Macromol. Symp. **143**, 243–255 (1999)

Flash Hydrolysis Deinking of Laser Print Using Degradable Toner Resin

El-Medhi Debzi, Robert H. Marchessault*

*McGill University, Chemistry Department and Pulp & Paper Research Centre, 3420 University Street, Montréal, Québec, Canada H3A 2A7

Gérard Excoffier, Henri Chanzy

Centre de Recherches sur les Macromolécules Végétales - CNRS, BP 53, 38041 cedex 9, France

SUMMARY: The choice of vinyl polymers as the plastic matrix for the pigment in xerographic toner did not anticipate the deinking thrust which has swept the paper industry. The hydrolytic stability of the carbon-carbon bond in vinyl and diene copolymers has prevented the use of a plastic degradation strategy for toner removal. New toner resins based on alkali degradable plastics have been shown to allow up to 97% toner removal. Based on polyimide and polyesterimide toners (either magnetic or non-magnetic) developed by Xerox, this study uses flash hydrolysis in the presence of 0.5% alkali to repulp. The process operates on 200-300 second batches at 190-210°C. The best results were obtained using alkaline repulping and magnetic deinking coupled with washing. The alkali also inhibits the hydrolytic degradation of cellulose although it negatively impacts the brightness. Thus the use of a polymer resin containing a chemically sensitive function allows conversion of the toner to pigment fragments and water soluble oligomers. The former is best separated by magnetic deinking while the latter is removed by washing.

INTRODUCTION

New environmental requirements have pressured pulp and paper companies to improve and promote their recycling activities. Small amounts of high quality fibre from office waste are included in the production of recycled paper but the demand for high grade recycled paper has revived interest in the deinking of xerographic-laser prints. These dry toner images are difficult to deink using conventional repulping, screening, cleaning, washing or flotation methods[1] and toner pigments are unbleachable. Different approaches have been, and are still, explored in order to perform an optimal fibre-toner separation. Several physico-chemical techniques such as spherical agglomeration[2], ultrasonification[3] or magnetic toner removal assisted by steam-explosion repulping[4] have shown promising results but their feasibility on an industrial scale is not yet demonstrated.

Another deinking "strategy" involves the synthesis of toners with built-in degradation

 CCC 1022-1360/99/$ 17.50+.50/0

properties. Xerox has developed such toners, called "ecotoners", based on polyimide[5-6] and polyesterimide[7] resins. These materials are characterized by good thermooxidative stability, excellent mechanical properties and ease of fabrication leading to several high-temperature applications[8-9] as films, matrix resin coating, adhesives... Some chemical formulae of these polymers are shown in Fig. 1. These toners are degraded in the alkaline media[10-11] which are generally used in the first stages of repulping and, therefore, can be readily separated by washing or flotation, depending on the size of the detached toner particles. They can also dissolve with biodegradable surfactants. Japanese companies have also developed toners based on polyester resins[12-13]. Using bacterial polyesters (polyhydroxyalkanoates) as a toner resin[14] is an alternative approach that implies the potential use of depolymerase enzymes as deinking agents.

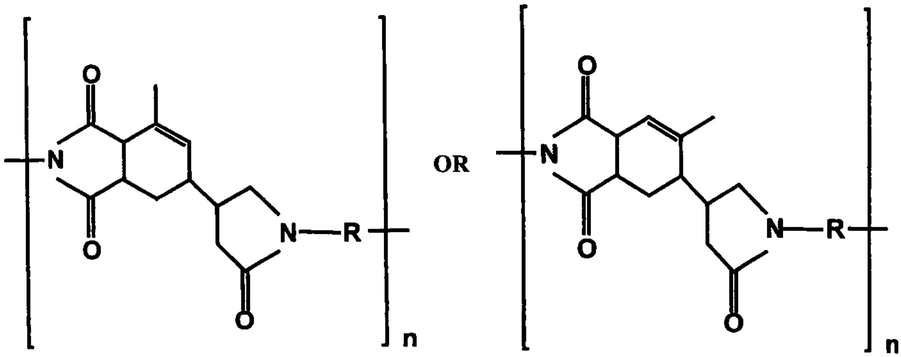
Our previous efforts[4] on deinking of copier prints have investigated the use of steam-explosion as a repulping tool and the magnetic susceptibility of the ferrite in black toner for the fibre/ink separation. The toner removal was quasi-complete for the whole range of particle sizes and the process efficiency for laser print was much higher than with a classical flotation technique. The physical properties of the standard handsheets prepared from such recycled fibres were also measured and serious losses in the mechanical properties were observed. The goal of this study is to determine the effects of a thermomechanical treatment, e.g. steam-explosion, on the deinkability of prints made from degradable toners and the properties of the recycled paper fibres.

