DEINKING POSSIBILITIES IN THE REDUCTION OF MINERAL OIL HYDROCARBONS FROM RECOVERED PAPER GRADES

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The aim of the study was to compare the efficiency of two deinking methods in the reduction of mineral oil hydrocarbons from recovered paper grades, which are going to be used in production of food packaging paper. Old newspapers (ONP) printed with cold-set inks, supercalendered (SC) papers printed by rotogravure, and lightweight coated (LWC) papers printed with heatset inks were deinked by flotation and adsorption treatments. After each treatment, filter pads obtained from deinked pulps were analysed on the content of saturated and aromatic mineral oil hydrocarbons (MOSH, MOAH) by GC/FID measurements, as well as on the brightness and ash content. The results have shown that adsorption deinking is almost as efficient as flotation in ink removal in the case of ONP deinking, but less effective in the case of heatset and rotogravure inks (SC and LWC printed papers). However, for most tested samples adsorption deinking was found to be more successful in the reduction of mineral oils than the conventional flotation deinking method. The main conclusion was that over 60% and up to 80% of mineral oils can be removed from recovered papers by means of adsorption deinking.

Keywords: food packaging, recovered paper, mineral oil, flotation deinking, adsorption deinking

INTRODUCTION

Recycling is extensively encouraged in the paper industry, since it contributes to waste reduction, thus ensuring sustainability of our natural resources by providing economic and social benefits. Hence, paper is the most recycled packaging material in the EU with a recycling rate of 78%.[1] However, the recycling process may introduce a number of undesirable and often unknown compounds into the final packaging. When used as food packaging, recycled paper must be safe, i.e. it should not give rise to migration of substances in quantities that might endanger human health.

Recycled paper and board are nowadays mostly being used as secondary packaging for food products. However, even when not used in direct contact with foods, recycled paper can be a source of migration of many potentially harmful volatile compounds, which have the ability to pass via the gas phase through different layers of packaging materials into food. This phenomenon is known as contamination by secondary packaging. Recently, non-food grade mineral oils were found in paper packaging for food.[2] Mineral oils are multi-component mixtures of hydrocarbons. They are a complex mixture of mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH), some of which can have carcinogenic and mutagenic properties. The MOSH consist of linear branched alkanes and alkyl-substituted cyclo-alkanes, while the MOAH include mainly alkyl-substituted polyaromatic hydrocarbons.[3]

The transfer of mineral oil into food usually occurs via the gas phase by evaporation and condensation. In this respect, a cardboard is permeated during a few days and a polyethylene (PE) sheet within weeks or months.[4] That is the reason why a high transfer rate of mineral oil into food packed in folding boxes stored in outer packaging is commonly identified. Zurich's Official Food Control Authority has published two studies on the issue of mineral oil migration in 2010.[5,6] The research highlighted the inclusion of newsprint in recycled paper and board as the main source of the potentially harmful oils. Moreover, a recent monitoring of packaging of the German market has identified mineral oil contamination in 119 samples of dry food packed in paperboard boxes.[7]

The main source of mineral oil contamination is recycled paper or board. Mineral oils can be brought into the paper recycling loop through the use of old newspapers (ONP) and leaflets, which contain mineral oil based printing inks[5]. Mineral oils may thus come into direct contact with foodstuffs as substances contained within the recycled paper and board, unless the packaging is designed such that migration of the mineral oil is avoided. Other sources for contamination of food with mineral oil are mineral-oil containing printing ink in package printing and the additives used in paper production and converting.

The health risk assessment of mineral oils found in foodstuffs is hampered by the absence of data on the toxicity of substances detected in foodstuffs after migration from the packaging.[8] The European Food Safety Authority (EFSA) has estimated that we ingest between 0.03 and 0.3 mg saturated hydrocarbons (MOSH) per kilogram of body weight with our daily food, while children may ingest even more. The intake of aromatic hydrocarbons (MOAH) is estimated by the EFSA to be around 20% of the values for MOSH, i.e. between 0.005 and 0.06 mg per kg of body weight.[3] Moreover, a transition of the MOAH ($C_{10} – C_{25}$) is considered critical by EFSA because of their mutagenic and carcinogenic potential. For the protection of consumers, these compounds should be absent from food. However, there are currently no migration limits for mineral oils for the MOSH and MOAH or limits of these compounds in printing inks according to EU legislation.

