

# Deinking xerographic and laser-printed paper using block copolymers

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## Abstract

The deinking of various types of paper has been necessitated by governmental regulations as well as increasing public interest in recycling materials taken from our natural environment. The increasing volume of office waste makes it an important class of paper available for deinking. It presents unique difficulties for ink removal because of the manner in which ink is applied to the paper in photocopiers and laser-printers. In this study, we develop a simple deinking process for office waste using a block copolymer as the only deinking agent and employing the two-step process involving pulping and froth flotation. The block copolymers tested are commercially available triblock copolymers composed of polyethylene oxide (PEO) and polypropylene oxide (PPO), known as Pluronic. A variation in the relative proportions of PEO and PPO results in copolymers of different hydrophobic character and, consequently, variations in colloidal and surface chemical properties such as detergency, wetting, emulsification and foaming. For a number of block copolymer systems, we report the brightness of handsheets formed of deinked fiber, the amount and size distribution of residual ink specks on the handsheets, and the amount of fiber lost in the operations. The novelty of the process lies in the simplicity of the deinking chemical formulation (a single compound), the low concentrations at which the deinking agent is employed, and the good biodegradability characteristics of the block copolymers. Both from an economic point of view (the amount of chemicals consumed is 20 to 30 times smaller than that in conventional deinking chemical formulations) and from an environmental point of view (because of the reduced need to treat process water from deinking operations), this process appears attractive. © 1998 Elsevier Science B.V.

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## 1. Introduction

Governmental regulations, coupled with a greater awareness by the public to reduce the volume of waste in landfills, has necessitated research in the area of removing ink from paper fibers and the use of recycled fibers. A class of

paper which presents unique difficulties for deinking is office waste consisting of papers from office copiers and laser-printers. The ink formulations used in these papers are difficult to remove due to the manner in which they are applied. In xerography, a latent image is formed on a charged photoconductive surface and this image is then transferred to the paper. The paper surface is also charged and receives the light reflected from the document to be copied. The dark areas of the paper (areas where the image is being projected) retain their

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charge, while the non-print areas of the paper where the light is reflected off have the surface charge dissipated. Toner particles (which consist of the ink and some chemical transport vehicle) are charged oppositely to the paper and electrostatically adhere to the dark charged areas of the paper surface. Thus, a visible image is transferred from the document to the paper. A similar method is utilized in laser-printing, but a laser beam is involved in neutralizing the charge present on the non-print areas of the copy paper [1].

Once the toner particles have been placed onto the copy sheet, they are fused to the surface by a combination of pressure and heating. The vehicle in which the pigment is being carried is usually a thermoplastic copolymer of styrene and acrylate. During the heating process, the copolymer rises above its softening temperature and goes from a dry solid to a liquid. The copolymer vehicle may then seep in and wrap around paper fibers at the surface, where they dry to solid particles once again.

A combination of mechanical and chemical forces is often necessary to remove the ink particles from the fibers. The mechanical force is usually supplied by a pulper where the paper is beaten into its respective fibers. The ink particles are detached from the fibers by a combination of factors, including hydrodynamic flow of the liquid phase in the pulper, swelling of the fibers, flexing and bending of the fibers, and abrasion of the fibers against each other [2]. Often, the mechanical force in the pulper is not sufficient to bring about effective ink removal and chemicals are added in the pulper to increase the ink removal efficiency. Once the ink particles are detached from the fiber by the mechanical action, they are then separated from the fibers via a variety of operations, including washing, screening, flotation or a combination of the above. In general, as part of the deinking operation, many chemicals are added to the pulper to aid in ink detachment [3]. If flotation is employed for the separation of the ink from the fibers, then other chemicals are added to facilitate the flotation of the ink. The nature of chemicals added in a deinking process depends upon the type of ink to be removed, the nature of the paper

stock, and the manner of application of the ink to the paper during the printing process.

In the case of office waste, the unusual size and shape of the ink toner particles, as well as the strong bonding between ink and fiber, make their removal by conventional approaches difficult. In general, the relatively large size of the particles limits their removal via standard washing or combinations of washing and flotation, and their flat or plate-like shape hinders removal by screens and reverse-flow cleaners. Flotation is effective for removal of particles between 10 and 100  $\mu\text{m}$ , with the optimum range being 30–60  $\mu\text{m}$  [4], while the reported ink particle size distribution after repulping for non-impact printed paper lies between 40 and 400  $\mu\text{m}$ .

## **2. Our approach to deinking based on block copolymers**

A typical deinking chemical formulation involves multiple components, since each chemical species added can create problems requiring the addition of another chemical to counteract them [3]. As more chemicals are added, the role of each individual chemical becomes ambiguous because of synergistic or antagonistic effects. From a practical point of view, there are many disadvantages associated with conventional deinking formulations based on multiple chemical components. Firstly, the chemical formulation needed is quite complex and, because of the unknown interactional effects, the design of the formulation is largely empirical. Secondly, the total amount of deinking chemicals that should be added per unit mass of paper fiber is quite large, of the order of 2 to 3 wt.% based on the fiber mass. Thirdly, the water streams from the deinking process are contaminated by the numerous chemicals employed and will have to be treated. To overcome these economic and environmental concerns, we explore a novel approach which utilizes a single deinking chemical in place of the conventional multicomponent mixture formulations. The chemical used is a block copolymer, and its selection is motivated by the possibility of using it in very small concentrations, its good biodegradability properties (some

of the block copolymers used are approved by the FDA even as food additives), and the fact that these molecules exhibit a multitude of surface chemical characteristics that are essential for the deinking application.