Experimental Section

Flash Hydrolysis Process

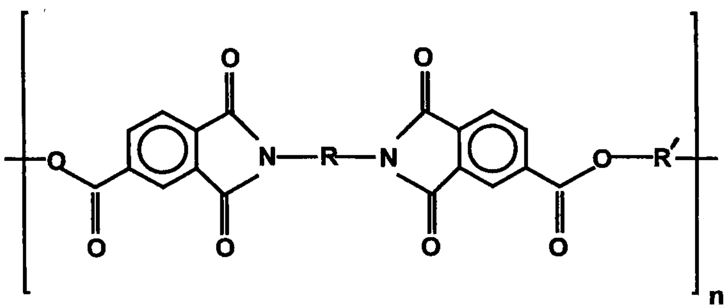
The EC 300 flash hydrolysis pilot unit (CNRS Licence) developed in the Centre de recherches sur les Macromolécules Végétales, Grenoble, France, was used for this study. A 20 kW steam generator supplies saturated steam at a pressure of 5 MPa maximum (the operating temperature is 265 °C maximum) in a 1 L reactor. A programmable controller is used to monitor the process (time, temperature, pressure) and to open/close a pneumatic valve from pre-heating of the reactor to decompression into a 50 L expansion chamber.

a)



wherein R *is alkylene, oxyalkylene, or polyoxyalkylene.*

b)



wherein R' *is alkylene; and* R *is independently selected from the group consisting of an oxyalkylene and polyoxyalkylene.*

Figure 1. Chemical structures of (a) polyimide [5] and (b) polyesterimide [7] resins.

Materials

Two types of toner from Xerox have been used to prepare the copies that were treated by steam-explosion : Non-magnetic M618 "Ecotoner" composed of 5 % carbon black (Regal 330), 85% polyesterimide resin, 6% of wax, 2 % of wax compatibilizer and 1.5% of surface additives (silica, titania and zinc stearate) and magnetic M 345 "Ecotoner": 3% carbon black (Regal 330), 81% polyimide resin, 16% Mapico black (iron oxide) and 0.24% DDAMS / DDABS (charge controller).A standard square dot pattern was chosen and Xerox 4024 paper was used for the prints, 26 g of strips (2 cm x 28 cm) were cut and pre-soaked for 30 minutes in various media : H_2O, NaOH 0.5% or Na_2SO_3 2%. At the end of the soaking, the samples were allowed to drip until constant weight before the steam explosion treatment.

Magnetic Separation of Toner

In the case of M 345 Ecotoner prints, the toner was separated from the fibres by immersing an Alnico U shaped magnet, purchased from Unimag (ref. 4344.01.21) in 1.5L of a 2g/L suspension of flash hydrolyzed pulp. A 7 minutes slow mechanical stirring of the slurry is performed during the separation.

Scanning Electron Microscopy

Scanning electron microscopy observations were made using a JSM 6100 JEOL microscope. The samples were suspended in water at a dilute concentration, dried on an aluminum holder, and then coated with gold.

Handsheet Formation

All handsheets were prepared using a British Handsheet machine designed to obtain samples having a diameter of 15.5 cm with a grammage of 60 g/m^2. The flash-hydrolyzed stock was diluted to about 0.3% consistency. The slurry was drained over the screen in the handsheet cylinder and couched off the screen on blotters. Handsheets were then pressed at 50 psi for 5 min and 2 min according to CPPA standard A.4 .The handsheets samples referred to as "control" or "repulped" in the different tables or figures of this study, were prepared using a Standard British Disintegrator to repulp sheets of white or printed paper before proceeding to the handsheet formation described above.

