DEINKING FLOTATION OF RECYCLED LINERBOARD FOR FOOD PACKAGING APPLICATIONS

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Brown packaging linerboard, made entirely from recovered pulp, was subjected to deinking flotation for evaluating the possible improvements in its chemical, optical and mechanical properties.

The increase in the rate of recovered paper utilisation, along with the tendency towards lower basis weights, in the packaging paper production, has created a growing need for the utilisation of secondary fibers of improved quality. To attain better quality fibers, flotation deinking of brown grades is being considered, along with the addition of primary fibers to recovered paper furnish. Numerous conducted studies, in which the flotation technology was used in the treatment of brown grades, support this idea. Most of them show that the quality of fibers is improved after flotation deinking, resulting in higher mechanical properties of the deinked handsheets and in lower amounts of chemical contaminants.

As to food and human health safety, packaging paper has to meet specific requirements, to be classified as suitable for its direct contact with foods. Recycled paper and board may contain many potential contaminants, which, especially in the case of direct food contact, may migrate from packaging materials into foodstuffs. In this work, the linerboard sample selected for deinking was made from recycled fibers not submitted previously to chemical deinking flotation. Therefore, the original sample contained many non-cellulosic components, as well as the residues of printing inks. The studied linerboard sample was a type of packaging paper used for contact with food products that are usually peeled before use, *e.g.* fruits and vegetables.

The decrease in the amount of chemical contaminants, after conducting deinking flotation, was evaluated, along with the changes in the mechanical and optical properties of the deinked handsheets. Food contact analysis was done on both the original paper samples and the filter pads and handsheets made before and after deinking flotation. Food contact analysis consisted of migration tests of brightening agents, colorants, PCPs, formaldehydes and metals. Microbiological tests were also performed to determine the possible transfer of antimicrobial constituents.

Keywords: food packaging, recycled linerboard, deinking flotation, food contact analysis

INTRODUCTION

Large quantities of recycled fibers are used in the production of packaging paper and board. Some European countries, like the Netherlands, UK and Germany, manufacture paper and board packaging grades from 100% recycled fibers.[1] According to CEPI Key Statistics 2008,[2] packaging papers utilize about 60.9% of the total volume of recovered paper, *i.e.* nearly two thirds of the total recovered paper consumption are used in packaging production. Most of the collected paper for packaging production is recycled without using deinking flotation, applied only in individual cases and mainly in the production of the white top layer of board.[3] Particularly, this means that a certain amount of non-fibrous contaminants, like clay, ink particles, stickies, etc., will remain in the pulp after recycling and, consequently, will induce a decrease in the fiber bonding potential.[4] Since deinking was not, most likely, performed during the previous recycling stages, the accumulation of ink and inorganic particles is intensified as recycling is repeated. In the production of corrugated containers, testliners and corrugated media are usually made of 100% recycled fibers, mostly by combining old corrugated containers (OCCs) and mixed paper grades. OCCs are used because they contain some softwood kraft fibers, which are essential in providing the required strength properties. However, if low-quality OCCs are used, the pulps will most likely contain a considerable amount of low-length fibers, with increased shares of inorganic and sticky substances.[5] Also, these pulps might contain a larger proportion of fines than the long fibers. The fines content increases as recycling is repeated, due to fiber hornification, which finally affects the reduced bonding capacity of the reprocessed fibers.[6] Therefore, to improve the strength properties of the recovered paper pulp, the utilization of strength additives, such as starch,[4] is especially important.

The continuous trend towards lower basis weights in paper and board production, as well as increased paper machine speeds, could possibly lead to the addition of higher quality recycled fibers to the furnish mix, for reaching the necessary strength properties. To obtain a better fiber quality, flotation deinking of brown grades is considered, along with the addition of primary fibers to the recovered paper furnish.

Müller-Mederer, Putz and Gottsching conducted research on the possible quality improvement of mixed/brown packaging grades by flotation, namely, by flotating seven different industrial pulps used in the production of corrugated board and folding box board.[3] They concluded that flotation improves the mechanical characteristics of the sheet to a certain extent and decreases the content of both chemical contaminants and macro-stickies.

In a recently finished German research project[7] (No. IW 060113), the integration of the flotation stage in the stock preparation of packaging paper was investigated. The results obtained showed that the amounts of inorganic matter (ash) and hydrophobic contaminants present in these pulps can be reduced by flotation, an increase in paper strength being thus obtained.

