Report of the Short Term Scientific Mission

DETERMINATION OF MINERAL OIL CONTENT IN RECYCLED PAPERS

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Introduction

Paper is the most recycled packaging material in the EU with a recycling rate of 78% [1]. 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 primarily used for the secondary packaging of food products and are known sources of mineral oils as well as other different contaminants that have ability to migrate into foods at levels which are unacceptable according to present toxicological assessments.

Consumers are exposed to a range of mineral oil hydrocarbons (MOH) via food. Mineral oils concerned are complex mixture of mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH), some of which can have carcinogenic and mutagenic properties. Mineral oil saturated hydrocarbons (MOSH) consist of linear and branched alkanes, and alkyl-substituted cyclo-alkanes, whilst mineral oil aromatic hydrocarbons (MOAH) include mainly alkyl-substituted polyaromatic hydrocarbons [2]. The mineral oil mixtures evaporate and from the packaging pass into the foodstuffs. The health risk assessment of mineral oils found in foodstuffs is hampered by the absence of data on the toxicity of the substances which were detected in foodstuffs after migration from the packaging [3].

Zurich's Official Food Control Authority has published two studies on the issue of the mineral oil migration in 2010 [4, 5]. 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 [6].

Main source of mineral oil contamination are recycled paper or board itself. Newspapers, leaflets printed by similar technique (offset coldset) are identified as predominant sources of mineral oil [5]. Mineral oils can be brought into the paper recycling loop through the use of the old newspapers (ONP) which contain mineral oil based printing inks. 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 transfer of the mineral oil is avoided.

The 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 has developed a new analytical method for the determination of hydrocarbons from mineral oil (MOSH & MOAH) in packaging materials and dry foodstuffs by solid phase extraction and GC-FID [7]. It is based on gas chromatographic analysis of the minerals following pre-separation by manual column chromatography.

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Purpose of the visit

The purpose of the visit was to learn a new analytical method used for the determination of the levels of mineral oils in the packaging materials. Moreover, a comparison of the effectiveness of two different deinking methods (adsorption deinking and flotation deinking) in reduction of mineral oil hydrocarbons from the defined recovered paper grades was also evaluated. The objective of the study was to investigate whether the conventional deinking process could be improved with regard to the removal of mineral oil components.

Description of the work carried out during the visit

Different types of recovered papers that are usually fed into the recycling process to manufacture paperboard for food packaging were analyzed for content of saturated and aromatic mineral oil hydrocarbons.

For the purpose of the investigation, the recovered paper samples consisting of three print and substrate combinations, were prepared and treated in laboratory conditions by means of two different deinking methods. Recovered papers consisting of old newspapers (ONP) printed with coldset inks (trial name - T1), rotogravure printed supercalendered (SC) papers (trial name - T2) and light weight coated (LWC) papers printed with heatset inks (trial name - T3) were submitted to a separate flotation deinking and adsorption deinking treatments. The characteristics of used recovered papers are shown in Table 1-2. After each conducted deinking treatment, the filter pads were prepared from corresponding deinked pulps and were subsequently analyzed on the content of aliphatic and aromatic components (MOSH, MOAH) by GC/FID measurements.

Table 1. Characteristics of recovered papers

Trial	Paper	Recovered paper content (%)	Grammage (g/m^2)	Age of the paper after publication
T1	ONP	100	45	2-4
	ONP	75-80	45	2-4
	ONP	100	42.5	2-4
T2	SC	*unknown*	54	3-4
	SC	*unknown*	54	3-4
T3	LWC	100	70	*

*Jack Wolfskin catalogue from 2012

Table 2. Dry and ash content of recovered papers (average value)

Trial	Paper	Dry content (%)	Ash Content (%)
T1	ONP	91	9.10
T2	SC	94	32.41
T3	LWC	94	42.61

The objective of this study was to evaluate the effectiveness of two different deinking methods, adsorption deinking and flotation deinking, respectively, in the reduction of the mineral oil content from the defined recovered paper grades.

The samples chosen to be recycled consisted of commercial prints. Newsprint sample (T1) was a combination of three newspapers printed in offset using mineral oil based coldset inks. For SC paper sample (T2) rotogravure printed catalogue was used, while for LWC paper sample (T3) a mix of two magazines printed with heatset inks was obtained.

The prints were recycled separately by means of two different deinking methods – adsorption deinking and flotation deinking. After each deinking trial filter pads were formed from their corresponding deinked pulps in order to be later analyzed on the content of mineral oil components (MOSH/MOAH) by GC/FID measurements. The content of MOSH and MOAH was also determined on the unprinted, reference papers, some of which had already contained a content of recycled fibers. Moreover, filter pads of undeinked pulp (pulp that was disintegrated prior to deinking process) were also prepared for reasons of evaluating the effectiveness of each deinking method in reduction of MOSH/MOAH.