Dirt Count Measurements

Dirt count measurements were performed on the handsheets using the Paprican Ink Scanner V.2.1 (OpTest Equipment Inc., Hawkesbury, Ont.). Typically, a total of 50 fields of 7.3 mm^2 were measured for each sample. The instrument, which has been described by Jordan *et al.*[15], allows ink particles of diameters above 10 μm to be detected on the surface of the paper. Due to the small field of view, the number of particles above 200 μm was not large enough to produce significant results. Thus, histograms of toner particles in the range 10 - 200 μm size range were analyzed.

Physical Measurements

The mechanical and optical measurements were performed by the Physical Testing Section of PAPRICAN, Pointe-Claire (Québec - Canada).

Results and Discussions

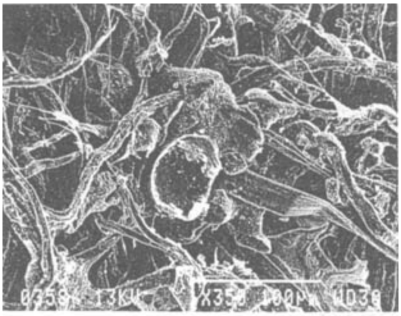
Yields

For steam-explosion treatments at 200-210°C for 200-300 sec. an unavoidable loss in fibre material takes place due to manipulation and process losses. For example some toner redeposition occurs as well as some fibre entrapment in molten toner which leads to fibre losses during magnetic deinking. Nevertheless, fibre yields for the flash hydrolysis process were between 71 and 89%. The yields obtained with sodium hydroxide presoaking are the lowest due to greater swellability of the cellulosic fibres in caustic solution compared to sodium sulfite or water. The more accessible is the substrate to saturated steam the more complete is the breakdown into smaller pieces during flash hydrolysis.

Morphology

The micrographs in Figure 2 illustrate the effect of a steam explosion treatment at 210°C for 300s on Polyesterimide Ecotoner (M 618) prints pre-soaked in different media. For the sample that was pre-impregnated in H_2O, large toner pieces (almost pixel size) are observable (Fig. 2a). Almost no remaining toner is observable in the case of the sample that was pre-soaked in 0.5% NaOH as only small aggregates are detected (Fig. 2b). Big melted toner aggregates were observable in the case of the prints that were pre-soaked in Na_2SO_3 2%.

a)



b)

FIGURE 2. Scanning electron micrographs of standard polyesterimide M618 Ecotoner copier prints steam-exploded (210°C for 300s) after presoaking in: **a)** - H_2O **b)** - NaOH 0.5%

Table 1. Dirt count data for standard handsheets made from steam-exploded copies printed with polyesterimide and polyimide (with or without subsequent magnetic toner removal) toners.

Experiment	Toner	Pre-soaking	T (°C)	t (s)	% coverage	% removed ink
1		H_2O	200	300	0.38	76.7
2	Non-Magnetic polyesterimide	H_2O	210	200	0.42	74.2
3	M 618	H_2O	210	300	0.37	77.3
4		NaOH 0.5%	210	300	0.05	96.9
5		Na_2SO_3 2%	210	300	0.37	77.3
6		H_2O	200	300	0.60	63.2
7	Magnetic Polyimide	H_2O	210	300	0.36	77.9
8	M 345	NaOH 0.5%	210	300	0.14	91.4
9	(No magnet)	Na_2SO_3 2%	210	300	0.55	66.3
10		H_2O	200	300	0.31	82.0
11	Magnetic Polyimide	H_2O	210	300	0.23	85.9
12	M 345	NaOH 0.5%	210	300	0.06	96.3
13	(Magnet used)	Na_2SO_3 2%	210	300	0.30	81.6
Control	REPULPED (No magnet)				1.63	