As a response to environmentally driven pressures, food board manufacturers often try to produce packaging with high content of recycled fibres. Paper and board, partly or fully produced from recycled fibers, are already being used in certain foodstuff applications in many European countries. Recycled paper is mainly used for direct contact with dry foodstuff, such as flour, grain, sugar, rice and pasta, as well as with foodstuffs that are usually washed, peeled or shelled before use, like vegetables, fruits and eggs. However, recovered paper is also used for direct contact with dry fatty foodstuffs, like pizza and other fast food products.[8] In Croatia, for example, in the production of take-away pizza boxes, the white top ply of the linerboard, which actually comes into contact with the food, is made of deinked pulp.

Nevertheless, since, in some cases, the origin and composition of recycled fibers may be unknown, recycled grades must be used with special caution for food contact products. Binderup *et al*.[9] cited a list of chemicals identified by the available chemical analyses of recovered paper. The list contains phthalates, solvents, azo-colorants, diisopropyl naphthalenes, primary aromatic amines, polycyclic aromatic hydrocarbons, benzophenone and others.

On the other hand, many manufacturers of recycled paper and board guarantee production of safe food packaging, thanks to the improved methods used in fiber selection and cleaning of recovered paper pulps. However, in the EU there is still no harmonized legislation on food contact paper and board applications, and on the use of recycled paper fibers in contact with foods. There is also no specific directive about paper and board coming into contact with foods. The main rule for paper and board food contact applications comes from the EU Framework Regulation[10] (EC) No 1935/2004 and the Regulation on Good Manufacturing Practice[11] (EC) No 2023/2006.

The Framework Regulation, covering generally food contact materials, provides that substances hazardous to human health must not be transferred from packaging into the packed food in quantities which could endanger human health or bring about an unacceptable change in the composition of the food or deterioration in its organoleptic characteristics (essentially its taste and smell). In the absence of a specific directive, some European countries have developed their own national provisions specific to paper and board (for example, France, the Netherlands and Germany).

In addition, the Council of Europe (COE) has published the non-legal binding Resolution on Paper and Board for Food Contact,[12] which acts as a reference for the countries that have not yet established their national regulations. The requirements included in the guidelines depend on the recycled paper source, decontamination processes and type of food contact application. Also, in these guidelines, the toxic compounds found or likely to be found in recovered paper are listed. In terms of overall (global) migration limits (OML) and specific migration limits (SML), different rules are applied for different types of foods. If packaging is intended to come into direct contact with fatty food, the limitations are far more restrictive than for dry food packaging applications.

EXPERIMENTAL

Brown packaging linerboard made entirely from recovered pulp was submitted to a deinking flotation process, for evaluating the possible improvements induced in its chemical, optical and mechanical properties. The linerboard sample under study was industrially made packaging used for contact with foods that are usually peeled before use, *e.g.* fruits and vegetables. The linerboard sample was unprinted, yet it contained a high amount of ink residues, fillers and other impurities in its structure, since it had been produced from recovered fibers which had not undergone chemical flotation. The deinking flotation procedure was applied for evaluating the possible decrease in the amount of ash and chemical contaminants, as well as for improving the properties of deinked paper (visual aspect, mechanical properties and suitability for food contact usage).

Laboratory deinking flotation was performed under the conditions and with the operation parameters described in the INGEDE Method 11 (pulping chemistry: 0.6% NaOH, 1.8% sodium silicate, 0.7% H_2O_2, 0.8% oleic acid; pulping: c = 15%, 20 min, 45 °C, 130 ppm Ca^{2+}; storage: c = 5%, 45 °C, 60 min; flotation c = 0.8%, 45 °C, 10 min). A Helico pulper was used instead of the recommended Hobart pulper N50. Handsheets and filter pads were made before and after deinking flotation, in accordance with the INGEDE Method 1.

After forming handsheets and filter pads, the optical characteristics (ISO brightness – ISO 2470, ERIC – TAPPI T 567 pm-97, and IE_{ERIC}) were measured for the samples made before and after the flotation stage, to evaluate the deinking flotation efficiency. Pulp brightness and effective residual ink concentration (ERIC) were measured with a Technibrite Micro TB-1C apparatus.

