Determination of mineral oil content in recycled papers

Sonja Jamnicki, PhD

"EFPRO-CEPI Innovation in Paper“ - Early Stage Researcher (ESR) Workshop
European PaperWeek, 13-15 November 2012, Brussels
Paper is the most recycled packaging material in the EU with a recycling rate of 78%.

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.

However, in the last few years we have witnessed several food scandals caused by migration of the mineral oils from the recycled paperboard packaging into food.

Recent studies have shown that in food packaging made from recycled paper and board, high amounts of mineral oils with saturated and aromatic hydrocarbons were detected.
Mineral oils are complex mixture of

- mineral oil saturated hydrocarbons (MOSH) &
- mineral oil aromatic hydrocarbons (MOAH),

some of which can have **carcinogenic** and **mutagenic** properties.

Contamination pathways for mineral oils into food packaging include printing inks (offset coldset) from newspapers and advertising brochures.

The mineral oil mixtures evaporate and from the packaging pass into the foodstuffs.

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.
**Objective**

*Determination of mineral oils in recycled papers* – a study conducted through the EFPRO Fellowship Short Term Scientific Mission (STSM) Hosted by Dr Rainer Spörl at Papiertechnische Stiftung (PTS) Heidenau (25/08/2012 - 08/09/2012)

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.

*Objective of the study:* to investigate if conventional deinking process could be improved with regard to the removal of mineral oil components.
Experimental

The recovered paper samples consisting of three print and substrate combinations, were submitted to a separate flotation deinking and adsorption deinking treatments (laboratory conditions).

Recovered paper samples (commercial prints):

- **T1** - old newspapers (ONP) printed with coldset inks
- **T2** - rotogravure printed supercalendered (SC) papers
- **T3** - light weight coated (LWC) papers printed with heatset inks

Table 1. Characteristics of recovered papers

<table>
<thead>
<tr>
<th>Trial</th>
<th>Paper</th>
<th>Recovered paper content (%)</th>
<th>Grammage (g/m²)</th>
<th>Age of the paper after publication</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>ONP</td>
<td>100</td>
<td>45</td>
<td>2-4</td>
</tr>
<tr>
<td></td>
<td>ONP</td>
<td>75-80</td>
<td>45</td>
<td>2-4</td>
</tr>
<tr>
<td></td>
<td>ONP</td>
<td>100</td>
<td>42.5</td>
<td>2-4</td>
</tr>
<tr>
<td>T2</td>
<td>SC</td>
<td><em>unknown</em></td>
<td>54</td>
<td>3-4</td>
</tr>
<tr>
<td></td>
<td>SC</td>
<td><em>unknown</em></td>
<td>54</td>
<td>3-4</td>
</tr>
<tr>
<td>T3</td>
<td>LWC</td>
<td>100</td>
<td>70</td>
<td>*</td>
</tr>
</tbody>
</table>

*Jack Wolfskin catalogue from 2012*
Deinking trials

**INGEDE Method 11p**

**Trial 1**
**Trial 2**
**Trial 3**

**Recovered paper**

**Pulping**
*Addition of: Deinking chemicals & Water*

**Storage**

**Deinking flotation**

**Undeinked pulp (UP) filter pads**

**Flotation Deinked pulp (FD) filter pads**

**Figure 1. Flotation deinking procedure scheme**

**Recovered paper**

**Soaking & storage**
*Addition of: Deinking chemicals & Water*

**Pulping & Adsorption deinking**
*Addition of: Polymer beads*

**AD**

**Adsorption Deinked pulp (AD) filter pads**

**Adsorption - Deinked pulp**

**Figure 2. Adsorption deinking procedure scheme**
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. PP beads were added to the special laboratory pulper (Hobart pulper) together with the printed samples and deinking chemicals (identical to those used in flotation process).

The polymer/paper mass ratio was 1:1.
After each conducted deinking trial, **filter pads were formed** from the corresponding **deinked pulps** in order to be analyzed on the content of **mineral oil components (MOSH/MOAH)** by **GC/FID measurements**.

The filter pads were also formed from the **unprinted** (reference) **papers**, as well as from the **undeinked pulp** (recovered paper pulp disintegrated prior to deinking process).

**Filter pads analyzed on the content of MOSH/MOAH:**

- Unprinted (reference) papers – ONP\textsubscript{REF}, SC\textsubscript{REF}, LWC\textsubscript{REF},
- Undeinked papers (worst case) – ONP\textsubscript{WC}, SC\textsubscript{WC}, LWC\textsubscript{WC},
- Adsorption deinked papers – ONP\textsubscript{AD}, SC\textsubscript{AD}, LWC\textsubscript{AD},
- Flotation deinked papers – ONP\textsubscript{FD}, SC\textsubscript{FD}, LWC\textsubscript{FD}. 
Sample preparation:

2 g of homogenized sample (filter pads cut to pieces of app. 2 cm edge length) were extracted with 10 ml ethanol/hexane with addition of 20 μL internal standard mix (2 hours at room temperature).

In order to remove the ethanol, app. 4 ml of the extract was taken and shaken with 10 ml water. An aliquot of the supernatant hexane phase was taken for separation on a solid phase extraction cartridge.
**Determination of MOSH/MOAH**

The separation of the MOSH from the MOAH fraction was carried out using the solid phase extraction cartridge.

After the separation, the MOSH and the MOAH fractions were 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 and analyzed by GC/FID.
Main results obtained

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.
Main results obtained

Mineral Oil Content (MOSH + MOAH)

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)
Main results obtained

Adsorption of the ink particles on the PP beads

In case of SC papers, **adsorption deinking was not expected to be more efficient than the flotation process** as polymeric beads were not able to absorb the ink particles from the fiber slurry as efficiently as from the ONP pulp.
Conclusions

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.

Adsorption deinking was 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.

Thus, if implemented in packaging grades recycling, this novel method of deinking could be a possible solution for the reduction of substantial amounts of mineral oil hydrocarbons from the recovered papers.
References


[7] 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