Dirt Count Measurements

In order to quantify the deinking efficiency of the steam-explosion treatment on the Ecotoner prints, associated with the magnetic ink-fibre separation (case of polyimide M 345 toner) or without it (case of polyesterimide M 618 toner), particle size analysis of the standard handsheets made from the exploded samples was performed. The data listed in Table 1 show that for these degradable polymers steam-explosion provokes a substantial deinking as ink removal efficiencies from 63 to 97% are obtained. The coverage of residual toner particles diminishes when the time of steam treatment is increased (Table 1, exp.2-3). On the other hand, considering the same pre-soaking medium (Table 1, exp. 1 & 3; exp. 6-7 and exp. 10-11) increasing the steam temperature leads to higher deinking yields. For the same experimental conditions (210°C - 300s), NaOH pre-soaking (Table 1, exp.4, 8 and 12) leads to an improvement of deinking. This effect (illustrated in Fig. 3) is expectable and is due to the solubility of the polyimide and polyesterimide toners in this caustic medium. The magnetic fibre-toner separation (Table 1, exp.6,10 - 7,11 - 8,12 and 9,13) is also

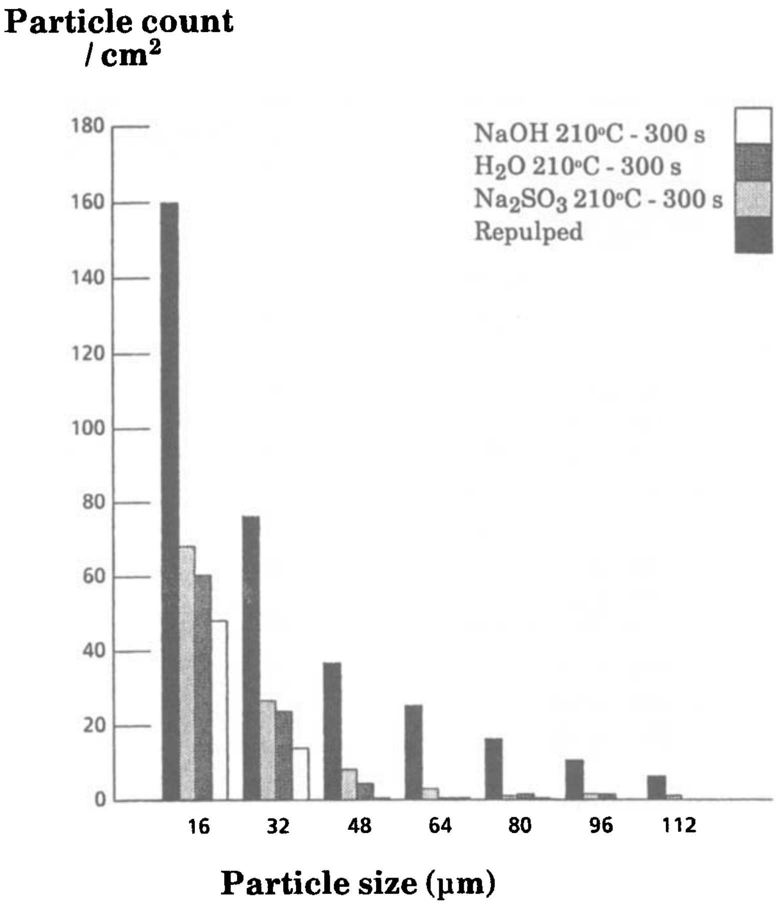


FIGURE 3. Effect of the pre-soaking pH on the particle size distribution of a standard polyesterimide M618 copier prints, steam-exploded at 210°C for 300s:
- repulped untreated print
- pre-soaked in Na_2SO_3 2%
- pre-soaked in H_2O
- pre-soaked in NaOH 0.5%