In addition, the mechanical properties of recycled handsheets, *i.e.* tensile breaking strength (TAPPI T 404 cm-92), internal tearing resistance – Elmendorf-type method (TAPPI T 414 om-98) and bursting strength of paper (TAPPI T 403 om-97) were measured.

The determination of the ash content at 900 °C (TAPPI T 413 om-93) was performed on handsheets and filter pads obtained both before and after flotation, as well as on the original linerboard sample and on the collected flotation froth.

As to the food contact analysis, all tested paper samples were compared with the quantitative restrictions laid down in the German BfR Recommendations[13] (chapter XXXVI) that they had to comply with. Even though the original linerboard sample was primarily used as dry food packaging, the food contact suitability was tested on direct fatty foodstuff application (such as pizza or pastry). Food contact analysis was done on the original paper sample, as well as on filter pads and handsheets made before and after deinking flotation. Food contact analysis involved migration tests of the brightening agents, colorants, PCPs, formaldehydes and metals. Microbiological tests were also performed, to determine the possible transfer of the antimicrobial constituents.

For the determination of metals, PCP and formaldehyde, cold-water extracts were prepared from all paper samples (original linerboard, and undeinked and deinked handsheets/pads). PCP extraction was made in accordance with EN ISO 15320. The PCP present in the cold-water extract was concentrated by solid-phase extraction on a phenyl column. The PCP was then eluted from the column with hexane, acetylated with acetic anhydride, and the amount of PCP present was determined by gas chromatography.

Formaldehydes were determined according to UNE-EN 1541, while the determination of the metal ions (cadmium, lead and mercury) in the cold-water extracts was carried out in accordance with the UNE-EN 12498 and UNE-EN 12497 standards. The detection of metals was done on an ICP-Spectrometer and the detection of formaldehydes – by spectrophotometry.

The fastness (migration) of the brightening agents (UNE-EN 648) and colorants (EN 646) from the food contact papers were tested with test fluids such as olive oil, 3% acetic acid, deionised water and saliva simulant. In these test procedures, the sample is brought into contact with glass fiber papers previously saturated with a test fluid (food simulant) and placed under a load (1 kg) for a given time period (24 h). The staining of the glass fiber paper was evaluated comparatively with a series of fluorescent-whitened papers (detection of FWAs) or against a blank or grey scale (color fastness).

For microbiological tests, Petri plates were prepared with the *Bacillus Subtilis* (bacterium) and *Aspergillus Niger* (fungus), then incubated for 3 days at 30 °C, and 5 days at 25 °C, respectively (UNE-EN 1104). When incubation was over, the occurrence of an inhibition zone (in the growth of flora) was indicative of the release of antimicrobial constituents.

RESULTS AND DISCUSSION

Optical properties

The results of brightness measurements, expressed separately for the lower and upper side of the original paper sample, as well as for the handsheets and filter pads, presented in Figure 1, evidence a certain increase in brightness after disintegration – of 20.3% in the case of handsheets (expressed as a mean value of both sides of the samples) and of 16.3% in the case of filter pads – which then slightly decreases after flotation (by 1-1.5% in both cases). These unexpected results can be explained by the fact that deinking flotation removed a certain amount of filler particles, causing a brighter visual aspect of the undeinked pulp, comparatively with that of the deinked one. These results can be correlated with the reduction in the ash content after the flotation stage (Fig. 2), which was reduced by 38.6% (handsheets) and 14.6% (filter pads), as determined for undeinked and deinked pulp handsheets/pads.

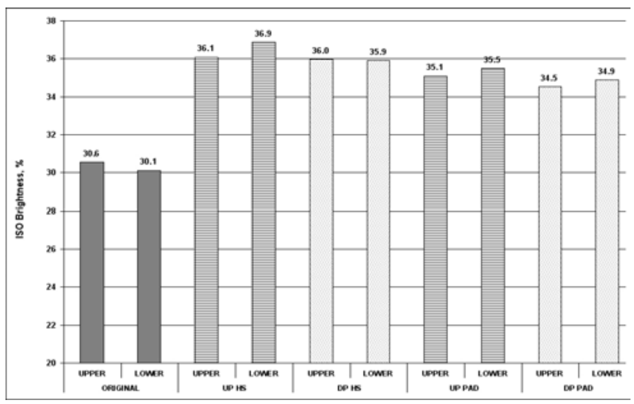

Figure 1: ISO brightness chart (ORIGINAL – original linerboard, UP HS – undeinked pulp handsheets, DP HS – deinked pulp handsheets, UP PAD – undeinked pulp filter pad, DP PAD – deinked pulp filter pad)

