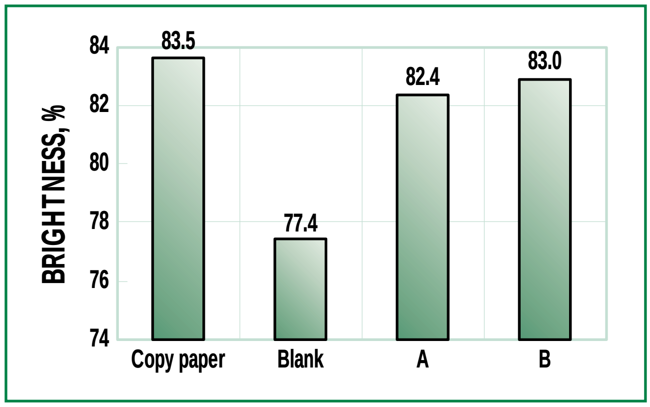
We printed a standard pattern on Yorktown Xerographic paper (75 g/m^2, Union Camp) on a Sharp SF-8300 copy machine. The filler content of the paper was approximately 12%. The printed paper then underwent accelerated aging (144 h, 60°C, 0% RH) according to the Papiertechnische Stiftung (PTS) standard method *(12)*.

Pulping

After the aging step, the pulp was slushed at 5% in a Beloit Jones Baracuda hydropulper at 60°C for 45 min. All enzymatic treatments and



1. Freeness values of selected samples: (A) no enzyme addition, 60 min reaction, and 0.3% flotation aid; (B) 1.0 NU/o.d. g pulp enzyme concentration, 60 min reaction, and 0.3% flotation aid



2. Brightness measurement of selected samples: (A) no enzyme addition, 60 min reaction, and 0.3% flotation aid; (B) 1.0 NU/o.d. g pulp enzyme concentration, 60 min reaction, and 0.3% flotation aid

deinking experiments were within one week after pulping the furnish. Unused pulp was stored during the experimental stages at 5°C.

Enzymatic treatment

The pulp suspension (80 g o.d. pulp) was transferred to the enzymatic reactor and diluted with warm water to achieve 3% consistency and 50°C. The pH was adjusted to 7.0 with reagent grade 1*N* HCl. A series of treatments was performed using various amounts of α-amylase. The reaction times with the α-amylase varied between 30 and 90 min. The enzyme reaction was stopped by increasing the pH of the suspension to 10.5 with reagent grade 6*N* NaOH—the pH used for the flotation deinking—and the pulp suspension transferred into the flotation cell.

Flotation

The flotation was performed in a 10-L Degussa flotation cell at a consistency of 0.8%. Various amounts of a nonionic, ethoxylated fatty acid flotation aid (DI-600, High Point Chemical Corp.) were added (0–0.3% on solids). The suspension was stirred at 1200 rpm for 15 min to allow the floatation aid to react with the toner particles. The flotation was performed for 5 min mixing the suspension at 1200 rpm with an air flow of 5 L/min. After the flotation, the pH of the pulp suspension was reduced to 7.5 with reagent grade 4*N* HCl. The rejects were collected for further analysis.

Sample	Tensile index, N•m/g	Burst index, kPa•m²/g	Tear index, mN•m²/g
Copy paper	–	2.1	–
Blank	37.1	2.4	11.8
No amylase	39.8	2.2	10.9
1.0 NU amylase	39.2	2.3	12.0

