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Article

Deinking of laser printing with ultrasound of intensive action to obtain high purity cellulose

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Abstract:

A study on the deinking of office waste paper printed with laser is presented, applying ultrasound of intensive action, combined with stages of flotation and washing. The treated material was evaluated to determine its use as a basis for generating soluble grade cellulose. The waste paper was manually torn and disintegrated at 1.2 % consistency, for 10 min. The disintegrated fiber was treated with intensive-action ultrasound. At this stage, a 2^k multifactorial experimental design was applied, in which the parameters time (min), consistency (%), temperature (°C) and time of pause of application by ultrasound were used; while the number of ink particles m^{-2} of paper, was the response variable. Low consistency and commercial surfactant were used in the flotation and washing steps. The deinked pulp was evaluated by analyzing various quality parameters such as α-cellulose content, brightness, CIE color L *, a *, b * and the residual particle count m^{-2}, using TAPPI standards. The obtained results indicate that the proposed deinking showed great efficiency in generating fragments of toner, of size between 25-50 and 50-100 μm. These particles were removed in flotation and washing. The best removal of ink m^{-2} of paper was obtained with 20 minutes of treatment, 0.5 % consistency, 25 °C and continuous ultrasound application. Finally, the properties of the pulp obtained under optimized conditions indicate that it can be reused in paper grade products and even to generate soluble grade cellulose by applying some subsequent bleaching.

Key words: High purity cellulose, deinking, flotation, washing, laser printing paper, ultrasonic intensive action.

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Introduction

The incorporation of secondary fiber into the paper making process is a strategy that has been used for decades. The information relating to the reuse of secondary fiber dates back to the 17th century in Denmark; however, it was not until the apparition of the paper machine, at the end of the 18th century —perfected by the Fourdrinier brothers and with progressive implementation throughout the 19th century—, that the secondary fiber began to be utilized on a large scale (Sánchez, 2000).

In the last 20 years, there was a sharp worldwide increase in the reuse of secondary fibers, which rose from 5.9 to 45 million tons per year (Costa and Rubio, 2005).

Recycled paper (secondary fiber) is used for the manufacture of toilet paper, tissue paper and paperboard, which is considered to be low quality. Indeed, the whiter the product, the better its quality; a less white hue is the result of the presence of ink residues in the recycled paper pulp (Alliot *et al*., 2004).

The development of information technology and the sustained growth in the use of personal computers have increased laser and xerographic printing, and therefore the consumption of paper, resulting in a good availability of high quality fibers for reuse. However, it should be noted that the deinking process is closely related to the printing method, the type of ink and the method utilized to dry the ink (Alzate y Alzate., 2012).

Manning and Thompson (2004) point out that the particles of ink used in laser printing are made of carbon black, iron oxide, polystyrene, polyamide and polyester, among other products that are used to adhere the carbon black to the paper when it melts during the printing process. According to Álvarez (2006), among the main problems related to the use of recycled printing paper by electronic methods, there is notably little information about the chemical characteristics and the physico-chemical properties of the residues of ink that are left after the deinking, and of the remnants after this process that can contribute to the formation of anionic impurities.

On the other hand, in countries like Japan and the United States of America, most of the plants normally use the washing process in addition to flotation; while, in regions of Europe and Canada only flotation is used, in an alkaline medium and at moderate temperatures(Theander y Pugh, 2004). The elimination of the ink in the flotation phase is one of the key points for obtaining high-quality deinked fiber (Pélach, 2015), through physico-chemical mechanisms. The success of the flotation process lies in three main characteristics: the detachment of the particles of ink on the fibers; the effective adhesion of the particles of ink to the air bubbles which are dragged to the surface of the cell; the elimination of the foam and inks. The use of surfactants in the flotation and washing phases can have a positive or negative effect on the deinking process. Its primary function is to release the ink particles from the fibers, as well as to stabilize them; this contributes to the elimination of inks and improves the properties of the surface of the fibers during flotation (Zhao *et al.,* 2004). Theander and Pugh (2004) indicate that the formation of foam and the hydrophilic-lipophilic balance (HLB) are important parameters, when using non-ionic surfactants, as these affect the whiteness, and also the efficiency of the washing and of the flotation.