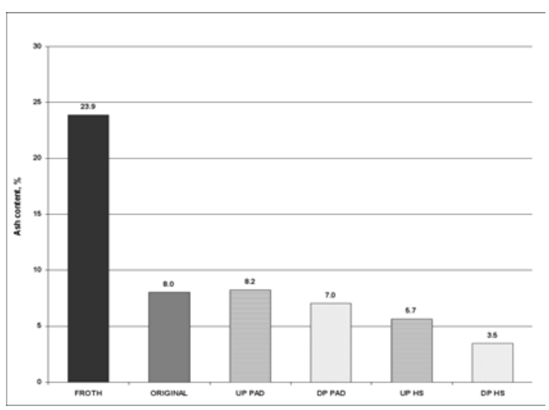

Figure 2: Ash content chart (ORIGINAL – original linerboard, UP PAD – undeinked pulp filter pad, DP PAD – deinked pulp filter pad, UP HS – undeinked pulp handsheets, DP HS – deinked pulp handsheets)

The results of the Effective Residual Ink Concentration (ERIC) measurements are presented in Figure 3. The ink elimination factor (IE_{ERIC}) calculated from the obtained results shows an ink elimination of 10.9% in handsheet samples, and of 7.3%, respectively, in filter pad samples.

Mechanical properties

The tensile strength results of recycled handsheets, expressed as breaking length (m) and presented in Figure 4, show a 30% increase in the tensile strength properties of the handsheet samples after deinking flotation, as compared to the undeinked ones.

The burst strength results of recycled handsheets, expressed as burst index and presented in Figure 5, show a 23.8% increase in the burst strength properties of the handsheet samples after deinking flotation, as compared to those of the undeinked handsheet samples.

The increase in the tensile and burst strength of the recycled handsheets can be correlated to the ash content reduction in handsheet samples after deinking flotation, which most likely contributed to the increase of the inter-fiber bonding potential of deinked fibers, thus increasing paper strength.

The internal tearing resistance results of recycled handsheets, expressed as tear index and presented in Figure 6, show that the internal tearing resistance of the handsheets after deinking flotation remained nearly the same.

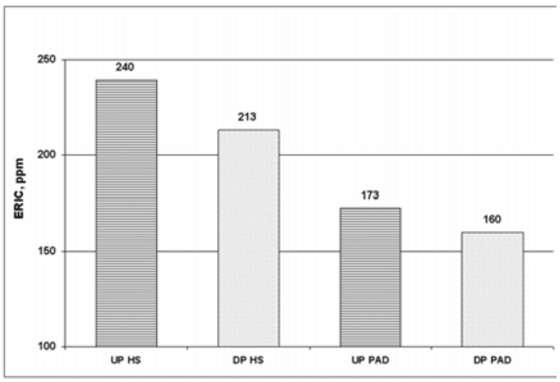

Figure 3: Chart of ERIC measurements (UP HS – undeinked pulp handsheets, DP HS – deinked pulp handsheets, UP PAD – undeinked pulp filter pad, DP PAD – deinked pulp filter pad)

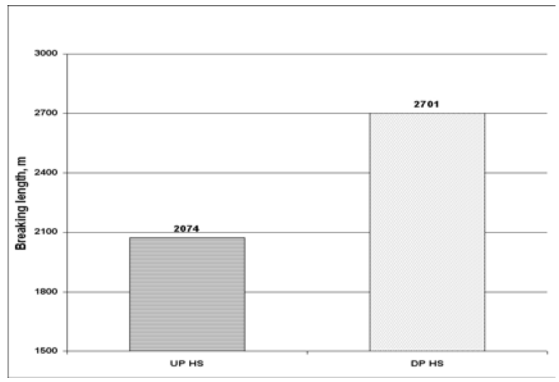

Figure 4: Tensile strength properties of recycled handsheets, expressed as breaking length, (UP HS – undeinked pulp handsheets, DP HS – deinked pulp handsheets)