The block copolymers employed are triblock copolymers of the polyethylene oxide (PEO)–polypropylene oxide (PPO)–polyethylene oxide (PEO)-type with the hydrophobic PPO block in the middle attached to the hydrophilic PEO blocks at the two ends. These are also known as poloxamers, and commercially as Pluronic. Many different physical properties and surface chemical functions are available in this family of block copolymers simply by changing the relative composition and molecular weights of the blocks in the copolymer [5,6]. Different poloxamers are chosen for their relative abilities in detergency, solubilization, foaming, defoaming, emulsification, wetting and surface/interfacial tension lowering. The experiments in this study are designed to examine a range of poloxamers with varying degrees of hydrophobicity in order to determine their effect on deinking performance.

### 3. Experimental methods

Deinking experiments were performed on papers which were xerographically printed on-site, and all contained the same image and, thus, the same ink content. In order to ensure that the paper feed-stock was the same, the test papers were prepared with the same image, a black circle approximately 15.3 cm in diameter, printed on a standard 21.5 cm × 28 cm sheet. The amount of paper used in each deinking run was determined by the percent consistency desired in the flotation cell. The consistency is defined as the weight in grams of oven-dry fiber in 100 g of pulp–water mixture [7]. The flotation cell holds a volume of 3 l, so for a consistency of 1.0%, 30 g of paper is necessary. Deinking chemicals added to the process are typically specified as a percentage of the amount of paper added. In the process described here, a single block copolymer was added as 0.1% of the paper weight.

#### 3.1. Pulping

30 g of paper was added to a Hamilton Beach 14 speed Blendmaster blender which served as the pulper. The copolymer was weighed out and also placed in the blender. Water preheated to 43°C in the flotation cell was poured into the blender to fill the remaining volume. The flotation cell had heating tape wrapped around it on the outside, and this tape was connected to a variable auto-transformer. 3 l of tap-water was poured into the cell and heated by the heating tape to the desired temperature. In the blender, the contents were pulped together for a total of 4 min. At 2 min, the pulping was stopped momentarily to check that all the paper was being pulped (i.e. to make sure that none of the paper had wrapped around under the blades or along the sides of the blender wall, which would prevent its being pulped). After this check, pulping was continued for another 2 min. The water temperature did not change appreciably during pulping, even though there was no heating element connected to the blender. After pulping, the pH of the pulp in the blender was noted; for nearly all the poloxamers used, the pH of the pulp was approximately 8.5.

#### 3.2. Flotation

The pulp was then transferred to the flotation cell and mixed in the cell for approximately 1 min before checking the pH. After noting the pH, flotation was carried out for a total of 6 min by activating an air inlet located along the side of the stirring shaft. Depending on the particular poloxamer used, the froth formed quickly or slowly, was thick or thin, and had much ink or very little ink at the top. This froth was then scraped off the top of the flotation cell by hand using a small paddle. Care was taken to not scrape too deeply into the froth, as this raises the risk of collecting paper fibers along with the ink. Periodically, the sides of the cell and the impeller were washed down with water because ink and paper typically collect in these areas. In some cases the froth becomes thinner or sinks further down into the cell as flotation proceeds, so water had to be poured into the cell to raise the froth layer high

enough so that it could be scraped efficiently. Fig. 1 shows the two steps of the deinking procedure as employed in this study. After 6 min of flotation, the air flow was stopped by turning off the air inlet on the impeller. In order to determine the efficiency of deinking, the pulp has to be fitted into a form appropriate for testing; this is achieved by re-forming paper sheets (known as handsheets or brightness pads) from the pulp [8].

### 3.3. Preparation of handsheets

The deinked pulp from the flotation cell was carefully separated from the water by utilizing suction filtration in a Büchner funnel. The funnel used for this procedure was a 15 cm inner diameter funnel with a perforated plate and connected to a 4 l suction flask. After inserting and leveling the Büchner funnel into the neck of the suction flask, a sheet of white, rapid-draining, 18.5 cm diameter filter paper was placed into the funnel and wetted; suction was momentarily applied in order to seat the paper into the funnel. Once the filter was ready, the deinked pulp (including the pulp which had wrapped around the impeller blades and along the impeller shaft) was carefully poured into it. While the suction action pulled the water through, the sides of the funnel were washed down with water to collect any pulp which was clinging to

the sides. Once most of the water had been pulled through, the suction was discontinued and the deinked paper was removed from the funnel. A second piece of filter paper was placed into the funnel and this procedure was repeated once more. The deinked pulp was then set aside to dry overnight.

These two large sheets are not acceptable as handsheets because of their excessive mass and uneven ink distribution. They must then be formed into smaller sheets. The pulp was dried in the above manner in order to determine and control accurately the amount of paper in each handsheet which was to be formed. The dried pulp was weighed and then separated into smaller piles of approximately 3.6 g. It was these smaller piles which were used to make the handsheets. The procedure used to make the handsheets was devised by the Technical Association of the Pulp and Paper Industry (TAPPI) as the TAPPI Test Method T218 om-91 [9]. This test method suggested using 3 g of dried pulp to form the sheets, but it was found in our experiments that the handsheets formed from this amount of pulp were too thin and contained an uneven distribution of paper, forming thick and thin areas on the sheets. Instead, a 3.6 g value was used. Each 3.6 g pulp sample was placed separately into the blender and diluted to 1 l with distilled water. It was pulped

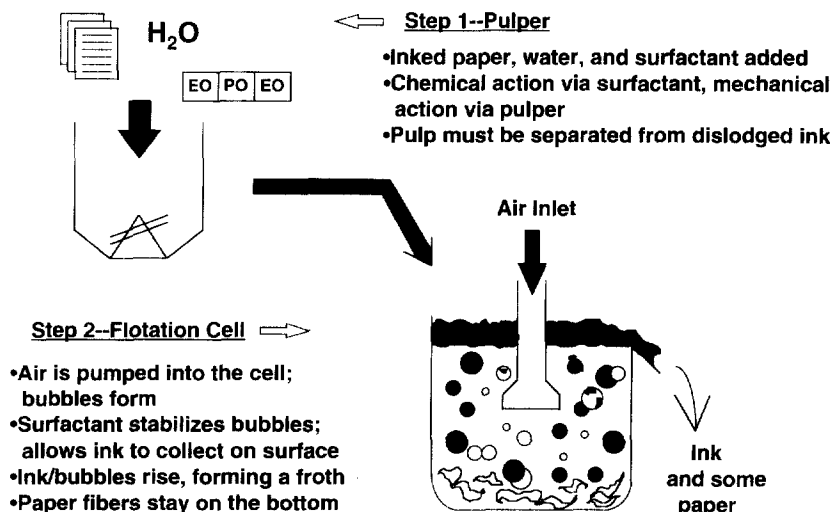


Fig. 1. Diagram showing the two-stage deinking process of pulping followed by flotation.

