Preferred citation: R. Gaudreault, C. Brochu, R. Sandrosck, P. Deglmann, H. Seyffer and A. Tétreault. Overview of practical and theoretical aspects of mineral oil contaminants in mill process and paperboards. In Advances in Pulp and Paper Research, Cambridge 2013, *Trans. of the XVth Fund. Res. Symp. Cambridge, 2013*, (S.J. l'Anson, ed.), pp 907–925, FRC, Manchester, 2018. DOI: 10.15376/frc.2013.2.907.

## OVERVIEW OF PRACTICAL AND THEORETICAL ASPECTS OF MINERAL OIL CONTAMINANTS IN MILL PROCESS AND PAPERBOARD

### *R. Gaudreault<sup>1</sup>, C. Brochu<sup>2</sup>, R.Sandrock<sup>3</sup>, P. Deglmann<sup>4</sup>, H. Seyffer<sup>4</sup>, A. Tétreault<sup>2</sup>*

<sup>1</sup>Cascades Canada ULC., Montreal, QC, Canada; <sup>2</sup>Cascades R&D Centre, Kingsey Falls, QC, Canada; <sup>3</sup>Reno de Medici, Arnsberg, Germany; <sup>4</sup>BASF-SE, GKP/M, Carl-Bosch-Str. 38, 67056 Ludwigshafen, Germany

### ABSTRACT

The paperboard industry is committed to consumer protection in food packaging and has assigned top priority to the issue of mineral oil hydrocarbons (MOH) as early as spring 2010. In this work, we have developed practical methods, using gas chromatography with a flame ionization detector (GC-FID) laboratory equipment, to characterize the level of mineral oil saturated hydrocarbons (MOSH) and aromatic hydrocarbons (MOAH) in European and North American newspapers, paperboards, and inks. As part of our validation protocol, several samples were analyzed by an external laboratory (ISEGA, Aschaffenburg, Germany) using Biedermann's protocol and an average deviation of 6% for the MOSH and 17% for the MOAH was observed between ISEGA and our method. Using the reference Tenax migration method (EN, 14338), the hexane or heptane vapour transmission rate (HVTR) method was developed to measure the barrier efficiency within one day, showing a very good correlation;  $R^2 = 0.80$ to 0.92.

Much higher MOH concentrations in newspaper printed areas infer that printing inks constituents are the most likely source of MOSH/MOAH in recycled paperboard. When processing such raw material, the drying section is one of the paperboard making process steps that significantly reduces the MOSH and MOAH level. Although low or free mineral oil printing inks would be preferable, the use of functional barriers can significantly reduce the migration of MOSH/MOAH, whenever necessary. Mineral oil migration barrier efficiencies of about 90% were obtained using polymeric functional barriers applied at the mill with conventional coating equipment. Finally, a first attempt was made to theoretically model the migration of mineral oil through model polyacrylate functional barriers. The correlation between calculated (theoretical) and experimental hexane permeabilities seems reasonable and a predictive discrimination between good and bad barrier polymers appears possible for acrylate copolymers ( $R^2=0.72$ ) within foreseeable limitations with respect to chemical composition.

**Keywords:** Mineral oil hydrocarbons (MOH), MOSH, MOAH, alkanes, aromatic hydrocarbons, sources of MOH, removal of MOH, mineral oil migration, functional barrier efficiencies, acceptable daily intake (ADI), food contact materials, hexane and heptane vapour transmission rate, modelling.

### **1 INTRODUCTION**

Following Grob et al. [1–5] findings related to mineral oil content in recycled paperboard for food packaging, the German Ministry of Consumer Safety have published a draft legislation requiring that the mineral oil saturated hydrocarbon (MOSH) contained in food does not exceed 0.6 mg/kg of food and 0.15 mg/kg of food for the mineral oil aromatic hydrocarbon fraction (MOAH). The 2nd ordinance was released the week of May 20th 2013 where the different share holders have to give there opinion on its content and implications. MOSH includes paraffins (straight chain and branched alkanes) as well as cyclic naphthenes and MOAH includes alkylated polyaromatic hydrocarbons with mainly 1–3 rings. Although the toxicity of MOSH is debatable, toxicity and the presence of MOAH in food remains a concern. However, unlike the polycyclic aromatic hydrocarbons (PAHs) that can be well resolved by gas chromatography (GC) and reported individually, the MOAH fraction is until now poorly resolved by GC and therefore reported as a sum of all components. The actual detection limit of

the procedure set up by Dr. Grob is in the range of 2-5 mg/kg of board which leads to a concentration in food (assuming 70% migration and a ratio of 1 kg of board for 10 kg of food) of 0.7 mg/kg of food, so higher than the proposed regulation [2]

The European Food Safety Authority (EFSA) identified the following or suspected sources of mineral oil [6]: 1) Food processing additives and aids; 2) Food packaging materials; and 3) Environmental contaminants. Although many of these sources were identified, few were documented. Only recycled paper and paperboard packaging and sisal bags were well characterized.