I. Strength properties of handsheets

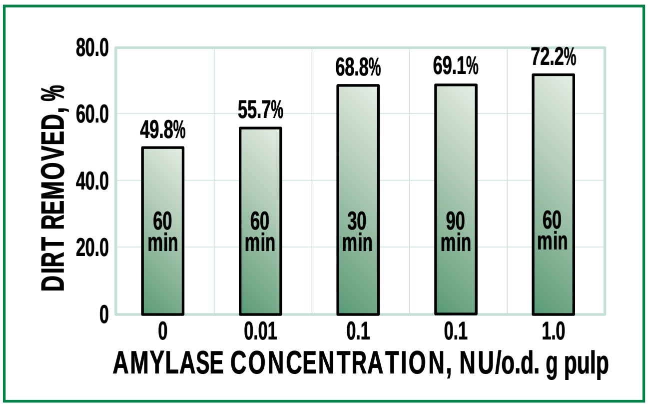
Handsheet preparation and testing

Pulp freeness was determined according to TAPPI Method T 227. Ash contents were determined according to TAPPI Method T 413 using the assumption that all the filler present in the paper was calcium carbonate. Handsheets of the pulp samples were made with a standard TAPPI handsheet mold according to TAPPI Method T 205. Physical testing of the handsheets was done according to TAPPI Method T 220. The brightness of the pulp was measured according to TAPPI Method T 452.

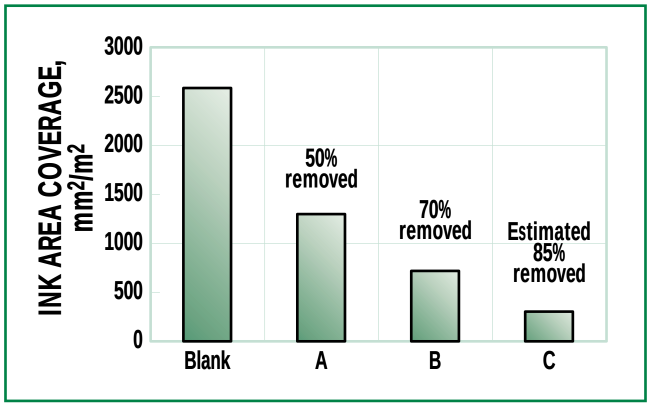
Image analysis—dirt count

Handsheets for image analysis of the toner particle content were prepared using a modification of TAPPI Method T 272. The modification omitted the filter paper cover. This procedure was chosen because it uses a large amount of pulp and a small quantity of water to make it more effective for retaining small ink particles.

A Microtek ScanMaker II HR flatbed scanner with an optical resolution of 1200 by 600 dpi was used to digitize the images of the toner particles containing handsheets. Adobe Photoshop version 2.5.1 software was used to interface with the scanner and to save the acquired images. Global Lab Image version 3.0 by Data Translation was used to count toner particles in the saved images. The threshold of the dirt particles was set to a constant value of 190 to allow the direct comparison of data from different experiments. The threshold value used corresponded to 5 standard deviations below the average gray scale value in the best deinking result. The minimum pixels per counted toner particle was set at 12. This corresponds to a particle size of 0.005 mm². The data generated from the dirt count were analyzed using spreadsheets in Microsoft Excel version 5.0. Particle size histograms represented the dirt size distributions within the sample.



3. Effect of enzyme concentration on ink dirt particle removal



4. Residual ink area coverage after the flotation of various samples: (A) no enzyme addition, 60 min reaction, and 0.3% flotation aid; (B) 1.0 NU/o.d. g pulp enzyme, 60 min reaction, and 0.3% flotation aid; (C) 1.0 NU/o.d. g pulp enzyme, 30 min reaction, and 0.3% flotation aid

The particle area summation was used to report total area coverage as parts per million (ppm) or mm^2/m^2. The ppm data generated should not be directly compared with the TAPPI standard dirt count in absolute terms. The procedure used in this analysis included particles below the TAPPI standard limit of 0.04 mm^2. The area coverage data will therefore be higher than comparable TAPPI area coverage data.

PROCESS DESCRIPTION

Pulp preparation

The recycled paper was produced by printing a standard pattern on a typical copy paper. After accelerated aging, the pulp was slushed in a hydropulper and immediately used for the experiments.

Enzymatic pretreatment with subsequent flotation

Each experiment used 80 g o.d. recycled pulp. During the enzymatic treatment of the pulp suspension, the α-amylase concentration varied was 0.01, 0.1, and 1.0 NU per o.d. g of pulp. The enzymatic reaction times were 30, 60, and 90 min.