for a total of 25 to 30 s, after which time it was poured into a beaker, taking care to rinse out the blender and collect all of the paper. The pulp slurry was then adjusted for pH; this entailed the addition of a prepared 10% acetic acid solution in small aliquots until the pH of the slurry was  $5.0 \pm 0.1$ . The handsheets were formed from this pulp slurry by once again utilizing the Büchner funnel. As before, the pulp was poured onto the seated filter paper in the funnel and the water was then drawn through by applying suction. Once all of the excess water had been removed, the vacuum was broken immediately to prevent drawing an appreciable amount of air through the pulp mat. The funnel was then removed from the suction flask and inverted over a piece of clean, white filter paper of 24 cm diameter. By blowing air into the funnel stem, the test sheet and its filter paper were transferred to the larger sheet of filter paper. Another sheet of the larger filter paper was then placed over the back of the test pad (on the side exposing the filter paper); another 3.6 g sample of pulp was treated in the same manner and was transferred from the funnel onto the large sheet of filter paper which was covering the first test sheet. Subsequent test sheets were prepared and placed over the last sheet in the same manner, so that there was always a larger piece of filter paper sandwiched between each test sheet. For a typical deinking experiment, a total of six test sheets were prepared.

Once the handsheets were prepared by filtration, each one had to have any excess water removed before being set aside to dry. This was done through the use of a machine press. A metal plate was placed on the base of the press, and a clean piece of the larger filter paper was placed on top of the plate. One of the handsheets (along with its piece of filter paper) was then placed onto the filter paper, and another piece of larger filter paper was placed over it. Finally, another metal plate was set over the filter paper. Thus, the entire stack from top to bottom consisted of one metal plate, a clean piece of filter paper, the handsheet and its filter paper, another clean piece of filter paper, and another metal plate. The press was lowered onto the top metal plate by a lever and pressure was applied for a total of 1 min to squeeze out as much

of the remaining water as possible from the handsheet. After pressing each handsheet, they were placed under a fan to dry completely.

### 3.4. Measurement of fiber loss

After drying, the sheets were ready to be tested for ink removal efficiency. The efficiency of the process is determined not solely by the amount of ink removed, but also depends on how much paper fiber is lost during the process most of which occurs during flotation. The amount of paper before deinking was weighed without ink printed on it, the assumption being that the deinked paper would have the majority of ink removed and would, therefore, most closely resemble the clean paper. The percent fiber loss was determined simply by subtracting the amount of deinked paper from the amount of original clean paper, dividing this by the amount of clean paper and multiplying by 100.

### 3.5. Measurement of brightness

In addition to determining the amount of paper fiber lost, a measure of ink removal is necessary. This is done through the use of brightness tests, which are common paper industry tests used to measure numerically the degree of reflectance of a paper sample when exposed to blue light at a wavelength of 457 nm [10]. In general, as more ink is removed from the paper, brighter sheets are obtained. A brightness meter was available at the International Paper Company's facility in Lock Haven, PA; handsheets were taken there for brightness testing. The tests consisted of calibrating the brightness meter using a small magnesium oxide plate of a certain brightness, then placing an area of the handsheet over the meter aperture, which was about 2 to 2.5 cm in diameter. A 500 g weight was placed over the sheet to ensure that no light escaped from the aperture. A digital readout reported the percentage brightness of the sheet at the point over the aperture. A total of five measurements were made at different points on a handsheet. The measurements were then averaged to get an average brightness value for the experiment.

### 3.6. Ink specks analysis and dirt count

Apart from the brightness gain, it is also necessary to determine the amount of visible ink specks on the deinked handsheets. This latter measure is considered even more important than the brightness gain for the deinking of office waste. The standard tests for dirt count in pulp [11] and in paper and paper board [12] developed by TAPPI count only ink particles larger than  $0.02 \text{ mm}^2$  or approximately  $160 \text{ }\mu\text{m}$  in diameter. The methods provide a measure of the apparent dirt area on a background using the TAPPI Dirt Estimation Chart. Although a well-trained operator can estimate the dirt area with good repeatability, the job is very tedious, time-consuming and often vulnerable to human errors. Image analysis with computers can improve the determination of the dirt count, thereby eliminating operator errors and increasing the resolution to well below  $160 \text{ }\mu\text{m}$ . An image analyzer detects images on a digitized pixel basis, the pixel being the smallest element in a picture. For images scanned at a resolution of 1200 dpi (dots per inch), the image size is calculated from the number of pixels, via the relation: image size in micrometers =  $24 \times (\text{number of pixels})^{1/2}$ . Most analysis algorithms are based on the differences in gray level intensity between ink spots and the background. It is common to have 256 gray levels, 0 being the darkest and 255 being the brightest value. Images below certain threshold gray level are recognized as dirt, while the rest is considered the background.