Moreover, EFSA [6] reported that the estimated MOSH exposure ranged from 0.03 to 0.3 mg/kg of body weight per day, or 0.6 to 6.0 mg/kg of food per day assuming the body weight of an adult is 60 kg which consumes 1 kg of contaminated food/day. EFSA also reported that: a) exposure to MOSH via food was considered of potential concern, and b) foodborne MOAH with three or more, non- or simple alkylated, aromatic rings may be mutagenic and carcinogenic, and therefore of potential concern. Revision of the existing acceptable daily intake (ADI) for MOSH/MOAH is then suitable.

Biedermann et al. [1] showed that corrugated board transport box did increase the MOH concentration into taglioline (fine noodles), which were contaminated with 2.5 mg MOSH/kg of noodle already before packaging, illustrating that there are other sources of mineral oil violating the 0.6 mg/kg of food limit.

In December 2012, the German consumer organisation Stiftung Warentest [7] published test results according to which most chocolates in 24 tested advent calendars in Germany contained mineral oil hydrocarbon residues. Stiftung Warentest also mentioned recycled cardboard packaging as the source of those residues. An analysis of the Technical Darmstadt University showed that this conclusion was incorrect, since 23 out of the 24 calendars tested were made of virgin fibres, only one contained recycled fibres. There are several possibilities of how mineral oils can get into chocolate and the root cause still needs to be determined. As potential sources, Darmstadt University listed additives and processing chemicals used during food production and other packaging materials, e.g. plastic trays, as well as potential contamination during transportation and storage.

The "Mineral Oil Regulation" [8] proposed by the German Federal Ministry, where the anticipated regulation for the migration of MOSH and MOAH ( $C_{10}$  to  $C_{25}$ ) into food is limited to 0.6 and 0.15 mg/kg of food respectively, gives rise to serious legal aspects and challenges in the food packaging industry, which needs significant investments and time to be implemented.

Although one of the root causes of this issue is the offset inks, the newsprint industry has been reluctant to use low or free mineral oil inks. Moreover, the recycled paper industry claims that selective sorting of newspapers is neither practical nor economically viable. Nevertheless, the level of mineral oil in recycled papers and paperboards can be minimized in different ways. Preliminary results showed that papermaking process may remove some of the MOH, e.g. deinking, drying [2], and process water clarification.

In this work, we have developed a practical method to characterize the level of mineral oil (MOSH and MOAH) in European and North American newspapers, paperboards, and inks. The removal of MOH in a paperboard mill process was investigated. A quick procedure was also developed to evaluate the migration of MOH based on the hexane and/or heptane vapour transmission rate (HVTR) through a coated paperboard. Functional barrier efficiencies applied at the mills and pilot plants, to prevent MOH migration, are reported. Finally, a first attempt was made to understand the underlying mechanisms by theoretical modelling of the mineral oil migration through polyacrylate functional barriers and to correlate it with the HVTR method, which is more practical and faster for quality control in paperboard mills.

### 2 EXPERIMENTAL METHODS

### 2.1 Mineral oil: analytical method

In 2009, Biedermann and Grob [3] published an analytical method for the fractionation and determination of saturated and aromatic hydrocarbons of mineral oil origin in food that was rapidly adapted for the analysis of paperboard packaging [2,4]. The approach developed by the Swiss researchers requires a high performance liquid chromatograph (HPLC) system coupled with a gas chromatograph with a flame ionization detector (GC-FID) that can be very complex and expensive. A practical method has been developed based on the extraction of mineral oils from paperboard with a mixture of hexane/dichloromethane followed by the fractionation of MOSH/MOAH on a silica/alumina column. The extraction of mineral oil was performed with the Accelerated Solvent Extractor (ASE) from Dionex. As opposed to Biedermann [3] who used a mixture of hexane/ethanol aiming at a limited extraction efficiency for high molecular hydrocarbons which tend to disturb their HPLC-GC system, this procedure used a mixture of hexane/dichloromethane (50/50) for a full recovery of all hydrocarbons. The ASE allowed the extraction of solid samples with a mixture of solvents at high temperature (150°C) and high pressure (1500 psi). Typically, 1.5 g of paperboard sample requires 20 ml of solvent. Following the extraction, the extract is concentrated to 3 ml prior to the separation of MOSH/MAOH. The separation of these two classes of mineral oil was developed using the same markers as Biedermann [1]. Therefore a mixture of

markers including n-alkanes C12, C14, C16 and chloestane were used as MOSH representative molecules and tri-tert-butyl benzene (TBT), hexyl-benzene (6B), nonyl-benzene (9B), biphenyl (BP) and perylene were used as MOAH representative molecules. The MOSH and MOAH were fractionated in a glass column (I.D. 9 mm) using 4 g of a mixture of silica (60-120 mesh)/alumina (70-230 mesh) in a ratio of 2:1 deactivated with 2% of water. As specified by Biedermann [3], the separation of MOSH/MOAH was adjusted with the chloestane that served to establish the end of the MOSH fraction and the TBT and perylene were used as markers for the beginning and the end of the MOAH fraction respectively. These markers were added to all samples for the verification of adequate performance of the procedure. Chloestane has to be present with a high recovery absent in the MOSH fraction and in the MOAH fraction. whereas TBT should be in the MOAH fraction with a high recovery. Typically, 8 ml of hexane was used to elute the MOSH and 15 ml of hexane/dichloromethane (40/60) was used to completely recover the MOAH fraction. Each fraction was then concentrated to 3 ml prior to an injection on GC-FID with a DB1-MS ( $30m \times 0.25 \text{ mm I.D.} \times 0.10 \mu \text{m film of dimethylpolysiloxane}$ ) with an on-column injector (1  $\mu$ l – oven track mode). The oven temperature was programmed at 20°C/min from 70°C (2 min plateau) to 325°C (5 min plateau) and the FID was heated at 370°C. In a similar way as Biedermann [3], the quantification of the MOSH fraction was based on the response of the C14 marker and the MOAH fraction was based on the response of the nonyl-benzene (9B).