According to research carried out in the mid-90s on the use of ultrasonic devices with frequencies of 22, 23 and 54 kHz as a new method (Norman *et al.*, 1994), the ink particles are not easily removed from the fibrous suspension by conventional methods, due to their large size. Norman *et al*. (1994) proved that the low frequencies (22 kHz) were more effective to break ink particles larger than 400 μm, while the high frequencies facilitated the removal of small particles by flotation. In a study of bond paper deinking at a frequency of 40 kHz with laser printing, Ramírez (2004) points out that the best conditions to separate particles of less than 100 μm were: 0.5 % of consistency, high modulation in ultrasound, 55 °C of temperature in the fibrous suspension, a pH of 5, and 20 minutes of ultrasound treatment. An increase of 91 % of the ink particles in the 1-50 μm interval, and of 27 % in the 50-100 μm interval was achieved; this facilitated efficient separation of the toner particles through flotation and washing.

The purpose of the present study was to evaluate the effect of deinking laser printing paper, through the application of intensive action ultrasound and in the later phases of flotation and washing; to understand the phenomena associated with the deinking process, and to determine the optimal values of the parameters involved in the process in order to achieve the highest efficiency per m^2 in the removal of ink particles.

Materials and Methods

The study was carried out with Maxbrite™ letter-size bond paper sheets of 75 g m^{-2}. In order to standardize the amount of ink deposited on each sheet, one of their faces was printed, using a laser printer (HP LaserJet 1022), with the following legend: Deinking of laser printing, using sequences with intensive action ultrasound, oriented toward the production of high purity cellulose, which is repeated several times until 45 rows were completed; a size 12 bold Times New Roman font was used at double space. An approximate amount of 0.1872 g of toner was thus deposited on each paper sheet.

Aging process of the sheets

In preliminary tests, it was observed that the ink particles newly deposited by laser printing on paper did not show sufficient adhesion, compared to laser-printed waste paper stored for a long time. The sheets with a longer storage time retained a larger amount of toner during their disintegration than newly printed paper. Therefore, newly print paper underwent an aging process through exposure to UV light, in order to promote a better adhesion of the ink particles and simulate the characteristics of waste paper with a long storage time.

The freshly printed sheets of paper were exposed to UV light in a (RPR-100 Rayonet™ photoreactor) with 16 lamps of a 350 nm wavelength and an 8 compartment rotating carousel used to hold the paper samples and provide a uniform exposure to ultraviolet light. The paper sheets were cut into strips of approximately 28 × 7 cm, and exposed to ultraviolet light during 60 minutes.

Finally, the aged bond paper was cut manually into pieces of about 2 × 2 cm and stored in plastic bags.

Disintegration

The raw material was disintegrated in the Frank™ equipment at 3 000 RPM, to a 1.2 % consistency, during 10 min, according to the T 205 sp-12 norm (TAPPI, 2012a). Subsequently, the fibrous suspension was transferred to a 5 000 mL glass beaker, prior to the treatment with high-gain ultrasound.

Formation of test sheets

130 g m² sheets were made in the laboratory in conformity with the T 218 sp-11 norm (TAPPI, 2011a). The sheets were made in a Büchner porcelain funnel with a 20 cm diameter, using a base made of No. 6 Whatman™ filter paper with 3- μm diameter pores. Each sheet was placed in a wooden frame (as a tensor), to dry at room temperature for

a period of 24 h. The sheets obtained from the fibrous suspension in the disintegration phases were considered as control targets.

Treatment with high-gain ultrasound

The fibrous suspension was treated with high gain ultrasound using a 500 watt and 20 kHz VCX-500 Sonics^{TM} ultrasound processor. During the treatment, a high-gain bar with a 1 inch diameter was utilized, and a cooling system for exhaust gas recirculation was connected to the equipment in order to maintain the temperature of the system close to 25 °C.