The laboratory deinking flotation was carried out according to the conditions and operation parameters described in the INGEDE Method 11p [8], with small variation regarding the use of the pulping chemistry: the H_2O_2 was excluded from the process in order to avoid the bleaching effect for future better comparison of two deinking methods in the ink elimination process.

The adsorption deinking is a novel method of ink removal from recovered paper slurries developed by the scientists at the Professorship for Paper Technology at 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 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 flotation process. The polymer/paper mass ratio was 1:1.

The flotation deinking and adsorption deinking workflow is shown in Figures 1-3.

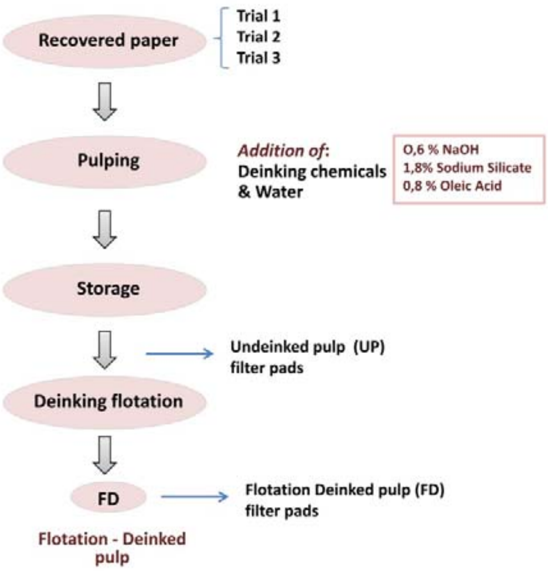

Figure 1. The flotation deinking procedure scheme

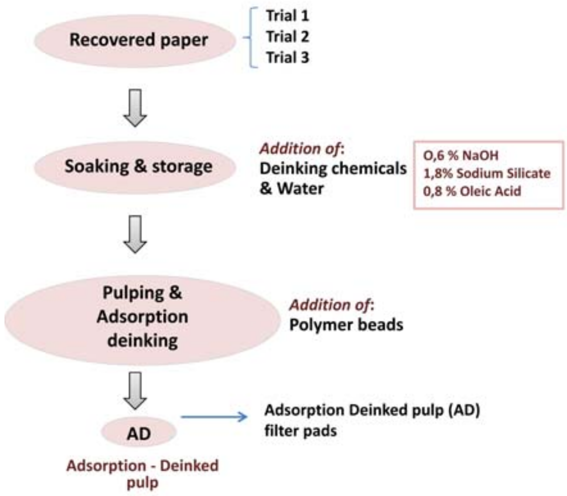

Figure 2. The adsorption deinking procedure scheme

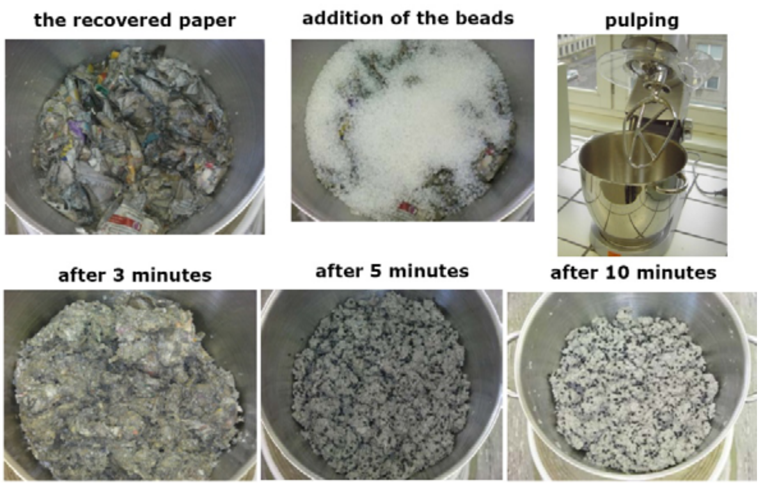

Figure 3. The adsorption deinking process steps

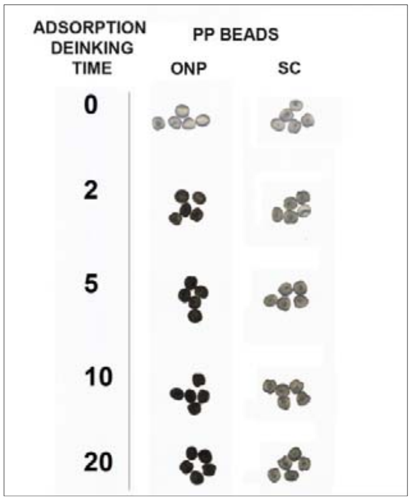

Figure 4. Adsorption of the ink particles on the PP beads after a given period of time