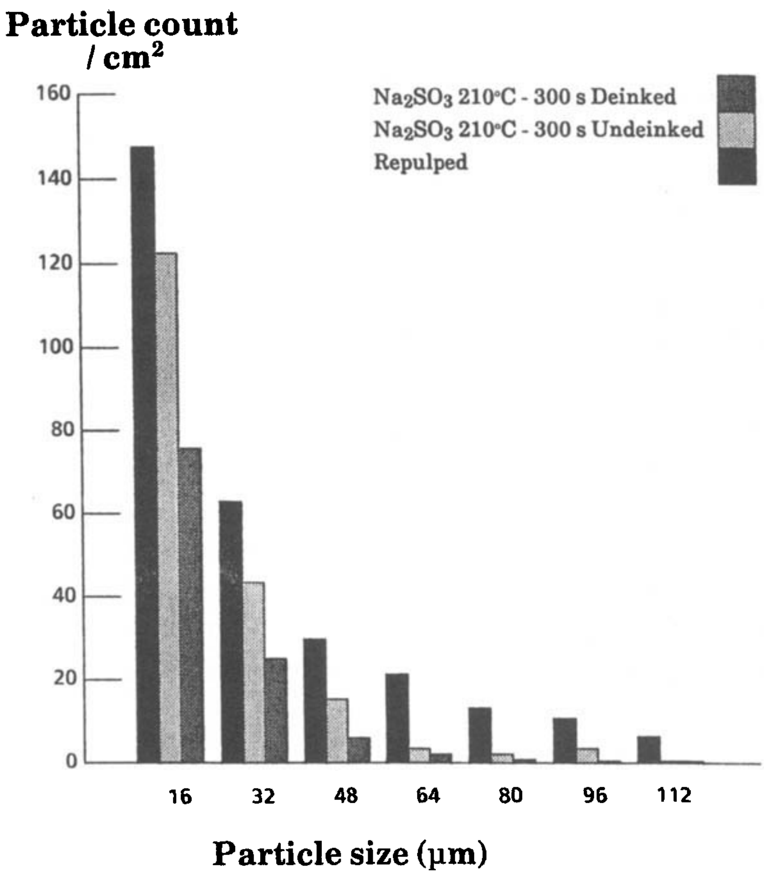


FIGURE 4. Effect of the magnetic toner removal on the particle size distribution of a M 345 toner print pre-soaked in Na_2SO_3 2% and steam-exploded at 210°C for 300s:
- repulped untreated print
- undeinked
- magnetically deinked

favorable to better deinking efficiencies (Fig. 4).

Physical Properties

The main optical and mechanical properties, indicative for the potential use of the recycled paper, of the standard handsheets made from the recovered fibres are listed in Table 2.

Increasing treatment time (Table 2, exp. 2-3) or temperature (Table 2, exp. 1,3 ; 6-7 and 10-11) is detrimental to the optical and mechanical properties of the recycled fibres. As observed in a previous study[4], the protective role of NaOH on the cellulose degree of polymerization[16] implies that the best mechanical characteristics are obtained in the case of the caustic pre-soaking (Table 2, exp. 4,8 and 12). However, the optical properties (low brightness and important yellowing of the handsheets) are poor in comparison with those of the initial basepaper. The optical characteristics are well preserved by a pre-soaking in Na_2SO_3 2% (Table 2, exp.5,9 and 1,3) but the loss in mechanical properties are significant. The same observations are to be made in the case of the water pre-soaking (Table 2, exp. 3,7 and 11).

Table 2. Mechanical and optical properties of standard handsheets from steam-exploded copies printed with M 618 non-magnetic polyesterimide toner and M 345 magnetic polyimide toner.

Experiment	Toner	Pre-soaking	T (°C)	t (s)	Breaking length (km)	Elastic modulus (km)	Brightness (%)	b*
1	Non-Magnetic polyesterimide M 618	H_2O	200	300	1.2	204	80.9	1.7
2		H_2O	210	200	1.7	329	80.6	1.4
3		H_2O	210	300	1.1	212	79.3	2.1
4		NaOH 0.5%	210	300	2.0	311	67.8	4.6
5		Na_2SO_3 2%	210	300	1.4	253	79.0	2.1
6	Magnetic Polyimide M 345 (No magnet)	H_2O	200	300	1.7	264	80.2	0.5
7		H_2O	210	300	1.5	261	78.4	1.1
8		NaOH 0.5%	210	300	2.3	363	71.3	2.0
9		Na_2SO_3 2%	210	300	1.7	223	79.6	-0.7
10	Magnetic Polyimide M 345 (Magnet used)	H_2O	200	300	1.9	268	82.4	0.3
11		H_2O	210	300	1.7	294	80.3	0.8
12		NaOH 0.5%	210	300	2.2	347	73.1	1.6
13		Na_2SO_3 2%	210	300	1.8	266	82.3	-0.4
Control	REPULPED (Unprinted)				3.5	477	84.0	-0.2