A 2^k factorial experimental design with the following parameters was used: time of application (5 to 20 minutes), consistency (0.5 to 2.0 %), % of pause during the ultrasound (0 %, when continuous, and 37.5 and 75 % when paused), and temperature (25 to 80 °C). The number of residual particles of ink m^{-2} in the 25-50 and 50-100 μm intervals was considered as the response variable. Table 1 shows the total number of experiments and the conditions in each one of them. The experiments were carried out in duplicate. The collected data were analyzed using the statistical package Statgraphics Centurion XVII (Statgraphics, 2012).

Table 1. Experimental design applied to the deinking process with ultrasound; factors involved in the process.

Run	Time (min)	Consistency (%)	Temperature (°C)	Pause time of ultrasound application (%)
1	5	2	25	75
2	5	2	80	0
3	5	0.5	25	75
4	5	2	25	0
5	5	0.5	80	75
6	20	0.5	80	0
7	20	0.5	25	75
8	5	2	80	75
9	20	2	25	0
10	20	2	80	0
11	20	0.5	25	0
12	20	2	25	75
13	20	0.5	80	75
14	12.5	1.25	52.5	37.5
15	12.5	1.25	52.5	37.5
16	5	0.5	80	0
17	20	2	80	75
18	5	0.5	25	0

Flotation phase

After each experiment of the previous treatment, a flotation process was carried out with specifications according to the PTS-RH010/87 method; the Barnant Mixer cell was used, with an air supply of 60 ± 5 L h^{-1}, a stirrer speed of 1 500 ± 60 RPM, a flotation period of 10 ± 1 min and a consistency of 0.80 %. The quantity of surfactant ISTEMUL-780 added was 0.16 % for dry basis cellulose, dissolved in 80 mL of deionized water.

Washing Phase

After the flotation phase, the fibrous suspension was submitted to a washing sequence, with 0.5 % of ISTEMUL-780 for cellulose dry basis, as dispersing agent. This stage was held in a Degussa cell during 10 min, with a water flow of 1 L min^{-1}, a consistency of 0.4 %, and a 200 mesh washing sieve inside the cell.

Characterization of the raw material

The bond paper sheets were analyzed using standardized techniques of the American Association of Technicians of the Pulp and Paper Industry (TAPPI), in order to determine the properties of interest: the moisture content, based on the T 412 om-11 norm(TAPPI, 2011b); ash content, with the T 211 om-02 technique (TAPPI, 2002); whiteness and opacity, with an Elrepho 3000 (Datacolor International) spectrophotometer, according to the norm T 452 om-08 (TAPPI, 2008); and the color of the paper, with the T 527 om-07 technique (TAPPI, 2007).

In addition, the content of α, β and γ-cellulose was evaluated based on the T 203 cm-09 norm (TAPPI, 2013).

Characterization of the test sheets

Once the evaluation sheets were developed, the number of residual ink particles per m² and the whiteness, opacity and color were assessed. The residual particles m^{-2} were calculated based on the norm T 563 om-12 (TAPPI, 2012b), with a Perfection V700 Epson™ Photo scanner, coupled to a software specialized in the analysis of dirty areas in pulp and paper (Techpap, Simpalab-Laboratory dirt analyzer™).

Based on the results of the statistical analysis, a non-conventional deinking process was carried out using a treatment with high-gain ultrasound according to optimized values. In each phase of the deinking process (disintegration, ultrasound treatment, flotation and washing) evaluation sheets were generated with the Büchner's funnel method, for which the following optical properties were determined: number of residual ink particles per m², whiteness, opacity and color, as well as their content of α, β and γ-cellulose and % of ashes.

Results and Discussion

Tables 2 and 3 show the optical characteristics and the chemical analysis of the bond paper sheets, respectively. The information in Table 2 indicates that the paper contains non-degraded cellulose (α-cellulose) and relatively high hemicelluloses (β and γ-celluloses). There is also a high Kappa number, which implies an unusually high lignin content for a bleached chemical pulp. Both values suggest that the raw material may include mechanical pulp mixed with chemical pulp in its composition.

The quantity of ashes in the sample is not very high, which suggests that the amount of mineral loads in the paper corresponds with the limits considered as normal in a bond paper formulation.

Table 2. Analysis of the content of α, β and γ-cellulose, Kappa number and ash content, in the bond paper without laser printing.