As part of our validation protocol, several samples were analyzed by an external laboratory (ISEGA, Aschaffenburg, Germany) using Biedermann's protocol and an average deviation of 6% for the MOSH and 17% for the MOAH was observed with this protocol. Figure 1 shows typical chromatograms of MOSH/MOAH from a European recycled paperboard obtained with this protocol. The detection limits for the MOSH and MOAH are estimated at 20 mg/kg.

### 2.2 Mineral oil migration using Tenax

The European method EN-14338 [9], for paper and board intended to come into contact with food was used as a reference method for migration studies. This procedure uses a modified polyphenyloxide polymer (Tenax) as a substitute simulant for fatty contact. Each sample was covered with Tenax for 10 days at 40°C, followed by an extraction of the adsorbent using a mixture of hexane/acetone (50/50) instead of hexane/dichloromethane because the Tenax would be degraded when exposed to dichloromethane. The extract was then processed as described in section 2.1.



Figure 1. Typical chromatograms of MOSH/MOAH from a European recycled paperboard. \* indicates markers added to all samples. Diisopropyl naphthalene isomers (DIPN) were subtracted from MOAH concentration.

## 2.3 Mineral oil migration using Hexane/Heptane Vapour Transmission Rate (HVTR)

A standard approach to verify the performance of a functional barrier is to analyze the foodstuff after a certain storage time. The equipment and time required for migration studies may prevent the use of those analytical methods for regular production and quality control of packaging materials. This section presents an effective way to assess the barrier performance of packaging materials that can be used for quality control and product development purposes. This method is based on the gravimetric determination of the vapour transmission rate of a volatile model compound through a functional barrier coated on a paperboard surface.

Until now, the mineral oil migration into food, for MOSH or polyolefinic saturated hydrocarbons (POSH), are related to a range of alkanes from *n*-hexadecane ( $C_{16}$ ) to *n*-tetracosane ( $C_{24}$ ) [10]. Although *n*-hexadecane is liquid, its vapour pressure at 25°C (100 Pa) is far below the vapour pressure of smaller size *n*-alkanes such as pentane, hexane, heptane or octane. Consequently, hexane and heptane were chosen to simulate faster mineral oil migration at room temperature.

The determination of the hexane vapour transmission rate (HVTR) is performed in a permeability cup (evaporation chamber) with a sealable closure fixable with screws (Figure 2). The closure has an open surface area which is sealed with the barrier material. This method can be used to evaluate plastic films, paperboard and laminated structures of plastic films or combinations of plastic films and paperboard. The thickness of the barrier layer can vary between 1 $\mu$ m up to 400 $\mu$ m. A volume of hexane or heptane (9–10 ml) is filled into the evaporation chamber



Figure 2. Experimental method to measure the Hexane/Heptane Vapour Transmission Rate (HVTR).

Barrier material	Substrate	<i>HVTR after</i> $4hrs g/(m^2 day)$	Barrier performance
Aluminium foil	same as harrier material	0.00	ideal
Paper (Magnostar 59.9 $g/m^2$ )	same as barrier material	8137	none
PE film (91um)	same as barrier material	818	insufficient
Epotal A 816 (23um)	PE film (91 $\mu$ m)	103	medium
Ultramid PA6 film (15µm)	same as barrier material	2	high
Ecovio FS paper (16g/m <sup>2</sup> )	fresh fibre board $(210g/m^2)$	1	high

Table 1. HVTR of selected materials

onto a sponge (to reach a liquid/gas equilibrium as quickly as possible) and the weight of hexane/heptane vapour that goes through the exposed surface of a functional barrier, is expressed in gram per square meter of the surface area per day. The barrier samples can be prepared by using a template or a punch. The samples have to be visually inspected to see if there are any surface defects (e.g. specks) or damage (e.g. creases, pin holes). At least three replicates for every coated surface should be tested.