Conclusions

Dirt count measurements have shown that the copies made from the Xerox polyimide and polyesterimide degradable toners considered in this study, can be readily deinked using "mild" steam-explosion conditions. For different pre-soaking media, in the case of degradable toners containing ferrites, the association of the magnetic deinking to the thermomechanical process improves the results *vs.* deinking of toner copies by steam-explosion only. The best deinking and mechanical properties retention are obtained when the samples are pre-soaked in a low concentration caustic medium. However, optical properties are degraded by caustic pre-treatment. Retention of mechanical properties has been previously observed in the case of steam-exploded laser prints[4)] and is due to the protective role of the caustic with respect to the hydrolysis reaction induced by the acidity of the steam at high temperature[16)]. The sulfite pre-soaking leads to the best optical characteristics while water pre-soaking leads to intermediate results. Future work should emphasize the improvement of the physical properties of the recycled fibres by optimizing the steam-explosion conditions (temperature and time) and the pre-soaking phase.

ACKNOWLEDGMENTS

This work was supported by the France-Québec exchange program and the NSERC Strategic Grant No. STR-149756. The authors would like to the thank Dr. G.G. SACRIPANTE from Xerox Corp. for providing the samples that were investigated in this study. The technical help of Mrs D. DUPEYRE from the Centre de Recherches sur les Macromolécules Végétales (CERMAV- CNRS) in Grenoble (France) as well as the contribution of Dr. W. BICHARD from PAPRICAN Pointe-Claire (Québec-Canada) for the physical tests, are gratefully acknowledged.

References

1. W.F Carr.,*1990 Pulping Conference Proceedings*, Atlanta, USA, 11 (1990).
2. C.R Olson., S.K. Richman, F.J. Sutman, M.B. Letscher, *Tappi J.*, **76**, 136, (1993)
3. J.C.Norman, N.J.Sell, N.Danelski, *Tappi J.*, **77**, 151, (1994)
4. R.H.Marchessault, E.M. Debzi, G. Excoffier, *Pulp Paper Can.*, **98:5**, 59, (1997)
5. G.G. Sacripante, B.W.A. Yeung, T.B. McAneney, J.S. Kittelberger, Xerox corp., US Patent 5,411, 829, (1995)
6. G.G. Sacripante, S.V. Drappel, Xerox corp., US Patent 5,411,831, (1995)
7. G.G. Sacripante, S.V. Drappel, Xerox corp., US Patent 5,348,831, (1994)
8. J.A.Cella, *Polym.Deg.Stab.*, 36, 99, (1992)
9. M.J.M. Abadie, B. Sillion Eds., *Polyimides and other High Temperature Polymers,* Elsevier, Amsterdam, (1991)
10. R.A. Dine-Hart, D.B.V. Parker, W.W. Wright, *Br.Polym.J.*, **3**, 222, (1971)
11. J.S. Kittelberger, G.G. Sacripante, S. Malhotra, *Xerox Discl.J.*, **21**,5, (1996)
12. A. Misawa, M. Ajioka, Mitsui Toatsu Chemicals Inc., US patent 5,387,665, (1995)
13. H. Kubota, E. Ozeki, Tomegawa Paper Co. Ltd - Shimadu Corp., European Patent Appl., 0 640 882 A1, (1995)
14. J.T. Fuller, R.H. Marchessault, T.L. Bluhm, US Patent 5,004,664, (1991)
15. B.J. Jordan, N.G. Nguyen, R.J.R. Trepanier, *Tappi J.*, **76**, 110, (1993)

16. E.M. Debzi, G. Excoffier, B. Toussaint, M.R.Vignon "Steam-explosion pretreatment of wood: effects of pressure and time on cellulose behaviour" in *Steam Explosion Techniques: fundamentals and Industrial Applications*, B.Focher, A.Marzetti and V.Crescenzi Eds., Gordon and Breach Science Publishers, Philadelphia, 141, (1991)