The filter pads that were formed in order to be analyzed on the content of mineral oil components are following:

- Unprinted (reference) papers – ONP_{REF}, SC_{REF}, LWC_{REF},
- Undeinked papers (worst case) – ONP_{WC}, SC_{WC}, LWC_{WC},
- Adsorption deinked papers – ONP_{AD}, SC_{AD}, LWC_{AD},
- Flotation deinked papers – ONP_{FD}, SC_{FD}, LWC_{FD}.

Determination of hydrocarbons from mineral oil (MOSH & MOAH)

For the sample preparation 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. 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 to remain 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 separation on a solid phase extraction cartridge.

The separation of the MOSH from the MOAH fraction was carried out using the solid phase extraction cartridge. The subsequent work flow for separation of the MOSH from the MOAH fraction is illustrated in the following figures (Figure 5).

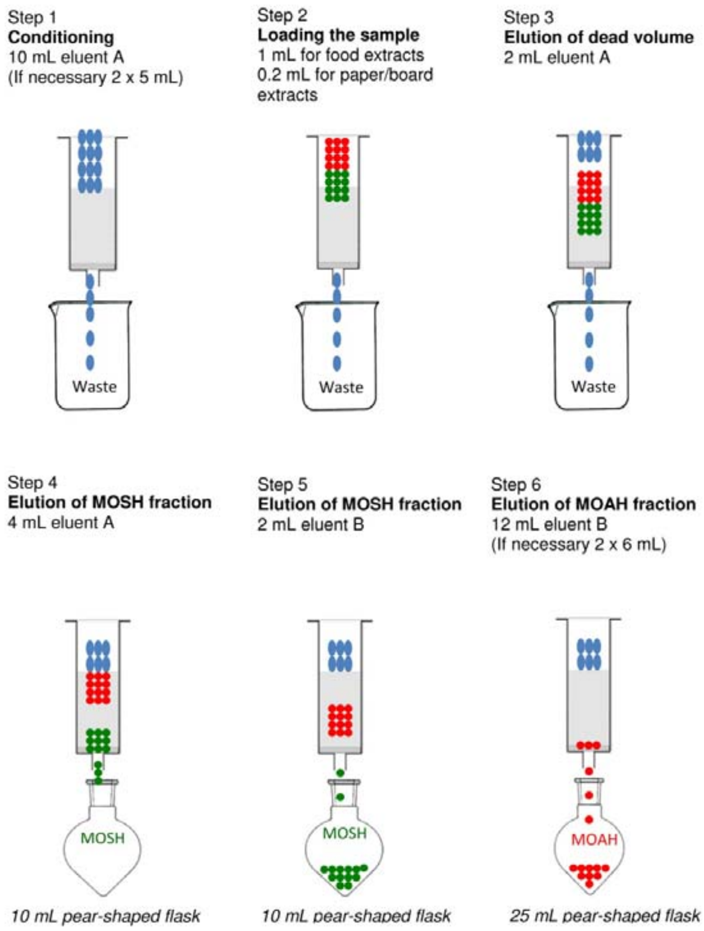

Figure 5. Solid phase extraction procedure [7]

After the separation procedure, the MOSH and the MOAH fractions had to be concentrated to a volume of 250-300 µL using a rotary evaporator. Thus concentrated MOSH and MOAH fractions were finally transferred to GC autosampler vials in order to be analyzed by GC/FID.

Table 3. GC conditions

(GC-2010)		
Injection Temp.	**280 °C**	
Injection Mode:	**Splitless**	
Sampling Time:	**1.50 min**	
Flow Control Mode:	**Pressure**	
Pressure:	**80.0 kPa**	
Total Flow:	**76.8 mL/min**	
Column Flow:	**1.75 mL/min**	
Linear velocity:	**47.3 cm/sec**	
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 msec**	
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/sec**	

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Main results obtained

Table 4 provides an overview of the MOSH and MOAH concentrations found in all analyzed samples. For each sample analysis, 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 before n-C_{24} are relevant for the migration into dry foods via the gas phase at ambient temperature [4]. Presented results are mean values of two subsequent measurements.