In this study, three groups of recovered papers, chosen with respect to paper type and printing technique were treated under laboratory conditions by means of two different deinking methods: conventional flotation deinking and adsorption deinking. The objective was to compare the efficiency of the two deinking methods in the reduction of mineral oil hydrocarbons from specific recovered paper grades. The analysis of mineral oil (MOSH and MOAH) concentrations in deinked pulp was carried out by solid phase extraction and GC-FID, a new analytical method that was developed by the German National Reference Laboratory for Food Contact Materials at the Federal Institute for Risk Assessment (BfR) in cooperation with the Laboratory of the Canton of Zurich. It is based on gas chromatographic analysis of the minerals following pre-separation by manual column chromatography.[9]

EXPERIMENTAL

Recovered paper samples

For the purpose of the investigation, recovered paper samples consisting of three print and substrate combinations were prepared and treated under laboratory conditions by means of two different deinking methods. Recovered papers (RP) consisting of old newspapers (ONP), supercalendered (SC) papers and light weight coated (LWC) papers were submitted to separate flotation and adsorption deinking treatments. All the samples were commercial prints. Newsprint sample (trial – T1) was a combination of three newspapers printed in offset using mineral oil based inks. For SC paper sample (trial – T2), a mix of two magazines printed by rotogravure was used, while a catalogue printed in offset using heatset inks was used for the LWC paper sample (trial – T3). The characteristics of recovered papers used in each trial are shown in Table 1.

Table 1
Characteristics of recovered papers

Trial	Paper type	RP content (%)	Basis weight (g/m^2)	Dry weight (%)	Ash content (%)
T1	ONP	100	45	91	9.1
	ONP	75-80	45		
	ONP	100	42.5		
T2	SC	n/a	54	94	32.4
	SC	n/a	54		
T3	LWC	100	70	94	42.6

Deinking procedures

Laboratory deinking flotation was carried out according to the conditions and operation parameters described in the INGEDE Method 11p,[10] with a small variation regarding the use of the pulping chemistry: H_2O_2 was excluded from the process so as to avoid any possible bleaching effect for a subsequent better comparison of the two deinking methods in the ink elimination process (Figure 1).

Adsorption deinking is a novel method of ink removal from recovered paper slurries developed at the Professorship for Paper Technology at the Dresden University of Technology. The principle of adsorption deinking is based on the ability of certain polymers to extract ink and other hydrophobic components from the pulp. In this deinking method, the polypropylene (PP) beads serve as a "dirt catcher" instead of air bubbles used in the flotation deinking. The polypropylene (PP) beads were added to the special laboratory pulper (Hobart pulper) together with the printed samples (recovered papers) and deinking chemicals, which were identical to those used in the flotation process (Figures 2-4). The polymer/paper mass ratio was 1:1. The mode of operation of this special pulper makes it necessary to interrupt the pulping process from time to time in order to remove clods of partly slashed paper and polymeric beads from the stirrer and vessel walls. As soon as this was no longer necessary it took approx. 15 min to sufficiently disintegrate – and due to the effect of the polymeric beads – simultaneously deink the furnish.

After each conducted deinking treatment, filter pads were prepared from the corresponding deinked pulps. Filter pads were also prepared from the pulp that was disintegrated prior to the deinking process (named hereafter as undeinked samples), as well as from unprinted (plain) papers (named hereafter as unprinted samples). The complete trial design is shown in Table 2.