In our laboratory, Genius ColorPage-I<sup>®</sup> was used to capture the images of the handsheets, and PhotoFinish<sup>®</sup> to process the images, and Mocha<sup>®</sup> image analyzing software to perform the dirt count. For each handsheet made from the deinked pulp, five sample regions chosen randomly, each with  $2.54 \text{ cm} \times 2.54 \text{ cm}$  area, were scanned at a resolution of 1200 dpi; therefore, ink specks with diameter as low as  $24 \text{ }\mu\text{m}$  can be detected. Calibration using known amounts of ink specks and their image analysis showed that by choosing any threshold in the range of 160 to 200 on the gray scale (for the image to be counted as dirt), one can get a satisfactory linear relationship between the amount of ink specks and the dirt

count obtained from image analysis. The ink counts for each experiment given here are based on a representative handsheets made from that particular experiment and using a threshold value of 160 on the gray scale.

## 4. Results and discussion

A total of 17 different poloxamers with diverse physical properties were tested for their effectiveness in deinking. These poloxamers were Pluronics, obtained as a gift from BASF Corp., Parsippany, NJ, and were used as-received. The fiber loss and brightness results are presented on the Pluronic grids, which provide a graphic representation of the relationship between the copolymer structure, physical form, and surfactant characteristics [6]. These grids are designed by plotting the molecular weight ranges of the hydrophobe vs. the percent of hydrophile in the molecule. In assigning their names, the letters P, F or L refer to the state of the polymer being a paste, solid or liquid respectively. The last digit when multiplied by ten gives the mass percent PEO block, whereas the remaining number is indicative of the molecular size of the PPO block.

### 4.1. Results on fiber loss

The percentage of fiber lost is indicated on the Pluronic grids (Figs. 2 and 3). The results range from a low 6.84 wt.% fiber loss with P123 to a very large loss of 30.5 wt.% with L35. Deinking processes described in the literature for various kinds of paper and ink suggest that fiber loss should be below about 15 wt.% for a reasonable deinking operation. Those Pluronics at the top of the grid have higher PPO molecular weights; those at the top left-hand corner have low amounts of PEO present. This is the area corresponding to the lowest fiber losses. Thus, it appears that the more hydrophobic the copolymer is, the lower the fiber losses. As one moves to the most hydrophilic area on the grid, corresponding to low PPO molecular weights and high percentages of PEO (i.e. the lower right-hand corner), the fiber losses increase.

What is it about the structure of the copolymer

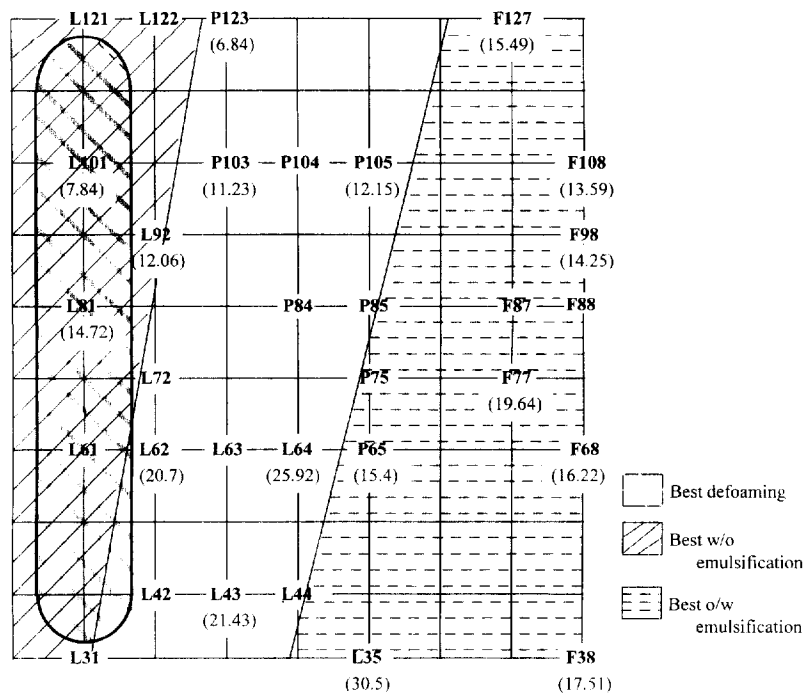


Fig. 2. Pluronic grid formed by plotting the molecular weight of the hydrophobe (PP0) vs. the percent hydrophile (PEO) present in the molecules. The percent fiber losses are shown in parentheses below the corresponding Pluronic. The shaded areas identify the Pluronics for best defoaming and emulsification.

that contributes to fiber losses? A probable explanation is based on the relative hydrophilic nature of the copolymer. The paper fibers themselves are hydrophilic in the flotation cell, and if a largely hydrophilic copolymer is added this may interact with the fiber more strongly than a hydrophobic one. Chemical interactions, such as hydrogen bonding between the copolymer and the cellulose fiber, may make it possible to carry the paper fiber up into the foam layer at the top of the flotation cell.

Besides this mechanism, other physical properties of the block copolymer may also be responsible for the higher fiber losses. If one examines the area on the Pluronic grid showing the best defoamers, one notices that most of this area includes Pluronics which exhibit low fiber loss. Conversely, Pluronics known as good foamers have some of the higher fiber losses. This is reasonable if one considers what is occurring in the flotation cell. A thicker foam generally means that there is a greater

likelihood for trapping paper fibers and collecting them with the ink, thus resulting in higher fiber losses. Thinner foams do not trap as much paper and, therefore, exhibit lower fiber losses.

Another physical property which seems to contribute to lower fiber losses is wetting. Pluronics considered the best for wetting have some of the lowest fiber losses, but this may also be attributed to the fact that the best wetters are also some of the best defoamers. A clearer understanding of which property contributes to low fiber losses, or even if the properties work together somehow to keep the fiber loss down, is not available at this time.