Table 4. Overview of MOSH, MOAH and mineral oil (MOSH+MOAH) concentrations in analyzed samples

Type of material	mg/kg paper						
Reference (unprinted)							
	MOSH ≤ C_{24}	**MOSH >C_{24}≤C_{35}**	**SUM**	**MOAH ≤ C_{24}**	**MOAH >C_{24}≤C_{35}**	**SUM**	**Mineral oil (MOSH+MOAH)**
ONP_{REF}	282	105	**387**	94	35	**129**	**516**
SC_{REF}	65	49	**114**	29	22	**51**	**165**
LWC_{REF}	65	75	**140**	101	100	**201**	**341**
Worst case (undeiked)							
	MOSH ≤ C_{24}	**MOSH >C_{24}≤C_{35}**	**SUM**	**MOAH ≤ C_{24}**	**MOAH >C_{24}≤C_{35}**	**SUM**	**Mineral oil (MOSH+MOAH)**
ONP_{WC}	575	377	**952**	250	229	**479**	**1431**
SC_{WC}	337	313	**650**	50	47	**97**	**747**
LWC_{WC}	395	219	**614**	145	107	**252**	**866**
Deinked by adsorption							
	MOSH ≤ C_{24}	**MOSH >C_{24}≤C_{35}**	**SUM**	**MOAH ≤ C_{24}**	**MOAH >C_{24}≤C_{35}**	**SUM**	**Mineral oil (MOSH+MOAH)**
ONP_{AD}	234	137	**371**	94	86	**180**	**551**
SC_{AD}	33	35	**68**	29	31	**60**	**128**
LWC_{AD}	81	75	**156**	31	49	**80**	**236**
Deinked by flotation							
	MOSH ≤ C_{24}	**MOSH >C_{24}≤C_{35}**	**SUM**	**MOAH ≤ C_{24}**	**MOAH >C_{24}≤C_{35}**	**SUM**	**Mineral oil (MOSH+MOAH)**
ONP_{FD}	326	131	**457**	152	96	**248**	**705**
SC_{FD}	87	57	**144**	28	19	**47**	**191**
LWC_{FD}	61	54	**115**	46	56	**102**	**217**

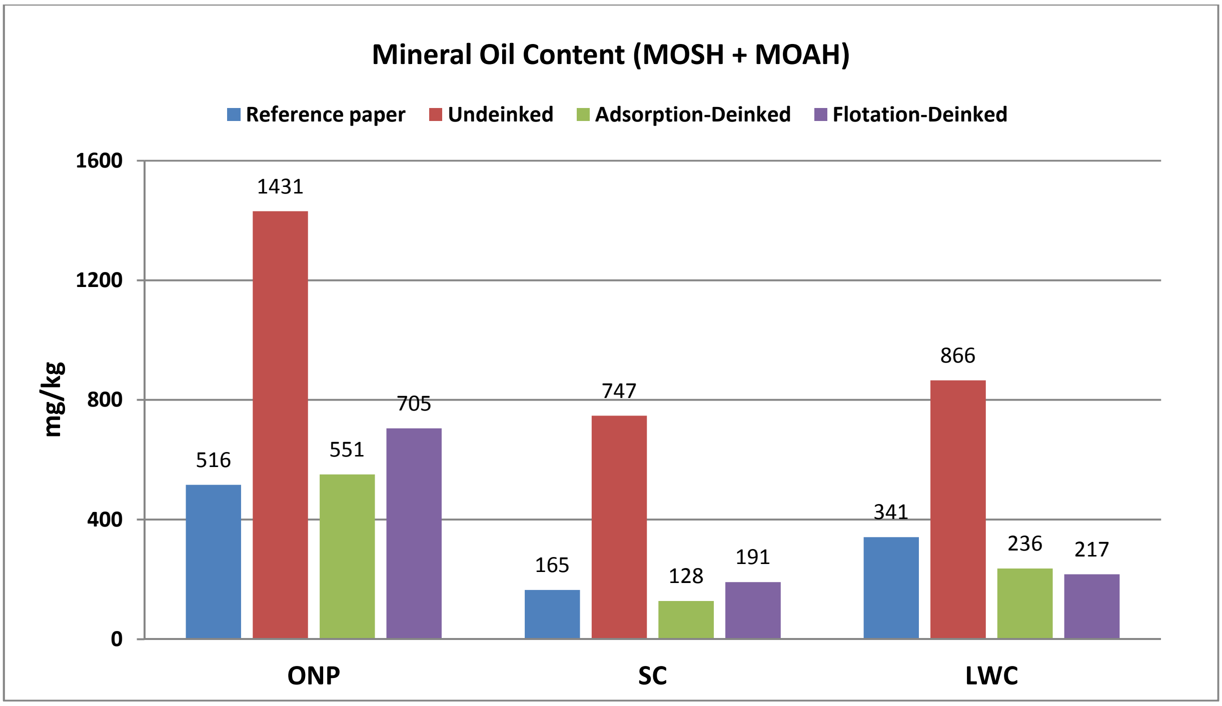

Figure 6. Mineral oil content (MOSH + MOAH) in analyzed papers
(ONP – old newspapers printed with coldset inks, SC – rotogravure printed supercalandered papers, LWC – light weight coated papers printed with heatset inks)