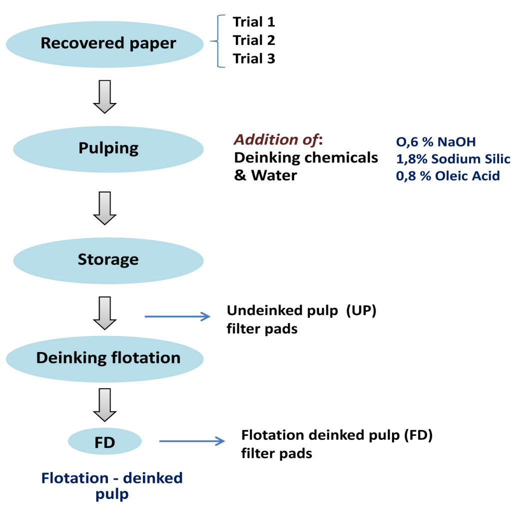

Figure 1: Flotation deinking process steps

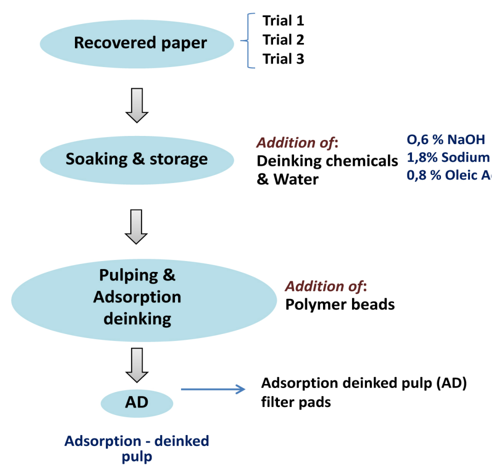

Figure 2: Adsorption deinking process steps

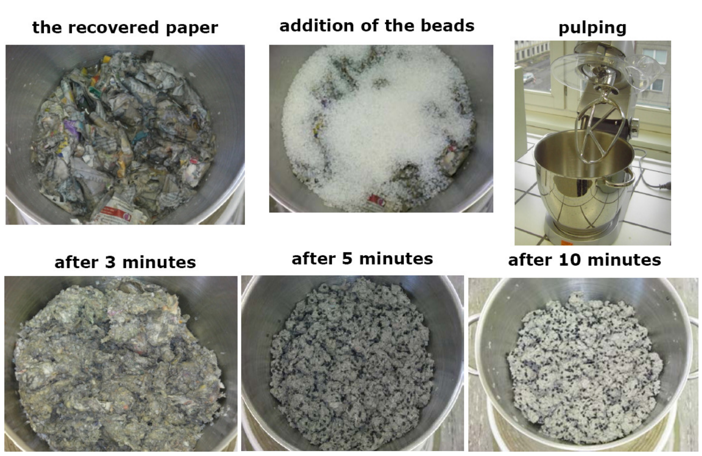

Figure 3: Images of adsorption deinking process steps

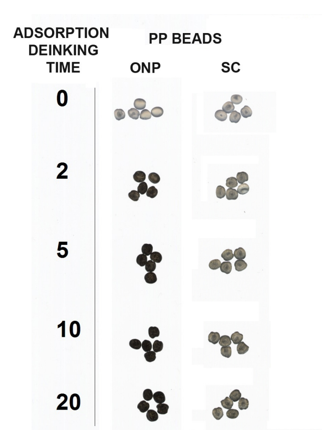

Figure 4: Ink adsorption on PP

Table 2
Trial design: preparation of filter pads

Recovered paper grade	Unprinted samples	Undeinked samples	Flotation deinked samples	Adsorption deinked samples
T1 (ONP)	x	x	x	x
T2 (SC)	x	x	x	x
T3 (LWC)	x	x	x	x
	3	3	3	3
Σ = 12 samples				

All obtained filter pads were subsequently analyzed at to the content of aliphatic and aromatic components (MOSH, MOAH) by GC/FID measurements. In addition, they were also compared with respect to the deinking quality properties, such as brightness and ash content.

Analysis of deinked pulps

Mineral oil (MOSH and MOAH) content

The content of hydrocarbons from mineral oils (MOSH and MOAH) was determined on pulp samples prepared as follows: filter pads (free of filter paper) were cut to pieces of approximately 2 cm edge length. The 2 g (± 0.1 g) of the homogenized sample was then weighted into a 70 ml screw cap glass test tube, where 20 µL internal standard mix and 10 ml ethanol/hexane (1:1; v/v) were added. After that the tube was vigorously shaken, and was left at room temperature for 2 hours. Prior to sampling the extract, the tube was agitated over again. In order to remove the ethanol, approximately 4 ml of the extract was taken and shaken with 10 ml water. Finally, an aliquot of the supernatant hexane phase was taken for the separation on a solid phase extraction cartridge.