#### 4.2. Results on brightness

The brightness results are also shown on Pluronic grids as they were for the percent fiber losses (Figs. 4 and 5). A clean paper containing no ink has a brightness of 83 on this scale, whereas

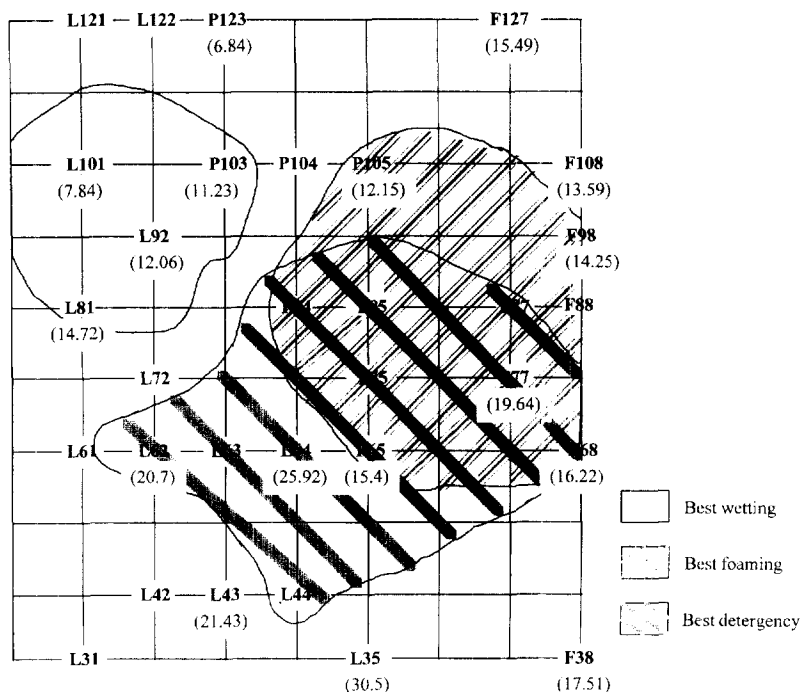


Fig. 3. Pluronic grid showing the molecular weight of the hydrophobe vs. the percent hydrophile in the molecules. The percent fiber losses are shown in parentheses below the corresponding Pluronic. The shaded areas show the Pluronics best-suited for detergency, foaming, and wetting.

the test paper used in the experiments (after pulping and reforming the sheet but without any ink removed) had a brightness value of 64.9. The deinking performance can be judged by how close the brightness of the deinked sheet is to that of the clean paper. The Pluronic grids show that the brightest values are generally found in the middle of the grid, corresponding to mid-range PPO molecular weights (from approximately 1800 to 2300). As the molecular weight of the PPO becomes either too low or too high the brightness values drop dramatically. An attempt was made to correlate the highest brightness values on the grid with the physical properties of the copolymers to gain a clearer understanding of which properties are most desirable for ink removal.

The first grid (Fig. 4) groups together the properties of defoaming and emulsification. These properties do not completely fit into the area for highest brightness, so they were deemed as not very important for brightness. However, the other properties

of detergency, foaming, and wetting on the other grid (Fig. 5) all lie, for the most part, in the desired region for highest brightness, and thus were deemed as most important for ink removal and higher brightness.

Pluronics with good detergency properties would almost naturally be assumed to provide higher brightness values. In addition, those Pluronics which are known as good foamers seem to be logical candidates for giving higher brightness values; after all, a thicker foam in the flotation cell makes it possible to remove more ink from the pulp slurry. These properties seem to work together in increasing the amount of ink removed if one realizes that the higher brightness values lie in the area where these two properties overlap.

Wetting also seems to make logical sense as a good property for higher brightness; in fact, wetting of the paper and ink by a surfactant solution is an important step in reducing adhesion of the ink particles to the cellulose fibers, thus making it



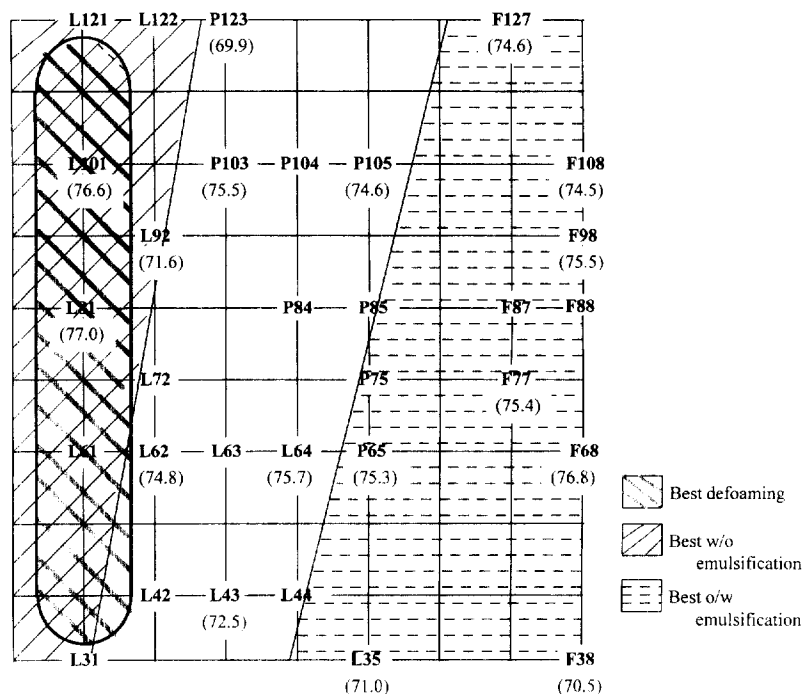


Fig. 4. Pluronic grid showing the brightness values for the Pluronics studied. The shaded areas indicate the best Pluronics for defoaming and emulsification.

easier to remove the ink. Further, many surfactants which are used as effective detergents also possess good wetting and foaming characteristics; therefore, it is no accident that these three properties are grouped so closely together on the Pluronic grid.

One property which did not cover an appreciable amount of the grid was the probability of micelle formation. The formation of micelles is dependent upon the concentration of the surfactant in solution and upon the temperature; at the temperature and the dilute concentration at which these experiments were conducted, many of these copolymers were well below their cmc, making the formation of micelles impossible. The only exceptions to this may be the Pluronics in the upper right corner, such as Pluronic P123 or F127.