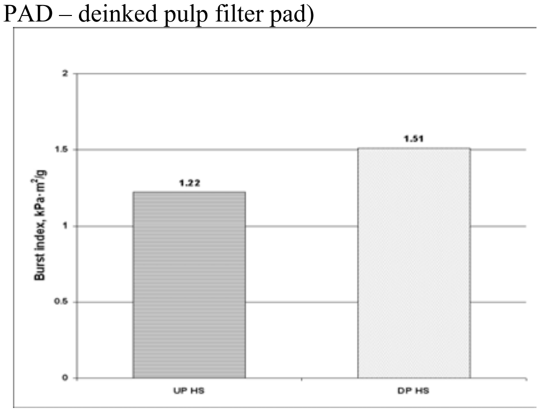

Figure 5: Burst strength properties of recycled handsheets, expressed as burst index, (UP HS – undeinked pulp handsheets, DP HS – deinked pulp handsheets)

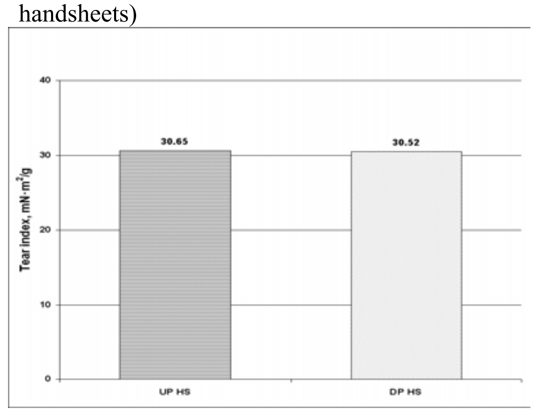

Figure 6: Internal tearing resistance of recycled handsheets, expressed as tear index, (UP HS – undeinked pulp handsheets, DP HS – deinked pulp handsheets)

Food contact analyses

According to the BfR Guidelines, the amount of pentachlorophenol (PCP) in finished paper should not exceed 0.15 mg of PCP per kg of paper. The results on the detected amount of PCP in cold-water extracts are presented in Figure 7. Although, for all samples, the detected amount of PCP is below the food contact limit, the results show that the amount of PCP in deinked samples is reduced, when compared to that of undeinked samples, as it is the case of *e.g.*, filter pad samples, which show a 32% decrease in the PCP content after flotation.

According to the BfR Guidelines, the finished paper must not exceed 1.0 mg formaldehyde per dm^2, as detected in the water extract. Table 1, listing the results of formaldehyde determination analysis, indicates that all detected amounts are well below the food contact limit.

According to the BfR Guidelines, the transfer of metal ions to foodstuffs must not exceed 0.5 µg per gram of paper (Cd); 3 µg per gram of paper (Pb); 0.3 µg per gram of paper (Hg). The analysis of the metal ions transfer tests is not necessary for the paper or paperboard intended for contact with dry, non-fatty foodstuffs.

The results of metal ions determination in the water extracts, presented in Table 2, show that the amounts detected in all recycled samples are well below the food contact limits.

As to the tests on the migration (bleeding) of brightening agents and colorants into food stimulants, all samples were found suitable for food contact applications. No bleeding was detected, not even on the original sample (linerboard). Microbiological tests, performed for determining a possible transfer of the antimicrobial constituents, show similar results. All tested paper samples were found suitable for food contact applications, as no release of antimicrobial constituents was observed (no inhibition zone present in the growth of flora, Fig. 8).

Table 1
Amounts of formaldehyde determined in cold-water extracts (ORIGINAL – original linerboard, UP PAD – undeinked pulp filter pad, DP PAD – deinked pulp filter pad, UP HS – undeinked pulp handsheets, DP HS – deinked pulp handsheets)

Sample	Concentration (mg/dm^2)	Limit (mg/dm^2)
ORIGINAL	0.004	1
UP PAD	0.012	1
UP HS	0.002	1
DP PAD	0.008	1
DP HS	0.001	1

Table 2
Amounts of metal ions determined in cold-water extracts (ORIGINAL – original linerboard, UP PAD – undeinked pulp filter pad, DP PAD – deinked pulp filter pad, UP HS – undeinked pulp handsheets, DP HS – deinked pulp handsheets)