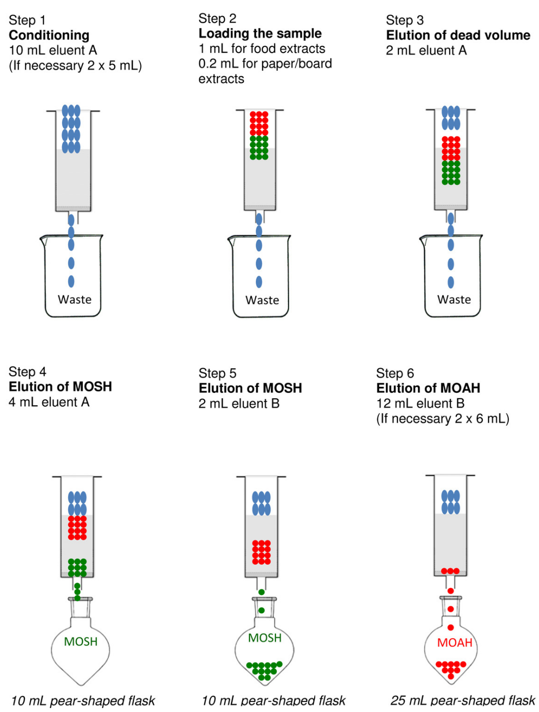

Figure 5: Solid phase extraction procedure[9]

The separation of the MOSH from the MOAH fraction was carried out using the solid phase extraction cartridge. The subsequent work flow for the separation of the MOSH from the MOAH fraction is illustrated in Figure 5. After the separation procedure, the MOSH and the MOAH fractions were concentrated to a volume of 250-300 μL using a rotary evaporator. Concentrated MOSH and MOAH fractions were finally transferred to GC auto-sampler vials in order to be analyzed by GC/FID. GC conditions are shown in Table 3.

Brightness and ash content

For the evaluation of the efficiency of each deinking method, the filter pads were compared with respect to their ISO brightness values and ash content. The ISO brightness measurements (ISO 2470) were conducted on filter pads obtained from unprinted samples, undeinked samples, flotation deinked and adsorption deinked samples. Similarly, the ash content was measured on all obtained filter pads. The ash content was determined by ignition at 525 °C (ISO 1762).

Table 3
Gas Chromatography conditions

(GC-2010)		
Injection Temp.:	280 °C	
Injection Mode:	Splitless	
Sampling Time:	1.50 min	
Flow Control Mode:		
Pressure:	80.0 kPa	
Total Flow:	76.8 mL/min	
Column Flow:	1.75 mL/min	
Linear velocity:	47.3 cm/s	
Purge Flow:	5.0 mL/min	
Split Ratio:	40.0	
High Pressure Injection:	ON	
High Press. Inj. Pressure:	250.0 kPa	
High Press. Inj. Time:	1.50 min	
Carrier Gas Saver:	OFF	
Oven Temp. Program		
Rate	Temperature (°C)	Hold Time (min)
-	65.0	9.00
25.00	330.0	12.00
(FID)		
Temperature:	370.0 °C	
Makeup gas:	He	
Makeup Flow:	30.0 mL/min	
H2 Flow:	35.0 mL/min	
Air Flow:	550.0 mL/min	
Signal Acquire:	ON	
Sampling Rate:	200 ms	
Stop Time:	31.60	
Subtract Detector:	None	
Delay Time:	0.00 min	
Auto Frame On:	OFF	
Auto Frame Off:	ON	
Reignite:	OFF	
Auto Zero after Ready:	ON	
Inj. Temp.	280 °C	
Inj. Volume	50 μl	
Inj. Speed	100 μl/s	

RESULTS AND DISCUSSION

Ink and ash removal

Figure 6 shows the results of brightness measurements. The highest levels of brightness were obtained on unprinted paper filter pads and were therefore used as reference values. The lowest levels of brightness were measured on undeinked samples due to the high concentration of the ink particles remaining attached to the fibres after disintegration. The applied flotation deinking on chosen prints resulted in the highest values of brightness achieved after the deinking process and were thus set to be the target brightness values. The innovative adsorption deinking almost reached the target value in the case of ONP sample. However, in the case of the SC and LWC samples, the brightness level was similar to that of the undeinked sample. This leads to the conclusion that the adsorption deinking process is almost as efficient as the flotation deinking in the removal of mineral oil-based newspaper ink, however it doesn't work well in the recycling of heatset (SC) and rotogravure (LWC) prints since the brightness analysis showed a poor elimination of those inks.