#### 4.3. Results on dirt count from image analysis

The image analysis was performed on the handsheets prepared before deinking (denoted as the

Master sheet) and the handsheets from two experiments involving Pluronic L101 and Pluronic P123. The two Pluronic samples were chosen because one led to the highest brightness values (L101) while the other resulted in the lowest brightness (P123) among the 17 block copolymers investigated. Figs. 6 and 7 correspond to the Master sheet without any ink being removed. In Fig. 6, the total area of ink spots having a given gray scale intensity is shown as a function of the gray scale levels from 0 (darkest) to 160 (threshold value chosen). All the specks that have intensities in the gray scale range indicated are treated as dirt and are counted as such. The size distribution of these specks is presented in Fig. 7. One can notice the presence of large specks in appreciable numbers (note: 1 pixel = 24  $\mu\text{m}$ , 100 pixels = 240  $\mu\text{m}$  and 200 pixels = 340  $\mu\text{m}$ ). Figs. 8 and 9 are for sheets deinked with Pluronic L101 and Figs. 10 and 11 are for sheets deinked with Pluronic P123. A comparison of Figs. 6, 8 and 10 shows that the darker spots (intensity values or gray scale levels

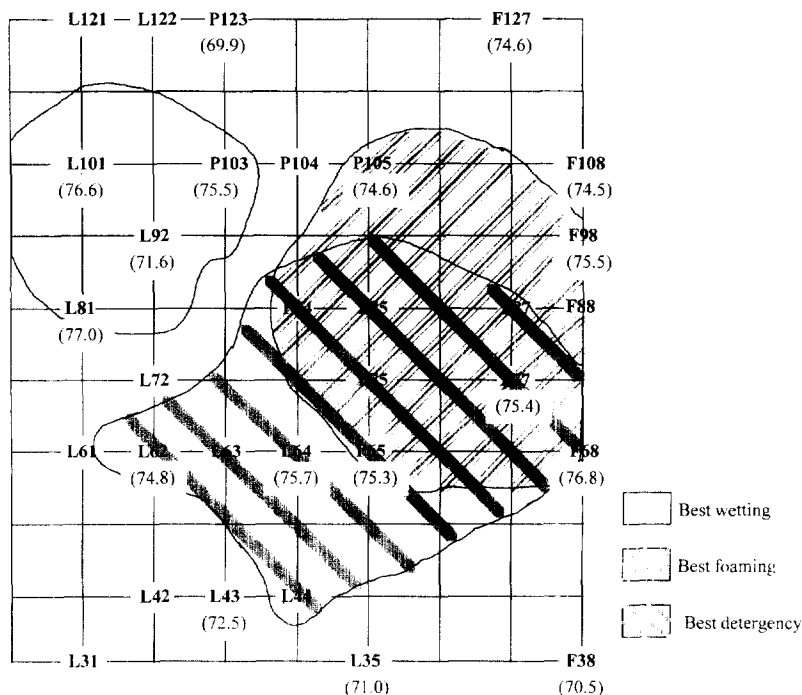


Fig. 5. Pluronic grid showing the brightness values for the Pluronics studied. The shaded areas indicate the best Pluronics for detergency, foaming, and wetting.

are small) from the original paper have been effectively removed on deinking by both the block copolymers, the performance based on L101 being superior. Similarly, a comparison of Figs. 7, 9 and 11 shows that, over the entire size range of ink spots, the number of ink spots in the original has decreased dramatically following deinking in the case of both block copolymers. One may observe that, contrary to the conventional wisdom about the flotation process being not suitable for the removal of toner ink particles because of their larger sizes, the use of block copolymers makes the flotation process effective. The data in these figures can be used to calculate the ink removal efficiency defined as the percentage reduction in the total ppm of ink area. Table 1 summarizes the ink particle size distribution for the two deinked handsheets and provides the total ppm of ink area calculated from the size distribution. Noting that the master sheet had an ink area of 14 160 ppm, the efficiency of ink removal is 99.2% in the case

of Pluronic L101 and 96.7% in the case of Pluronic P123.

#### 4.4. Results based on conventional deinking chemicals formulation

The use of Pluronics as the only chemical employed for the deinking leads to brightness values in the range between 73 and 76. Some of these Pluronics were also tested as part of more complex chemical formulations involving other conventional deinking chemical additives. For example, a deinking formulation included the block copolymer at 0.1% of paper weight besides 2.0% NaOH, 0.8% H<sub>2</sub>O<sub>2</sub> (a bleaching agent), and 0.2% EDTA (ethylene diamine tetra-acetic acid, a chelating agent). The brightness values obtained for the deinked sheets using this formulation were on average at least one brightness point higher, with some Pluronics delivering brightness values as high as 80. This appears to be an upper limit