Content of carbohydrates			Kappa number	Ash content
α-cellulose (%)	**β-cellulose (%)**	**ϒ-cellulose (%)**		
87.33±0.10	6.69±0.08	19.35±0.19	27.42	13.45±0.03

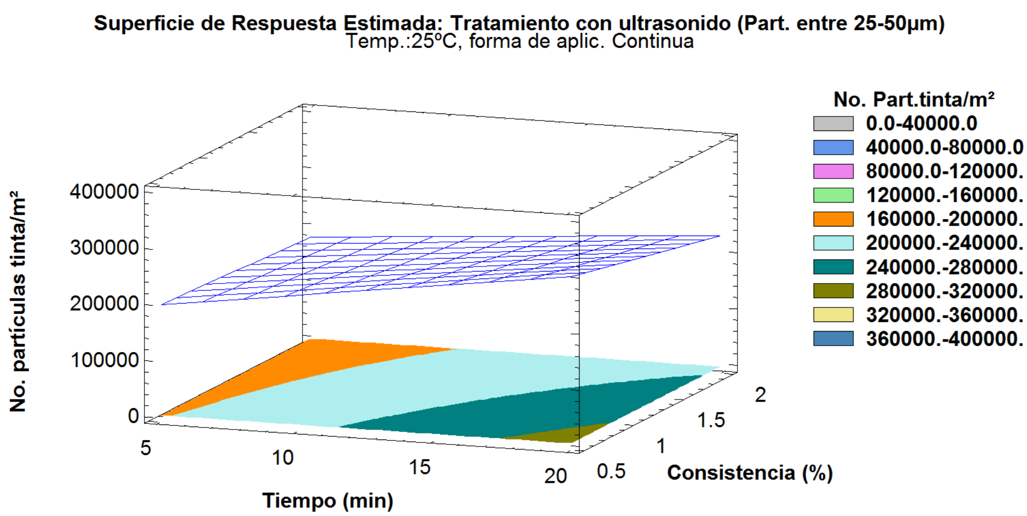
Table 3 shows the whiteness and the parameters of color, according to the space of the 1976 CIE L*, a*, b* hues, measured on the bond paper. An average whiteness of 94.41 % ISO is observed, with a brightness or luminosity (L) of 91.54 %, and a coloring within the red/blue color plane, leaning more toward the blue color (b=-10.73). This trend reflects the fact that the paper is bleached using an oxidative process combined with the use of optical brighteners, which would account for the high level of whiteness observed.

Table 3. Optical properties of the bond paper, without laser printing.

Whiteness % ISO	The CIE color parameters		
	L*	**a***	**b***
94.41±0.95	91.54±0.29	2.49±0.04	-10.73±0.13

One of the main objectives of this research was to apply an ultrasound treatment in order to promote effective fragmentation of toner particles, in such a way that it will generate the greatest possible amount of ink particles, with sizes between the intervals of 25-50 and 50-100 μm, to facilitate its removal by the flotation and washing stages.

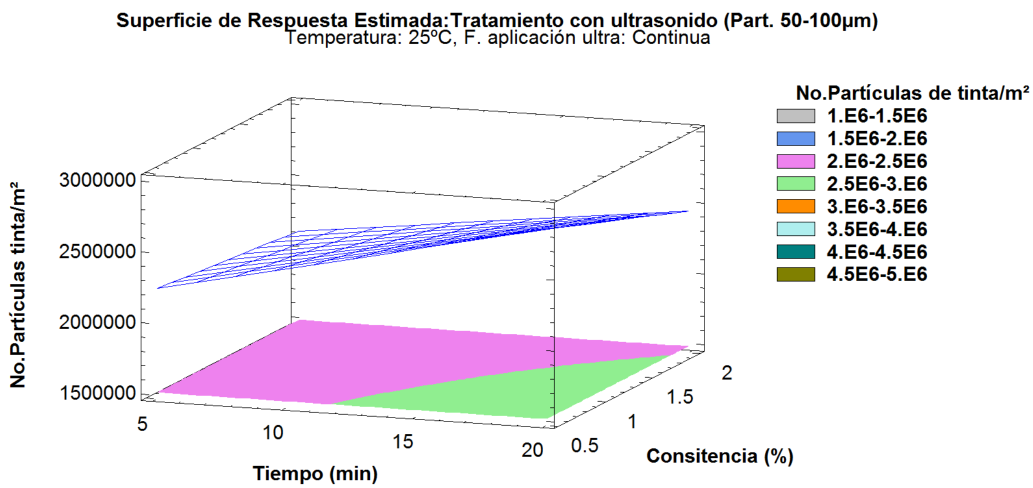
Figure 1 shows a response surface graph based on the statistical analysis of the particle size distribution data, obtained through the application of experimental design at the treatment phase with high-gain ultrasound. The response variable considered was the count of residual ink particles per m² in 25-50 μm. It is evident that in order to generate a larger quantity of ink particles per m², it is necessary to work using 20 min time periods, consistencies of 0.5 % at a temperature of 25 °C and with a continuous application of ultrasound.