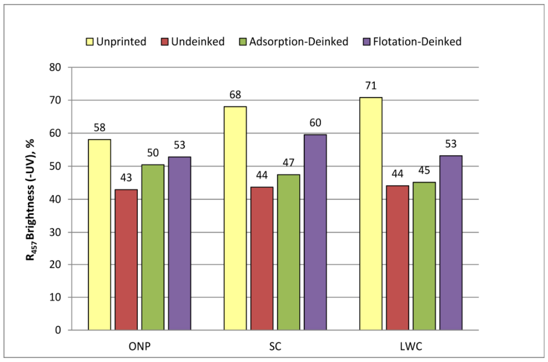

Figure 6: ISO Brightness chart of analysed pulp samples

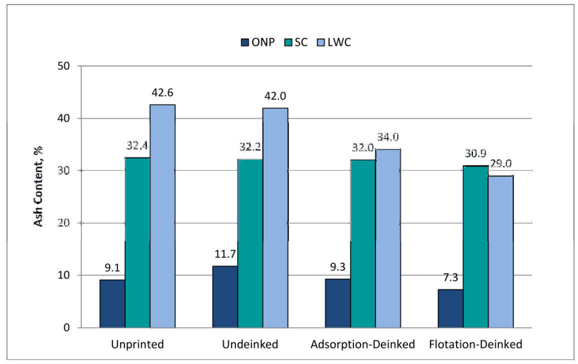

Figure 7: Ash content of pulp samples tested

The possible reason why adsorption deinking works better on newsprint samples printed with coldset inks than on the SC and LWC magazine papers is probably due to a different composition of the papers. Papers used in printing magazines (SC and LWC papers) usually contain substantial amounts of mineral pigments in the form of fillers or coatings applied on the top of the substrate. It is possible that the minerals contained in the magazine paper are adsorbed on the surface of the polymer beads during deinking, thus resulting in reduced surface availability for ink particles adsorption. Moreover, colloids, surfactants, and dispersants possibly extracted from the recovered magazine paper are released during the pulping stage and are therefore present in the water. These particles can then be adsorbed by PP beads, leading to lesser available surface for ink adsorption. Also, adsorption of surfactants on the surface of the beads might shift the surface properties from hydrophobic to hydrophilic.

Figure 7 shows the results of the ash content. The ash content of the sample may consist of various residues from chemicals used in its manufacture, metallic matter from piping and machinery, mineral matter in the pulp from which the paper was made, as well as filling, coating, pigmenting and/or other added materials. The flotation deinking process does not remove only the printing ink particles, but also some inorganic components of the paper such as fillers and coating constituents. For this reason, deinking efficiency is also evaluated through the removal of the inorganic components present in ash. Results indicate that for the most tested samples flotation deinking was found to be slightly more effective in the reduction of inorganic components from the fibre slurry than the adsorption deinking process.

Removal of mineral oil hydrocarbons (MOSH and MOAH)

Figures 8-10 show the MOSH and MOAH concentrations found in analysed samples from each printing trial (T1-T3). For each sample, the concentration of the MOSH and the MOAH fraction was calculated separately for the hydrocarbons eluted from gas chromatography before n-C_{24} and for the hydrocarbons eluted after n-C_{24} up to n-C_{35}. Hydrocarbons eluted up to about n-C_{24} are relevant for the migration into dry foods via the gas phase at ambient temperature.[5] The results presented are mean values of two subsequent measurements.

In Figure 11, the sum of all measured MOSH and MOAH concentrations, expressed as the total mineral oil content, found in analysed pulps is given.

The concentrations of mineral oils found in undeinked samples (Figure 11) indicate that old newspapers (ONP) contained the highest amounts of mineral oils. This was not unexpected since the inks used currently for newsprint paper printing contain the highest concentration of mineral oil solvent (vehicle) when compared to the rotogravure and heatset inks. In the SC and LWC undeinked samples, the concentrations of detected mineral oils were almost twice lower. Even unprinted papers contained certain amounts of mineral oils due to the use of recycled paper fibres in production of those printing papers.