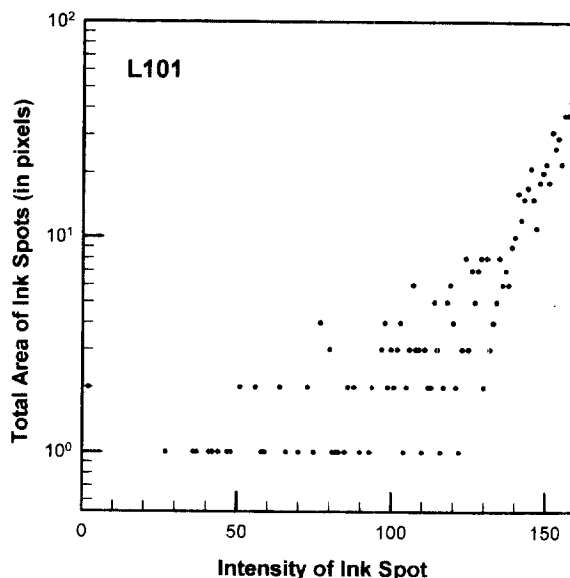
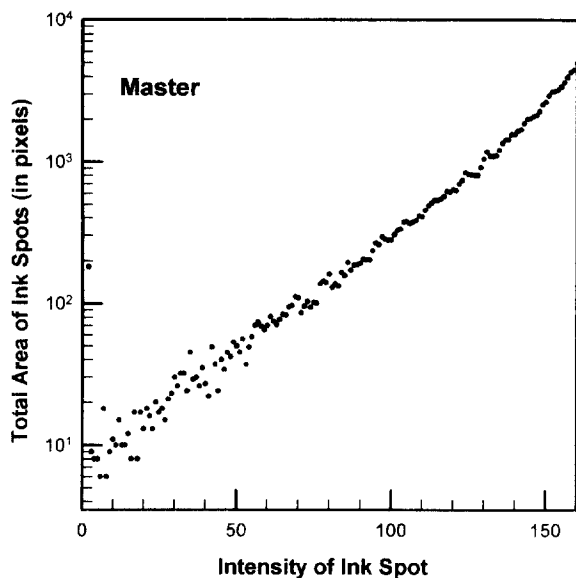


Fig. 6. Distribution of ink spots as a function of their intensity (gray scale level) in the master sheet (prepared by repulping the test paper and forming the handsheet). The gray scale value of 0 corresponds to the darkest spot and as the gray scale value increases, the spots become lighter.

Fig. 8. Distribution of ink spots as a function of their intensity (gray scale level) in the handsheet prepared from pulp treated with Pluronic L101. Note that most of the dark spots present in Fig. 7 have disappeared here. The remnant ink after deinking corresponds predominantly to larger gray scales, and hence to lighter spots.

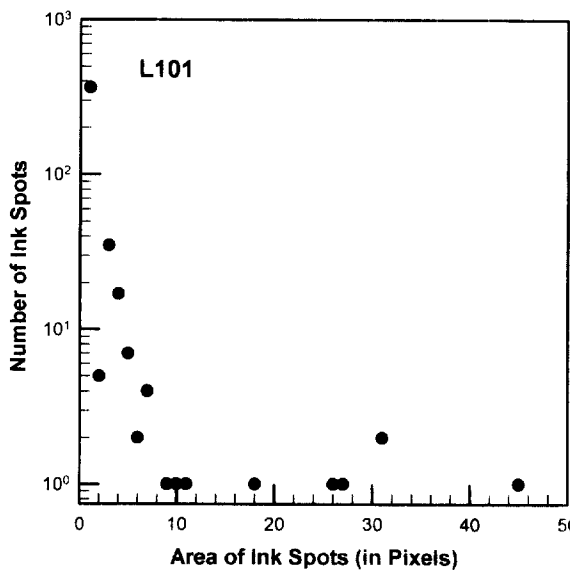
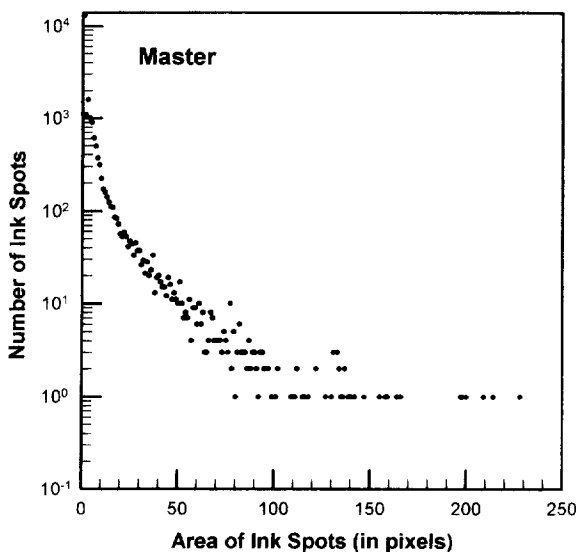


Fig. 7. The size distribution of ink spots on the master sheet. The ink spots are those that have intensities in the gray scale from 0 to 160 shown Fig. 6. See text for the relation between pixel and the size of the ink spot.

Fig. 9. The size distribution of ink spots on the handsheet prepared from pulp treated with Pluronic L101. The ink spots are those that have intensities in the gray scale from 0 to 160 shown Fig. 8.

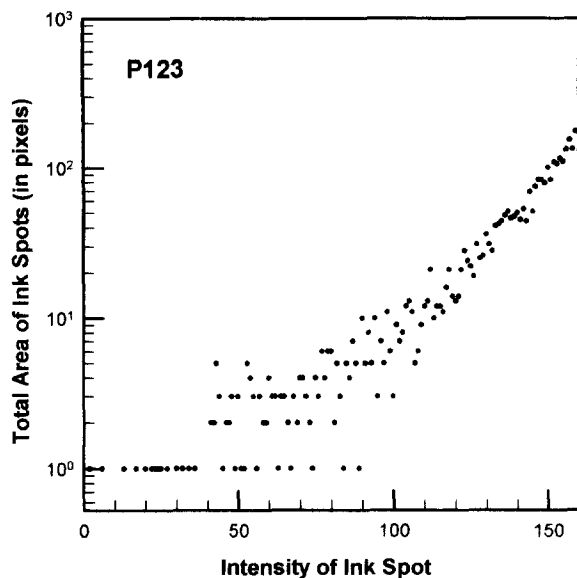


Fig. 10. Distribution of ink spots as a function of their intensity (gray scale level) in the handsheet prepared from pulp treated with Pluronic P123. Note that most of the dark spots present in Fig. 7 have disappeared here. The remnant ink after deinking corresponds predominantly to larger gray scales (or lighter spots).