No. partículas tinta/m^2 = Number of ink particles/m^2; *Tiempo* = Tiempo; *Consistencia* = Consistency; *Superficie de respuesta estimada* = Estimated response surface; *Tratamiento con ultrasonido* = Treatment with ultrasound*;* *Part entre* 25-50 μm = Particle between 25-50 μm*; Temp.* = Temperature; *Forma de aplic.* = Application form; *Continua* = Continuous*.*

Figure 1. Response surface for the ultrasound treatment phase with ultrasound for the detachment of ink particles per m² in the range of 25-50 μm, time *vs* consistency.

Figure 2 shows the response surface graph in the case of the statistical analysis, in which the response variable was the content of residual ink particles in the paper with size of 50-100 μm. The trend observed in Figure 2 indicates that in order to generate a greater amount of ink particles m² of 50-100 μm, a 20 min ultrasound treatment with a consistency of 0.5 % is required.



No. partículas tinta/m^2 = Number of ink particles/m^2; *Tiempo* = Tiempo; *Consistencia* = Consistency; *Superficie de respuesta estimada* = Estimated response surface; *Tratamiento con ultrasonido* = Treatment with ultrasound*;* *Part entre* 50-100 μm = Particle between 25-50 μm*; Temp.* = Temperature; *Forma de aplic.* = Application form; *Continua* = Continuous*.*

Figure 2. Response surface for the ultrasound treatment phase for the detachment of ink particles per m^2, 50-100 μm, time *vs* consistency.

Because the laser printing inks are usually made of a pigment and a thermoplastic resin, the polymers of the resin melt and become resistant to the action of chemicals, which renders the ink on the printed paper difficult to remove with conventional processes (Borchardt *et al*., 1998).

The statistical analysis of the data of the treatment phase with high-gain ultrasound revealed that the optimum conditions to maximize the number of ink particles, sized within the ranges of interest, were the following: treatment time of 20 minutes, consistency of 0.5 %, temperature of 25 °C and continuous application of ultrasound. These values were used to deink paper, under optimized conditions of treatment with ultrasound, and to analyze the general behavior of the proposed deinking process.

Once the paper was deinked under optimum conditions through a process that included disintegration, ultrasound, flotation and washing, the sheets were formed for their respective evaluation. Below are the results of tests for the determination of: α*,* β and γ-cellulose, and percentage of ashes (Table 4). The determination of α, β and γ-pulp was carried out under the norm T 203 om-88 (TAPPI, 1998).

Table 4. Determination of α, β and γ-cellulose for the bond paper with laser printing.

Result of α-cellulose %	**Result of β-cellulose %**	**Result of ϒ-cellulose %**	**Ashes %**
83.24	8.53	8.23	1.18

The ash content was determined according to the norm T 211 om-02 (TAPPI, 2002).

Table 5 shows the measures of whiteness and the L*, a*, b* of the formed paper sheets, made after the phases listed above. The degree of whiteness was measured with the Elrepho 3000 spectrophotometer.

Table 5. Values of whiteness (brightness) for laser printed bond paper.

Phase	Whiteness %	L*	a*	b*
Disintegration	77.61	86.76	1.47	-6.64
Ultrasound	71.15	83.77	1.36	-6.54
Float	83.74	89.48	1.45	-6.38
Washing	86.98	90.70	2.03	-6.60

Low values were registered for whiteness at the disintegration phase because only the paper was disintegrated (Table 5).