Amount in water extract	Hg	Cd	Pb
	mg/kg paper		
Limit	0.3	0.5	3
ORIGINAL	< 0.050	< 0.025	0.040
UP PAD	< 0.050	< 0.025	0.037
UP HS	< 0.050	< 0.025	0.031
DP PAD	< 0.050	< 0.025	< 0.025
DP HS	< 0.050	< 0.025	< 0.025

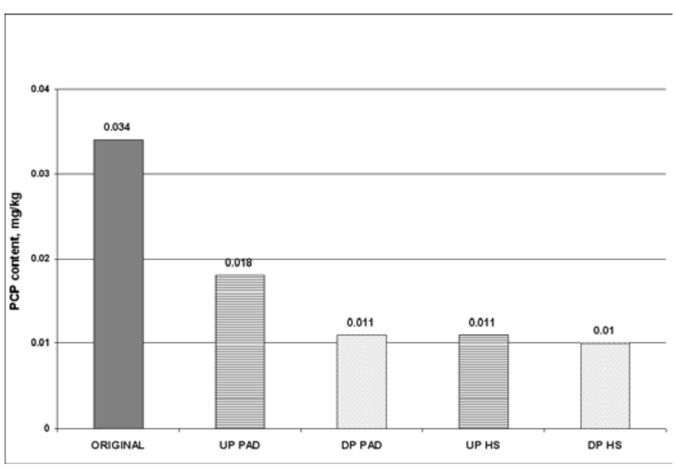

Figure 7: The PCP found in recycled pulp cold-water extracts (ORIGINAL – original linerboard, UP PAD – undeinked pulp filter pad, DP PAD – deinked pulp filter pad, UP HS – undeinked pulp handsheets, DP HS – deinked pulp handsheets)

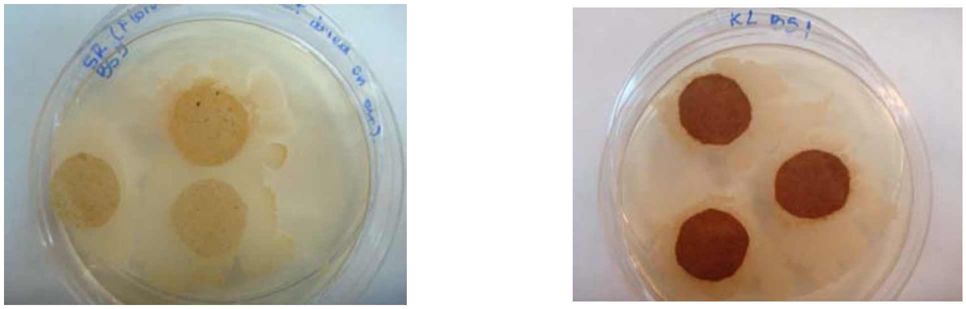

Figure 8: Paper samples placed into Petri plates prepared with *Bacillus Subtilis* (bacterium)

CONCLUSIONS

The deinking flotation, which was conducted on the brown packaging linerboard, had a positive influence on selected optical, mechanical and chemical properties of deinked pulp.

For the samples studied, the brightness increase in the deinked handsheet and pad samples, when compared to the original sample, occurred within the 15-17% range. The calculated ink elimination factor (IE_{ERIC}) was of 10.9%, in the case of handsheet samples, and of 7.3%, respectively, for filter pad samples. Deinking flotation also removed a significant amount of inorganic components, approximately 38% for handsheet samples and 15% for filter pads, respectively, which most likely contributed to increasing the bonding potential of deinked fibers. This was further confirmed by the results of mechanical tests, which showed an increase in the burst and tensile strength of the deinked samples (of 24 and 30%, respectively).

As to the food contact analysis, all studied samples (even the original linerboard sample) were found suitable for food contact applications. The amounts of all chemical contaminants detected in the analyses were well below the food contact limits. The amount of chemical contaminants detected by food contact analysis further showed that the original linerboard sample, which is primarily used in contact with dry foods, as well as all the other deinked and undeinked samples under investigation, are suitable for contacts with fatty foods. The efficiency of deinking flotation in removing impurities can be also seen from the reduction of the pentachlorophenol amount, especially in the case of filter pad samples.

Deinking flotation had a positive effect on the observed properties, showing that the quality of furnish is improved after deinking flotation, resulting in higher mechanical properties of the deinked handsheets and a lower amount of chemical contaminants.

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