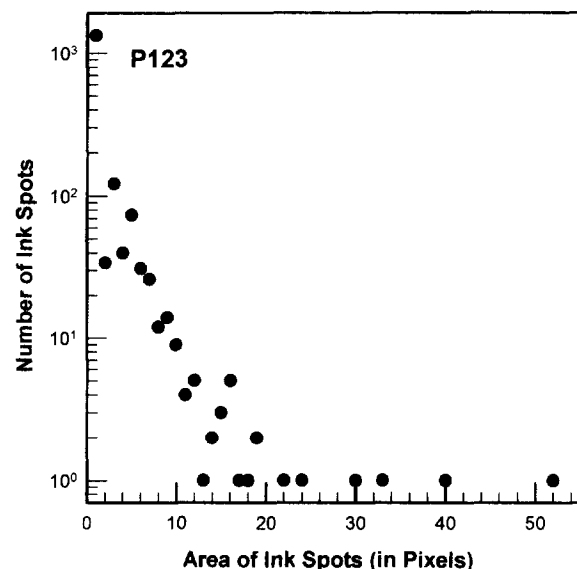


Fig. 11. The size distribution of ink spots on the handsheet prepared from pulp treated with Pluronic P123. The ink spots are those that have intensities in the gray scale from 0 to 160 shown in Fig. 10.

for brightness using this formulation at these concentrations; thus one can see how the addition of other chemicals really affects the brightness. However, the percent fiber losses obtained using these multicomponent chemical formulations were all higher than the fiber losses obtained with only the Pluronic; some of the losses were as much as 10% higher. These findings provide an important realization, namely that the addition of more chemicals may raise the brightness of the pulp, but at the expense of losing more paper fiber.

#### 4.5. Optimal selection of block copolymer

The results on fiber losses and brightness values are grouped together onto the same grid to determine some optimum range of Pluronics for deinking (Fig. 12). The last grid shows that there is an overlap of lowest fiber losses and highest brightness values between the Pluronic 80 series and the 100 series. To get the best results from a deinking operation, one would therefore wish to pick a Pluronic somewhere in this regime. In fact, it seems that Pluronic L101 in the upper left corner of this area provides a very low fiber loss coupled with a high degree of sheet brightness and high ink removal efficiency estimated from computerized image analysis.

## 5. Conclusions

A two-step deinking process involving pulping and flotation steps and utilizing a single block copolymer in very low concentrations, is developed here for Xerox and laser-printed papers. The addition of other chemicals may provide slightly brighter deinked pulp, but their use in a large-scale deinking process drives the cost up dramatically. Further, the use of a single chemical additive offers the opportunity to explore the connection between the surface chemical properties of the additive and its deinking performance.

Pluronics are seen to be effective surfactants for deinking, but one must choose carefully the best Pluronic for a specific application. The Pluronics which gave the lowest fiber losses were, in general, those with the most hydrophobic character; these were the ones with the highest PPO molecular

Table 1  
Ink particle size distribution

Handsheets	Number of particles in the size range					Total ppm ink
	20-40 $\mu\text{m}$	40-80 $\mu\text{m}$	80-120 $\mu\text{m}$	120-160 $\mu\text{m}$	> 160 $\mu\text{m}$	
Master	14108	5664	1192	487	356	14160
L101	369	68	1	4	1	108
P123	1365	332	22	3	1	463

Note: The number of particles listed in the table are per 5 in<sup>2</sup> area of the handsheet.

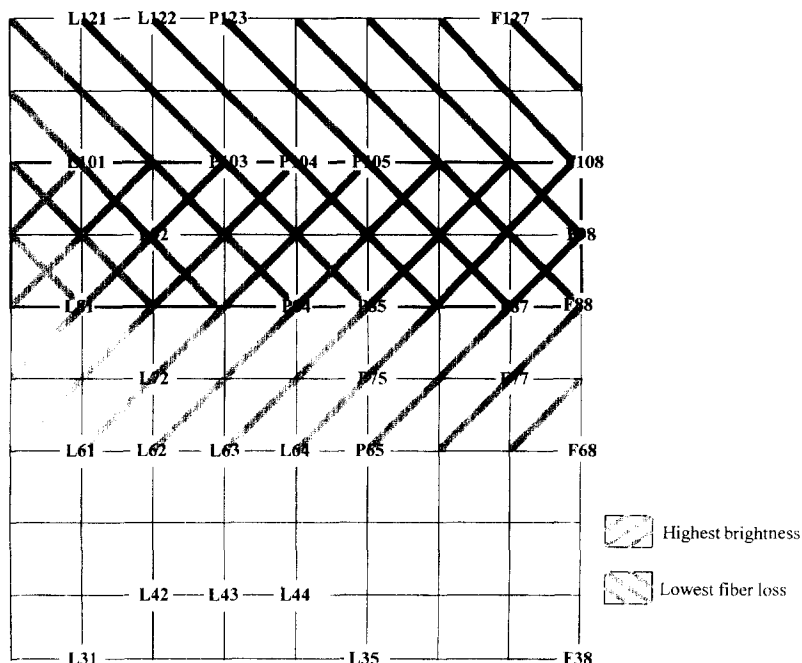


Fig. 12. Pluronics grid showing the areas of highest brightness and lowest fiber loss. The region where these areas overlap indicates the Pluronics which have the greatest deinking efficiency.

weights and the lowest percentage of PEO. They also had excellent wetting and defoaming characteristics. Those Pluronics which were noted as good foaming agents seemed to produce poorer results with larger fiber losses. Those Pluronics which provided the brightest deinked pulp generally had mid-range PPO molecular weights. These were noted as best for detergency, foaming, and wetting, and since these properties are all so closely related, it seems logical that they would all fall in the range where brightness values are highest. An ideal Pluronic would provide deinked pulp with a high degree of brightness and little fiber

loss. There is a narrow range of Pluronics exhibiting this behavior between the 80 series and the 100 series; the surfactant which seems to be the best in this range is Pluronic L101. The use of this block copolymer also led to very high ink removal efficiencies, as determined using computerized image analysis.

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