Under controlled experimental conditions  $(23^{\circ} \pm 1^{\circ}C \text{ and } 50 \pm 2\%$  relative humidity), the paperboard sample is fixed into the closure head, the barrier coating facing the inner side. The chamber should be closed as quickly as possible. The filled evaporation chamber is then weighed after 1, 2, 4 hrs and 1 day. The amount of hexane retained in the barrier is typically small with respect to the weight loss per hour, the HVTR is then calculated according to:

$$HVTR [g/(m^2 day)] = weight difference[g] * 10000[cm^2/m^2] * 24[h/d]/(area[cm^2] * time[h])$$
(1)

Table 1 shows examples of experimental HVTR for different types of barrier material. Any material that shows an HVTR higher than ~500 g/(m<sup>2</sup> day) is not considered as an effective functional barrier to mineral oil residues, whereas an HVTR lower than 10 g/(m<sup>2</sup> day) indicates high performance barrier.

### **3 RESULTS & DISCUSSION**

### 3.1 Mineral oil content in raw materials

Table 2 shows that the mineral oil concentrations differ a lot from the type and origin of the papers. Much higher concentrations in printed areas infer that printing inks constituents are the most likely source of MOH. Moreover, the trend observed for MOSH follows quite well the MOAH trend.

Origin of the sample	$MOSH \leq C24$ (mg/kg)	MOSH > C24 (mg/kg)	$MOAH \leq C24$ $(mg/kg)$			
North American Newspaper (n=3)						
Printed area	420–1500 (1000 ±550)	3000–3500 (3300 ±250)	250-360 (300 ± 80)			
Unprinted area	36–60 (49 ±12)	230–370 (290 ±70)	<20–34 (19±13)			
European Newspaper <sup>[5]</sup> (n=6)	1100–5700 (2800±1700)	500-890 (680±150)	400–1500 (830±480)			
Asian Newspaper <sup>[5]</sup>						
Printed area (n=6)	430-3700 (2100 ± 1100)	110-1250 (560 ±510)	15-670 (340±250)			
Unprinted area (n=2)	95–660	140–160	7–28			
Office paper <sup>[5]</sup> (n=5)	18–50	n.a.	n.a.			

**Table 2.** Mineral oil concentrations in European and North American raw materials used by the recycled paperboard industry. The range of data is reported as well as the average and standard deviation in brackets, if the number of samples is 3 or more

According to Harbin [11], 90 % of all process inks used in the USA for newspaper printing are wholly or partly soybean oil based, and the equivalent share of black inks is also increasing constantly, despite the higher prices for the pressready ink compared to mineral oil based inks. The use of soy based ink, or partly soybean – partly mineral oil, could be a reason why the level of MOSH/MOAH, ( $C_{16}$  to  $\leq C_{24}$ ) in North American newspapers is lower than European newspapers.

Because newspaper inks are highly contaminated by MOSH/MOAH, the reduction of this raw material can have a significant impact on the MOH concentration in the recycled paperboard packaging. In 2011, a mill trial was performed where newsprint was removed from the board's middle layer. Although before the trial (blank) there was 20% newsprint in the middle layer, which represents about 15% of total board basis weight, the MOSH and MOAH concentrations in paperboard were reduced by 43% and 54% respectively.

Interestingly, several ink formulations used by the folding carton industry were tested and results showed significant variation in MOSH/MOAH concentrations between suppliers and grades (Table 3). For example, ink #1 having a total mineral oil concentration of 26.4% was considered a typical product used prior to the issue of mineral oil with MOAH/(MOSH + MOAH) ratio of 31%, similar to those reported by Biedermann [2]. However, inks #2–6 were qualified as low mineral oil content or low migration mineral oil by suppliers.

Ink Series/Origin	MOSH≤C24 (%(w/w))	MOSH > C24 (%(w/w))	MOAH≤24 (%(w/w))	Total mineral oil (%(w/w))
Ink 1/Supplier 1	18.2	ND	8.2	26.4
Ink 2/Supplier 1	2.1	ND	1.2	3.3
Ink 3/Supplier 2	8.8	ND	0.3	9.1
Ink 4/Supplier 3	2.1	ND	1.6	3.7
Ink 5/Supplier 4	< 0.2	ND	0.9	1.1
Ink 6/Supplier 5	< 0.2	ND	< 0.2	< 0.2

 Table 3.
 Concentration of mineral oil in different types of ink (oil based) and suppliers.

\* This table does not intend to represent a statistical picture of the world wide distribution of ink products.

### 3.2 Mineral oil concentration in virgin and recycled boards

On average, European recycled boards have higher mineral oil content than North American boards. Although virgin boards have lower MOH concentration than recycled boards, it was not possible to compare virgin European and North American boards because of lack of data (Table 4).

# **3.3** Distribution of mineral oil concentration in paperboard making process

Mineral oil concentration was investigated in a North American 100% recycled paperboard mill to determine which process steps have an impact on the removal of MOH. During this investigation the percent recycled newsprint was between 25–30%. Figure 3 shows that MOH has a higher affinity for fibres since very little

Origin of the sample	MOSH ≤C24 (mg/kg)	MOSH >C24 (mg/kg)	MOAH ≤C24 (mg/kg)
North America Recycled Paperboards (n=26)	$160 \pm 50$	$770 \pm 250$	55 ± 22
Europe			
Recycled Paperboards (n=54)* <sup>[5]</sup> Virgin Paperboards (n=4)* <sup>[2]</sup> Virgin Paperboards (n=8)	$711$ $27$ $34 \pm 16$	n.a. n.a. 160 ± 170	134 <5 22 ±5