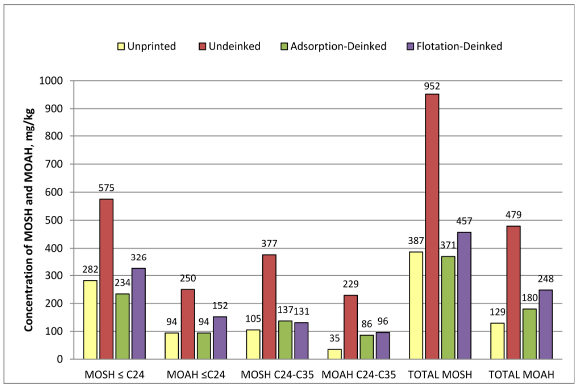

Figure 8: Concentration of mineral oil hydrocarbons (fractions ≤ C24, C24-35 and total) in ONP pads

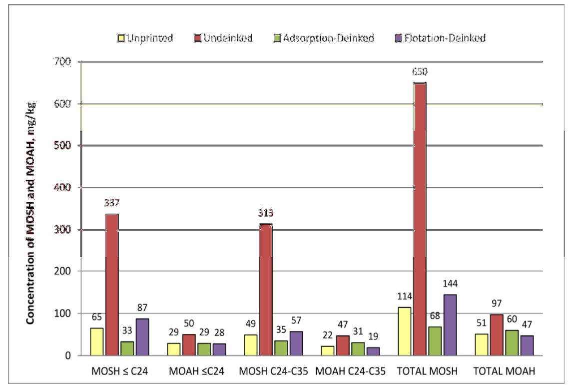

Figure 9: Concentration of mineral oil hydrocarbons (fractions ≤ C24, C24-35 and total) in SC pads

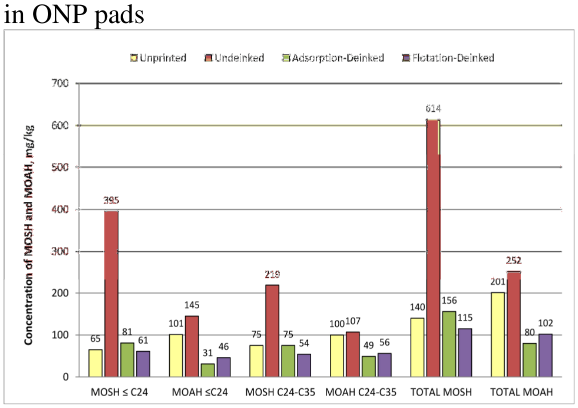

Figure 10: Concentration of mineral oil hydrocarbons (fractions ≤ C24, C24-35 and total) in LWC pads

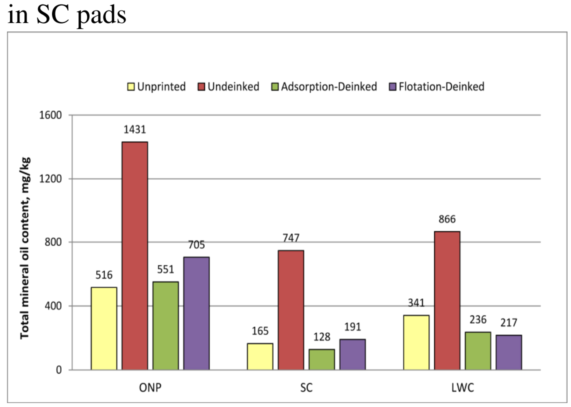

Figure 11: Total concentration of mineral oils (C_{15}-C_{35}) in analyzed pulp samples

Through adsorption deinking over 60% of mineral oils were removed from ONP fibre slurry, whereas in the case of the LWC and SC papers the reduction was even greater. Adsorption deinking managed to remove over 70% and 80% of mineral oils, respectively. Moreover, the results also indicate that in the case of the ONP and SC papers, the adsorption deinking was more successful in the reduction of mineral oils when compared to the conventional flotation deinking. More precisely, the adsorption deinking removed by about 11% more of mineral oils from ONP pulp in comparison with flotation deinking, and the same trend was noticed in the case of SC papers where the difference was of about 8%. However, in the case of LWC samples the flotation deinking was slightly more successful in the reduction of mineral oil than the adsorption deinking.