Prasad *(5)* reported an enzymatic deinking process for laser and xerographic office waste papers without the use of flotation chemicals. Preliminary flotation experiments showed that little flotation occurred without the use of a flotation aid. The importance of the flotation aid was therefore also studied. The concentration of the nonionic flotation aid was 0, 0.15, and 0.3% based on o.d. g of pulp.

RESULTS AND DISCUSSION

Freeness

The new enzyme-assisted flotation process did not affect the freeness of the pulp. **Figure 1** shows a small range of 265–285 CSF.

Sheet strength properties

Table I shows the values of the tensile, burst, and tear indices for handsheets made from the different pulp samples. The tensile index was 37.1–39.8, the burst index 2.1–2.4, and the tear index 10.9–12.0. The new enzyme-assisted deinking process had no deleterious effects on sheet properties.

Brightness

Brightness was measured on all the handsheets made from the deinking experiments and compared to the brightness of the original copy paper. **Figure 2** shows the brightness values measured on the handsheets of some selected runs.

Brightness values in the same range as the original copy papers were achieved using an amylase concentration of 1.0 NU/o.d. g of pulp, a reaction time of 60 min, and a flotation aid concentration of 0.3%.

Yield

The yields of the flotation experiments were very high under the conditions studied. Yields of 95–98% resulted. The ash contents of the accept and reject streams of the flotations were analyzed. The material lost consisted of approximately 20% fillers and 80% fiber and fines. This is the equivalent of reducing the amount of fillers in the system by approximately 8% and the amount of fibers and fines by approximately 3%.

The yields obtained with the novel amylase-assisted deinking process are higher than existing enzyme-enhanced deinking processes. The fibrils on the surface of the fibers and the fines do not degrade when using amylase as a pretreatment enzyme. This reduces the solid waste produced and therefore the landfill costs.

Residual toner particles

Effect of enzyme concentration and reaction time. α-Amylase concentrations of 0, 0.1, and 1.0 NU per o.d. g of pulp were used. The reaction times were 30, 60, and 90 min.

Figure 3 shows the efficiency of the toner dirt particle removal. All these runs used 0.3% flotation aid.

The percentage of toner dirt particle removal is based on the blank run. The pulp treated the same way except "no chemicals added" is the blank run.

The addition of 0.01 NU/OD g of pulp increased the toner particle removal efficiency from approximately 50% to 56%. Increasing the enzyme concentration to 1.0 NU/o.d. g of pulp increased the toner particle removal to approximately 73%.

The same trend—an increased toner particle removal at higher enzyme concentration—also occurred at 0.15% flotation aid. The overall toner particle removal efficiency decreased when using a lower flotation aid concentration.

An increase in the time of the enzymatic pretreatment of the recycled pulp had only minor effects on the removal of toner particles. **Table II** shows the effect of the increase in reaction time from 30 to 90 min on the residual ink area coverage.

The experiments using the highest concentrations of amylase and flotation aid showed the same tendencies. The lower reaction times are therefore preferred. From an economical viewpoint, it is better to have only short reaction times in a mixing chest before the recycled pulp is transferred to the flotation cell.

Effect of the flotation aid concentration. The flotations used the flotation aid at 0, 0.15, and 0.3% based on o.d. pulp. **Table III** shows the effect of the flotation aid concentration on the residual ink area coverage.

An increase in flotation aid concentration from 0% to 0.3% based on o.d. g of pulp reduced the residual toner particle area in the handsheets made by 58%.

Amylase is responsible for releasing the toner particles from the surface of the fibers. The enzyme is not responsible for separation of the released toner particles from the pulp suspension. The separation of the toner particles from the pulp suspension is done in the flotation cell. The higher concentration of flotation aid increases the efficiency of separating the released toner particles from the pulp suspension. A further increase in flotation aid concentration will result in total flotation. This means that fillers, fibers, and toner particles will be floated in the system.