**Table 4.** Mineral oil concentrations in typical European and North American virgin and recycled paperboards

\* Standard deviation not available



Figure 3. MOSH/MOAH distribution in a paperboard making process. All results are experimental with the exception of the losses in the drying section which were calculated\* (Cx: Pulp/paper consistency in weight %). Percent MOSH and MOAH are relative to the inlet concentration referred as «Pulp #1 & 2».

amount follows the white water streams and about one third of the MOSH/ MOAH are removed at the drying section. The calculated losses, MOSH (36.3%) and MOAH (31.9%), have not been analyzed in detail. In other words, the atmospheric emissions, condensation within the drying section and/or the precision of the mass balance could influence these values. Nevertheless, our results correlate with preliminary observations reported by Biedermann et al. [2].

# **3.4** Functional barriers applied in mill and pilot plant to prevent mineral oil migration

Although ink suppliers would have to provide low or free mineral oil inks, the use of functional barriers could significantly reduce the migration level of MOSH/ MOAH, whenever necessary. Figure 4 shows the efficiency of different functional barriers applied at the paperboard mills and pilot plants, measured over the last three years for different paperboards, basis weight, coating weight and functional barriers (chemistry), using different methods (Tenax, hexane or heptane). Heptane was then selected over hexane for further investigations, since it shows a better correlation ( $R^2$  of 0.92 versus 0.80 respectively), and it allows an easier discrimination between good and bad barrier (Figure 4, left and right).

If a board has been completely aged, the HVTR test is in equilibrium after a few hours, e.g. 2 to 4 hrs. However for fresh board coming off the machine, the HVTR should be tested after one day rather than than 2 to 4 hours, because a better precision is obtained (Figure 4). Maybe aging of the binders and/or a change



Figure 4. Mineral oil migration barrier efficiency, using Tenax, for: left) MOAH as a function of hexane/heptane permeability; and right) MOSH as a function of heptane permeability. Average board basis weight =  $230 \text{ g/m}^2$ ; coating weights =  $11-15 \text{ g/m}^2$ ; HVTR measured after one day at  $23^{\circ}$ C.

of the barrier's porosity occurs as a function of time. Figure 4, on the right side, also shows very good correlation between the laboratory ISEGA and our method as described in section 2.1.

# 3.5 Modelling of mineral oil migration through functional polymer barrier

For a rational development of polymers for functional barriers, it would be desirable to support synthesis and permeability measurements with theoretical molecular modelling. This means, a method has to be identified which establishes a link between computed molecular properties and barrier behaviour of polymer films with respect to longer molecular aliphatic and aromatic hydrocarbon species. For a comparison of computed permeabilities with experimental results, migration data like those obtained for the model hexane appear to be a good choice.

For small migrating species, typically gases, it has been shown that it is possible to directly study migration through polymer matrices using molecular dynamics simulations and that computed mobilities compare favorably with the experiment [12]. However, such atomistic molecular dynamics are computationally rather expensive methods, in particular if the motion of one larger species (like a molecular model for a heavier mineral oil constituent) in another (polymer chains of a barrier film) has to be described in a realistic manner. In addition, a careful benchmarking of the applied force fields would be required.

Thus, an alternative approach was chosen based on the computation of isolated migrating species and small but representative molecular models of the polymer matrix at the quantum level and a consideration of their interactions with the solvation model COSMO-RS.[13] The model was first calibrated and

benchmarked with gas permeabilities (methane), for which a larger amount of reliable experimental data are available and then applied to migration of the larger aliphatic hexane through polymeric barrier films.

Migration of small molecules through polymeric barrier film means a transport through macromolecular matrices which leads to different potential interactions between polymer and permeating entity. A general account of the basic physics behind transport phenomena through polymers has been reported by Li and Long [14]. In case of more complex glassy polymers which contain microvoids that significantly contribute to transport of dissolved species, "dual sorption theory", as described by Vieth and Sladek should be used instead [15]. A detailed derivation is given elsewhere, how these theories enter into the computation of the permeability (permeation constant) P [16]. This key property characterizes the disposition of a material to allow for migration of smaller species in it [16]. The approach is based on the following widely accepted definition: [17]

$$P = D \cdot S \tag{1}$$

Here, *D* denotes the diffusivity (diffusion coefficient) and *S* the available species for diffusion, i.e. solubility of the permeating molecules. Permeabilities assume the following dimension:

$$[P] = \frac{permeant \; quantity \times barrier \; thickness}{area \times time \times pressure \; drop \; in \; film} = \frac{cm^3(gas \; at \; 273K; 1bar) \times cm}{cm^2 \times s \times Pa}$$
(2)

The precise unit given here corresponds to the convention used in the polymer handbook [18]. It should be mentioned that permeation data as the above HVTR have to be divided by the barrier thickness to obtain permeabilities P.