In the ultrasound phase, the results for the whiteness and L*, a*, b*, appear to be low. However, the generation and division of the ink particles per m² at this stage corresponded to the intervals of 25 to 50 μm and 50 to 100 μm; these ink particles were easily removed by flotation and washing. The level of whiteness was low, and so were the L*, a*, b*, values that represent the tone of the fibrous suspension treated with ultrasound. L* was positive, with a blue-gray hue; a* was also positive, with a reddish-blue hue; conversely, b* was negative, with a blue-gray hue in a grayish fibrous suspension.

As a result of flotation, it was possible to obtain an optimal whiteness of 83.74 % without the use of any chemical reagent. The results for L*, a* and b* are good in the color scheme of the fibrous suspension; L* was positive, with a grayish-blue hue; a* was positive with a reddish-blue hue; and b*, was negative, blue-gray. These shades are reflected on the tonality of the fibrous suspension as positive in terms of the coloring and the whiteness obtained.

With regard to the washing phase, there has been an increase in the whiteness; with an optimal of 86.98 %, which confirms the removal of particles of ink through the use and deinking of bond paper with intensive ultrasound. According to Fricker *et al*. (2007), the washing phase is highly effective for removing particles sized under 10 μm. The results in the tonality of the L*, a*, b* fibrous suspension in the washing phase were positive, which increased the final coloring of the fibrous suspension even more.

Figure 3a shows the surface of a sheet with disintegrated paste before treatment with ultrasound. Figure 3b exhibits the image of the sheet prepared with an intensive ultrasound treatment. As can be seen, a large number of ink particles were generated, or many were fragmented, which led to a blue-gray coloration on the surface of the formed sheet.

A) Disintegration; b) Treatment with ultrasound; c) Floating; d) Washing.

Figure 3. Images of the surface of the sheets obtained using the deinking process with intensive ultrasound.

Figure 3c shows the surface of a sheet obtained with treated paste at the later stages of ultrasound and flotation, in which the elimination of a large amount of toner particles is evident. The surface of the sheet showed a reduction of the gray-blue shade originally observed. Finally, Figure 3d shows the properties of the sheet formed after the ultrasound, flotation and washing phases. This surface represents the highest reduction of ink particles, which gave a greater whiteness to the paper.

Conclusions

Deinking of laser printed bond paper is possible when previously treated with ultrasound of intensive action, since it made it feasible to generate a greater amount of ink particles per m² at intervals of 25-50 μm and 50-100 μm, which are easy to remove through flotation and washing.

There is an important relationship between the temperature and the detachment of the toner particles from the fibers; *i.e.* higher temperatures, of or above 80 °C, during the application of the ultrasound are not conducive to a good ink particle detachment from the fibers; this is reflected in a reduction of whiteness. However, a temperature of 25 °C results in a better removal of the toner particles present in the fibers; this is one of the main factors in the deinking process with ultrasound.

The treatment time, temperature, consistency and form of application of the ultrasound to the fibrous suspension are very important in the process. It was observed that 20 minute periods at a temperature of 25 °C, a consistency of 0.5 % and continuous application of ultrasound result in a better detachment of ink particles per m²; and in an improved whiteness at the later stages.

Flotation and washing are very important in the removal of particles of ink after the implementation of the process with ultrasound to the fibrous suspension; however, it is necessary to add a surfactant froth, as this allows the removal of the ink particles of 25-50 μm and 50-100 μm, respectively.

The properties of the pulp obtained under optimized conditions indicate that it can be used to generate high purity cellulose through subsequent bleaching.

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Conflict of interest

The authors declare no conflict of interest.

Contribution by author

Rogelio Ramírez Casillas: conception of the research topic, review of results of the experimental work, drafting and editing of the manuscript; Enrique Ramírez Valdovinos: development of the experiments, calculations, and statistical analysis; Artemio Carrillo Parra: review of the results and of the experimental work; Florentina Dávalos Olivares: participation in the development of the experiments and analysis of results; Fernando Navarro Arzate: review of the results, assistance in the planning of the manuscript.