Enzyme concentation, NU/g	Reaction time, min	Flotation aid concentraion, %	Residual ink area, ppm
1.0	30	0.15	1129
1.0	90	0.15	1119
0.1	30	0.3	816
0.1	90	0.3	808

II. Residual ink area coverage as a function of reaction time

Enzyme concentation, NU/g	Flotation aid concentraion, %	Residual ink area, ppm
0.1	0	1958
0.1	0.15	1196
0.1	0.3	816

III. Residual ink area coverage as a function of flotation aid concentrate

Analysis of experimental design

A second-degree polynomial experimental design *(13)* estimated the best conditions for the enzymatic-assisted deinking of white office waste by flotation:

$$y = b0 + b1X1 + b2X2 + b\ 3X3 + b11X12 + b22X22 + b33X32 + b12X1X2 + b13X1X3 + b23X2X3 \qquad (1)$$

where

y = various response factors
x_1 = enzyme concentration
x_2 = reaction time
x_3 = flotation aid concentration.

The optimum conditions for toner particle removal occurred at an α-amylase concentration of 1.0 NU/o.d. g of pulp, 30 min reaction, and 0.3% flotation aid. **Figure 4** shows the estimated results for the residual ink area coverage. Using the estimated optimum conditions for the enzyme-assisted deinking process, up to 85% of the toner particles could be removed.

ECONOMICS

This novel enzyme-assisted deinking process requires the addition of another chemical—the enzyme—before the flotation step compared with conventional flotation deinking. The enzyme pretreatment of the pulp requires a reaction time of 30 min in a mixing chest to degrade the surface starch before pumping the pulp suspension into the flotation cell. The inactivation of the enzyme will not contribute any additional costs. The increase in pH from 7.0 to 10.5 upon going to the flotation stage will inactivate the enzyme. The estimated increase in cost per ton of pulp by adding 1.0 NU α-amylase per o.d. g of pulp is only approximately US$ 0.04.

CONCLUSIONS

The advantages of the new technology result from a higher efficiency in the deinking process. The toner particle removal increases from approximately 50% to 70–85%. The higher efficiency could potentially avoid a second flotation step and therefore increase the yield of recovered fiber, reduce water usage, decrease the capital cost of the deinking plant and ancillary equipment, and reduce the sludge and its disposal costs. No losses of sheet strength properties or any negative influences on pulp properties occurred.

The enzyme treatment of the pulp is at neutral pH. Amylase will degrade starch to disaccharides and various oligosaccharides. This effect will reduce the BOD load in the

KEYWORDS

Amylase, deinking, enzymatic activity, flotation, ink, pretreatment, recycling, surface sized papers, toners, xerocopy papers.

waste water stream *(14)*. The pH of 10–10.5 during the flotation step causes the inactivation of the enzyme.

We propose a model for the increase in toner particle removal by enzyme-assisted deinking. The release of toner particles from the paper is enhanced due to degradation of the starch present between the toner particles and pulp fibers in the paper. Mechanical shear should aid the release of these particles. The toner particles are then separated from the pulp suspension during the subsequent flotation step.

FUTURE WORK

This study used commercially available xerographic paper with an unknown starch type. The effect of modified starch samples on the novel enzymatic-assisted deinking process requires investigation. Cationic or anionic substituents on the starch polymer may influence the starch degradation negatively. The reduced starch degradation could result in a reduced deinking efficiency.

Zeyer *et al. (15)* suggested a model for cellulase-assisted deinking. They postulated that fiber surface friction with the cellulase action increases the deinking efficiency. Putz *(16)* found that enzymatic treatment with soaking was sufficient for a proper ink particle release for offset printed newspaper. Further investigation is necessary to develop a new theory on the influence of fiber surface friction on toner particle release in enzyme-assisted deinking using amylase. Various degrees of mixing will be used during the enzymatic pretreatment of the pulp before flotation.

The novel deinking process has only used commercially available xerographic and laser printed recycled papers. The difference in deinking performance for paper made with starch as a surface-sizing agent and with starch as a wet-end additive will be analyzed. Different types of paper will be made on a pilot plant paper machine with and without wet- end starch and variations in surface sizing. These papers will be printed and recycled as before with the xerographic paper. TJ

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