A transport of small and rigid molecules (typically gases) will occur as a sequence of jumps between sorptive sites. In contrast, the transport of larger hydrocarbon molecules should represent a cooperative and stepwise movement of connected chain segments (reptation). However, it appears probable that also for mineral oil transport, which definitely takes place according to the latter mechanism, the same physics as for transport of small gaseous species apply (or – at least – a similar dependence on polymer matrix properties). For this reason, methods that derive D and S of gas transport should also allow the ranking of barrier properties with respect to mineral oil.

With respect to the temperature dependence of *P*, an exponential behaviour is typically assumed for both diffusivity and solubility:

$$D = D_0 \cdot e^{-\frac{E^D}{RT}}$$
(3)

and

$$S = S_0 \ e^{-\frac{E^3}{RT}} \tag{4}$$

Here,  $D_0$  and  $S_0$  represent pre-exponential factors,  $E^D$  is an activation energy (or rather a Gibbs free energy of activation) of diffusion and  $E^S$  the solvation energy (or – rather – the solvation Gibbs free energy) of the permeating species in the polymer, whereas R is the gas constant and T the absolute temperature. From various possible approaches to obtain D and S, free volume theory and computation of Gibbs free energies of solvation via COSMO-RS have been chosen here.

Cohen and Turnbull discuss how free volume theory can be applied to access diffusivity *D* of a low molecular weight species in others [19]. An application of this theoretical framework to polymeric systems was proposed by Vrentas and Duda [20]. For the considered copolymers, an additivity of (free) volume of the homopolymeric constituents was assumed, as suggested by Rezac and John [21].

An advanced treatment of solvation, allowing for a fast access to useful approximations for *S*, which is based on first principle methods, was proposed by Klamt in 1995 with the COSMO-RS approach [13]. Here, no attempt is made to explicitly compute partition functions in solution; instead, the Gibbs free energy is computed as the sum of van der Waals, electrostatic interactions of surface charges and hydrogen bonding contributions, where the latter two terms depend on charge profiles of the molecular surface. For these charge profiles, quantum chemical calculations, typically at a density functional level of theory (DFT) for all species involved are required [16].

Altogether, permeabilities P are computed as:

$$P = a \cdot e^{-s \frac{\Delta G^{solv}}{RT}} \cdot e^{-d \frac{V^*}{V^f}}$$
(5)

Here, *a*, *s* and *d* represent three adjustable parameters; *a* gathers the former  $D_0$  and  $S_0$ ,  $\Delta G^{solv}$  is the Gibbs free energy of solvation of migrating species in the polymer matrix environment (obtained via the aforementioned COSMO-RS solvation treatment), and  $V^*/V^f$  the quotient of volume of the permeating species divided by the free volume per polymer segment which is accessible from a combination of experimental macroscopic density data and microscopic estimates of molecular hard sphere volumes [16].

A validation of the predictability of the chosen approach for highly differing polymers was performed for methane as a gas where a number of experimental data are available in the Polymer Handbook [18]. For these methane permeabilities, about half of the experimental data refer to polymers with a significant degree of crystallinity which was taken into account as suggested by Mohr and Paul [22]. There is a good agreement between experimental permeabilities and those obtained from the correlation based on the above protocol. Considering that the compared polymers are significantly different materials (with glass transition temperatures that differ by around 100°C, low density polyethylene exhibiting the lowest value of around  $-125^{\circ}$ C), this suggests a general applicability (Figure 5). Typical deviations are around half a log unit, the correlation R<sup>2</sup> being 0.81. Experiment and prediction agree that polyvinyl fluoride and polyvinyl chloride exhibit good barrier properties with respect to methane, whereas permeation of polyole-fins is much higher.



**Figure 5.** Computed (correlated) versus experimental methane permeability (at 25°C) for various polymers. Permeabilities *P* are given in  $10^{13} \cdot \text{cm}^2/(\text{s}\cdot\text{Pa})$ . Abbreviations are PVC: polyvinyl chloride, HDPE: high density polyethylene, PIB: poly-*iso*-butylene, LDPE: low density polyethylene. For methane permeability calculation (with a volume of  $3.80 \cdot 10^{-29}$  m<sup>3</sup> for the permeating species), the optimized parameters within (5) are:  $a=2.14 \cdot 10^{59} \text{ cm}^2/(\text{s}\cdot\text{Pa})$ , s=1.55 and  $d=8.78 \cdot 10^{-28} \text{ m}^{-3}$  at room temperature (if as  $V_f$  the dimensionless fraction of free volume in the polymer is used and not the rather ambiguous quantity free volume per segment).  $\Delta G^{solv}$  are obtained via COSMO-RS theory; to derive

volume and free volume from the output of the cosmotherm software [16].

Thus, for a number of acrylic copolymers as potential mineral oil barrier materials, it was tried to correlate, via the same protocol, computed free volume and solubilities with experimental hexane permeation. These acrylic copolymers, some of which are commercialized BASF products, whereas others have been just recently developed (novel specialty acrylates), represent up to quaternary copolymers of esters of acrylic and methacrylic acid, having glass transition temperatures well below room temperature (Figure 6).

As statistic copolymers (i.e. there is a random sequence of co-monomers according to the overall composition), these acrylic copolymers typically exhibit a very low degree of crystallinity and a low glass transition temperature. This represents an important prerequisite for the computation, as generally crystallinities and hypothetical amorphous densities of research products will hardly be known. However, the agreement between experiment and theory is mediocre (Figure 7).