Figure 6 shows the total concentration of mineral oils (MOSH + MOAH) determined in analyzed samples. It was found that old newspapers (ONP) contained highest concentration of mineral oils which was not a surprise since the inks used for printing newspapers were actually mineral oil based, whereas in SC and LWC samples the concentrations of detected mineral oils were almost two times lower. Through adsorption deinking over 60% of mineral oils were removed from ONP fiber slurry, whereas in the case of LWC and SC papers the reduction was even greater - over 70% and 80% of mineral oils were removed through adsorption deinking process. Moreover, the results also indicate that in case of ONP and SC papers, the adsorption deinking was more successful in reduction of mineral oils when compared to the conventional flotation deinking. More precisely, the adsorption deinking removed about 11% more of mineral oils from ONP pulp in comparison to flotation deinking and the same trend was noticed in case of SC papers where the difference was at about 8%. In case of LWC samples the flotation deinking was for 3% more successful in reduction of MOSH and MOAH than the adsorption deinking which cannot be considered as a significant difference.

From the results of optical assessment undertaken in previous study we had already known that adsorption deinking is more efficient technique in removal of ink particles as far as coldset newspaper inks are concerned, therefore better removal of mineral oil content in case of newsprint sample was result that we had expected. However, in case of SC papers, we did not expect adsorption deinking to work better then flotation process as the polymeric beads were not able to absorb the ink particles from the fiber slurry as efficiently as from the ONP pulp (see Figure 4). However, results indicate that even when adsorption deinking is not efficient enough in removing printing ink particles from the pulp – it is quite effective in removal of mineral oils. Thus, if implemented in packaging grades recycling (where it is not necessary to achieve high brightness of the recycled pulp), this novel method of deinking - could be a possible solution for the reduction of substantial amounts of mineral oil hydrocarbons which is currently not possible with mechanical cleaning technology. Therefore application of this concept could provide manufacture of recycled paper and board with significantly lower concentrations of mineral oils that would ensure safer use of such materials as secondary packaging for food products.

The outcome of the STSM

- The results obtained through this research will be presented at this year's Joint EFPRO-CEPI Early Stage Researchers Workshop (ESR): "EFPRO-CEPI Innovation in Paper" that will take place in the frame of the CEPI European Paper Week (13th - 15th November 2012)
- It is also planned to publish an article in the peer-reviewed journal.
- Through bilateral scientific project "Treatments of Fibre Based Materials for Improved Food Packaging: IMPRO - FOOD - PACK" established between TU Dresden, Germany and Faculty of Graphic Arts, University of Zagreb, the research on the improvements of recycling methods with regard to better reduction of chemical contaminants from recovered papers will be continued, in order to further confirm the applicability of adsorption deinking in manufacture of food packaging applications.

Dr.sc. Sonja Jamnicki, dipl. ing

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Short summary

In this study, recovered paper samples consisting of three print and substrate combinations, were prepared and treated in laboratory conditions by means of two different deinking methods. Recovered papers consisting of old newspapers (ONP) printed with coldset inks, rotogravure printed supercalendered (SC) papers and light weight coated (LWC) papers printed with heatset inks were submitted to a separate flotation deinking and adsorption deinking treatments. After each conducted deinking treatment, the filter pads were prepared from corresponding deinked pulps and were subsequently analyzed on the content of saturated and aromatic mineral oil hydrocarbons (MOSH, MOAH) by GC/FID measurements. Aim of the investigation was to compare the effectiveness of two different deinking methods (adsorption deinking and flotation deinking) in reduction of mineral oil hydrocarbons from the defined recovered paper grades.

For most of the tested samples adsorption deinking was found to be more successful in reduction of mineral oils than the conventional flotation deinking method. Through adsorption deinking over 60% up to 80% of mineral oils were removed from recovered papers. It was also found that adsorption deinking was quite effective in reduction of amounts of mineral oils even in cases when it was not efficient enough in removing printing ink particles from recovered paper pulp.

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