As stated before, the results of undertaken optical assessment (Figure 6) indicated that adsorption deinking can be as efficient as flotation deinking in the removal of ink particles as far as newspaper inks are concerned. On top of that, adsorption deinking can be seen as a more efficient deinking method for the reduction of mineral oil content from ONP fibre slurry than the flotation process. We assume that the mineral oils adhere to the surface of the polymer beads better than on air bubbles. The same trend is observed in the case of SC papers: deinking by adsorption resulted in a better removal of mineral oils than the flotation deinking despite the poor elimination of ink particles that was observed during the analysis of the pulp's brightness. However, the heatset printing trial conducted on LWC papers showed similar mineral oil reduction in both applied deinking techniques.

CONCLUSION

A comparison of two deinking methods – conventional flotation deinking and innovative adsorption deinking – led to the following conclusions relating to their efficiency in the reduction of mineral oil hydrocarbons from specific recovered paper grades:

- The results of optical assessment indicate that adsorption deinking was almost as efficient as flotation deinking in the removal of ink particles, but only as far as newspaper inks were concerned, while in the case of heatset and rotogravure inks the brightness analysis showed a poor elimination of ink particles. However, for most tested samples adsorption deinking was found to be more successful in the reduction of mineral oils than the conventional flotation deinking method. Over 60% up to 80% of mineral oils were removed from recovered papers by means of adsorption deinking.

- When the results of chemical and optical assessments are compared, it can be seen that substantial amounts of mineral oils can be removed through adsorption deinking, even in the cases when printing ink particles are not efficiently detached from the recovered paper slurry. Thus, if implemented in packaging grades recycling (where it is not necessary to achieve a high brightness of the recycled pulp), this novel method of deinking could present a possible solution for the reduction of substantial amounts of mineral oil hydrocarbons, which is currently not possible with mechanical cleaning technology. Therefore, the application of this concept could provide manufacture of recycled paper and board with significantly lower concentrations of mineral oils, which would ensure a safer use of such materials as secondary packaging for food products.

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REFERENCES

[1] CEPI Press Release, Paper-based packaging recycling at 78%, CEPI, Brussels, 24 April 2012, Available at http://www.paper.org.uk/news/2012/CEPI%20paperbased%20packaging%20recycling%20final.pdf

[2] I. Tiggelman, Master's Thesis, Stellenbosch University, 2012, Available at http://hdl.handle.net/10019.1/20269

[3] EFSA Panel on Contaminants in the Food Chain (CONTAM), Scientific Opinion on Mineral Oil Hydrocarbons in Food, in *EFSA Journal* 2012;10(6):2704 [185 pp.]. doi:10.2903/j.efsa.2012.2704. Available at: http://www.efsa.europa.eu/en/efsajournal/doc/2704.pdf

[4] M. Toeniessen, "Mineral oil from the View of the Adhesive Manufacturer", Henkel, Product Safety & Regulatory Affairs Adhesive Technologies EMEA, Available at: http://www.feica.com/~feica/images/stories/downloads/feica_130620_mt_mineral-oil

[5] M. Biedermann, Y. Uematsu, K. Grob, *Packag. Technol. Sci.*, **24**, 61 (2011).

[6] M. Biedermann, K. Grob, *Eur. Food Res. Technol.*, **230**, 785 (2010).

[7] A. Vollmer, M. Biedermann, F. Grundbock, J.-E. Ingenhoff, S. Biedermann-Brem *et al.*, *Eur. Food Res. Technol.*, **232**, 175 (2011).

[8] Bundesinstitut für Risikobewertung (BfR), New analytical method for detecting the mineral oil contents in foodstuffs resulting from recycled cardboard (2011), Available at: http://www.bfr.bund.de/en/press_information/2011/36/new_analytical_method_for_detecting_the_mineral_oil_contents_in_foodstuffs_resulting_from_recycled_cardboard-127574.html

[9] Bundesinstitut für Risikobewertung (BfR), Determination of hydrocarbons from mineral oil (MOSH & MOAH) or plastics (POSH & PAO) in packaging materials and dry foodstuffs by solid phase extraction and GC-FID, Available at: http://www.bfr.bund.de/cm/349/determination-of-hydrocarbons-from-mineral-oil-or-plastics.pdf

[10] INGEDE Method 11p: Assessment of Print Product Recyclability - Deinkability Test, INGEDE (2009), Available at: http://ingede.com/ingindxe/methods/ingede-method-11p-2009.pdf