A trend becomes only obvious if the acrylic copolymers are divided into two groups: (I) and (II). Copolymers of group (II) contain a larger amount of lipophilic co-monomers like styrene and their hexane barrier properties do not seem to correlate with computed diffusivities and solubilities. The fact that group (II) experimental permeabilities are much larger than expected is explained, either by a bad processability (i.e. film formation with lower quality) or hexane induces swelling of the copolymers (thus lowering the density of these copolymers resulting in a further increase of copolymer permeabilities).

However, if only copolymers of group (I) are considered, the trend of superior hexane barrier properties of the novel specialty acrylates seems reproduced by the computations with an  $R^2$  value of 0.72, although the – up to now available – four data points are of course not sufficient to draw more general conclusions on the scope of the presented approach; more data points are necessary, here, to increase the level of confidence for this method. But at least in combination with its applicability to methane migration it can be assumed that theoretical calculations according to the above protocol will be helpful in the future to speed up product development. Of course, the observed limitations with respect to polymer classes clearly show that such virtual screening needs a thorough back up from the experiment.



**Figure 6.** Generalized formula of copolymers, for which computed hexane permeabilities were compared to experimental values. R', R", R" and R"" can be H or alkyl. Also styrene is sometimes used as a co-monomeric constituent.



**Figure 7.** Computed (correlated) versus experimental hexane permeation (HVTR at 25°C) for various acrylic copolymers. The permeation, g hexane/m<sup>2</sup>day, results from the experimental method described above. Here, permeation and not permeability is compared (the computation of permeability would require knowledge of barrier thickness, which is

difficult to determine if the barrier is applied as a layer on a rough substrate).

### 4 CONCLUDING REMARKS

Our method was developed using GC-FID laboratory equipment, and it correlates well with Biedermann's results. Barrier efficiency, using Tenax migration method, correlates well with the hexane/heptane vapour transmission rates (HVTR) obtained within one day.

Much higher MOH concentration in newspaper's printed areas infer that printing inks constituents are the most likely source of MOSH/MOAH in recycled paperboards, as previously reported by Grob et al. (Table 2). A reduction of recycled newspaper raw material significantly reduces the MOH content in recycled paperboard. The drying section is one of the paperboard making process that significantly reduces the MOSH and MOAH level.

Although ink suppliers would have to provide low or free mineral oil inks, the use of functional barriers can significantly reduce the migration level of MOSH/ MOAH, whenever necessary.

Mineral oil migration barrier efficiencies of about 90% were obtained using polymeric functional barrier applied at the mill with conventional coating equipment.

A first attempt was made to theoretically model the migration of mineral oil through model polyacrylate functional barriers. The correlation seems reasonable and a predictive discrimination between good and bad barrier polymers appears possible for the acrylate copolymers I ( $R^2 = 0.72$ ), but not for standard acrylate copolymers (II).

### **5 REFERENCES**

- M. Biedermann, J.E. Ingenhoff, M. Barbanera, D. Garbini and K. Grob. Migration of Mineral Oil into Noodles from Recycled fibres in the Paperboard Box and the Corrugated Board Transport Box as well as form Printing Inks: A Case Study. Packag. Technol. Sci. (2011).
- M. Biedermann and K. Grob. Is recycled newspaper suitable for food contact materials? Technical grade mineral oils from printing inks. Eur Food Res Technol. Vol 230, 5, pp.785–796, 2010.
- M. Biedermann, K. Fiselier and K. Grob. Aromatic Hydrocarbons of Mineral Oil Origin in Foods: Method for Determining the Total Concentration and First Results. J. Agric. Food Chem. Vol 57, pp 8711–8721, 2009.
- 4. M. Biedermann and K. Grob. On-line coupled high performance liquid chromatography-gas chromatography for the analysis of contamination by mineral oil. Part 1: Method of analysis. J. Chromatogr. A (2012).
- 5. M. Biedermann, Y. Uematsu and K. Grob. Mineral oil contents in paper and board recycled to paperboard for food packaging. Vol. 24, 2, pp. 61–73, 2011.
- 6. European Food Safety Authority (EFSA). Scientific Opinion on Mineral Oil Hydrocarbons in Food. EFSA Journal 2012; 10(6):2704.
- StiftungWarentestwebsite:http://www.test.de/Adventskalender-mit-Schokoladenfuellung-Mineraloel-in-der-Schokolade-4471436–4471488/
- 8. Twenty-second Regulation Amending the German Commodities Regulation, Germany, May 02, 2011.
- 9. DIN EN 14338. Conditions for determination of migration from paper and board using modified polyphenyl oxide (MPPO) as a simulant. March 2004.
- 10. Piringer, O. G.; Baner, A. L., Plastic Packaging Materials for Food, Wiley-VCH, Weinheim, (2000).

- 11. B. Fuchs; website http://www.ifra.com/website/specialr.nsf/wuis/8EBCB1828F66B F53C1256A23002C2AE5?OpenDocument&SR&)
- I. Cozmuta, M. Blanco and W. A. Goddard III. Gas Sorption and Barrier Properties of Polymeric Membranes from Molecular Dynamics and Monte Carlo Simulations. J. Phys. Chem. B Vol 111, pp 3151–3166, 2007.
- A. Klamt. Conductor-like Screening Model for Real Solvents: A New Approach to the Quantitative Calculation of Solvation Phenomena. J. Phys. Chem. Vol 99, pp 2224–2235, 1995. A. Klamt and F. Eckert. COSMO-RS: a novel and efficient method for the a priori prediction of thermophysical data of liquids. Fluid Phase Equilib. Vol 172, pp 43–72, 2000.
- N. N. Li and R. B. Long. Permeation through Plastic Films. AiChE Journal Vol 15, pp 73–80, 1969.
- W. R. Vieth and K. L. Sladek. A Model for Diffusion in a Glassy Polymer. J. Colloid Sci. Vol 20, pp 1014–1033, 1965.
- P. Deglmann, H. Heiler, H. Seyffer, H. Diehl and A. Esser. A Predictive Modelling Approach to Barrier Properties of Polymer Films. *In Proc. The Proceedings of the Fundamental and Applied Pulp & Paper Modelling Symposium*, Montreal, Canada, and August 61–73, 2011. Eds. R. Gaudreault, S. Robert and M.A. Whitehead, Desktop Publishing, Montreal (2012).
- 17. D. Feldman. Polymer Barrier Films. J. Polym. Environment Vol 9, pp 49–55, 2001.
- S. Pauly in J. Brandrup, E. H. Immergut, E. A. Grulke, A. Abe and D. R. Bloch, Polymer Handbook, 4th edition, pp VI/543–VI/569, John Wiley & Sons, Inc. (1999).
- M. H. Cohen and D. Turnbull. Molecular Transport in Liquids and Glasses. J. Chem. Phys. Vol 31, pp 1164–1169, 1959.
- J. S. Vrentas and J. L. Duda. Diffusion in polymer—solvent systems. I. Reexamination of the free-volume theory. J. Polym. Sci. Vol 15, pp 403–416, 1977. J. S. Vrentas and J. L. Duda. Diffusion in polymer–solvent systems. II. A predictive theory for the dependence of diffusion coefficients on temperature, concentration, and molecular weight. J. Polym. Sci. Vol 15, pp 417–439, 1977.
- 21. M. E Rezac and T. John. Correlation of penetrant transport with polymer free volume: Additional evidence from block copolymers. Polymer Vol 39, pp 599–603, 1998.
- J. M. Mohr and D. R. Paul. Comparison of gas permeation in vinyl and vinylidene polymers. J. Appl. Polym. Sci. Vol 42, pp 1711–1720, 1991.

### **Transcription of Discussion**

## OVERVIEW OF PRACTICAL AND THEORETICAL ASPECTS OF MINERAL OIL CONTAMINANTS IN MILL PROCESS AND PAPERBOARD

### <u>*R. Gaudreault*</u>,<sup>1</sup> *C. Brochu*,<sup>2</sup> *R. Sandrock*,<sup>3</sup> *P. Deglmann*,<sup>4</sup> *H. Seyffer*,<sup>4</sup> and *A. Tétreault*<sup>2</sup>

<sup>1</sup> Cascades Canada ULC., Montreal, QC, Canada;
 <sup>2</sup> Cascades R&D Centre, Kingsey Falls, QC, Canada;
 <sup>3</sup> Reno de Medici, Arnsberg, Germany;
 <sup>4</sup> BASF-SE, GKP/M, Carl-Bosch-Str. 38, 67056 Ludwigshafen, Germany

### Peter de Clerck Amazon-Papyrus Chemicals

It strikes me that you could do an awful lot of removal of this material in the de-inking stage in the process. Have you looked at de-inking as a means of reducing the amount of these materials in the furnish?

### Roger Gaudreault

We have not done it in our company, but it has been published already that de-inking can also be useful. The range of removal seems similar to what we found for the drying section.

*Janet Preston* Imerys Minerals (from the chair)

One of the most difficult things with this work is a successful scale-up to produce a good barrier layer on the board machine. How do you determine whether you have a good layer which will withstand cracking, folding, converting, and how do you get such a good layer?

### Discussion

### Roger Gaudreault

At the beginning we started with lower efficiencies and we looked at the quality of the coating surface. Sometimes we saw lots of bubbles which explained our lower efficiencies. We have since addressed this issue, sold some hundred tons as standard board and had not any remarks or complaints of creasing and glueability.

### Janet Preston

You did say that you have a quick method for measuring the heptane and hexane vapour transmission, do you know how long you actually have to run the test for to get a reliable result? Is it one hour, two hours, four hours or 24?

### Roger Gaudreault

First of all, if you have an aged paper, you can do the HVTR test after 1 or 2, or 4 hours and you should get the same results. However, if you test a board sample right off the machine, i.e. fresh board, the barrier characteristics are ageing, e.g. the porosity, hence you have to wait about one day to get constant HVTR results.