

## MIGRATION OF MINERAL OIL HYDROCARBONS FROM CELLULOSE-BASED PACKAGING TO FOOD: BARRIER vs SORBENT MATERIALS



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#### OUTLINES

- Mineral oil in paper-based food packaging toxicological challenge analytical challenge
- MOH in foodstuff
  - migration study and food servey
- Currently available technologies multilayer materials
- Patent description
- Future perspectives



#### MINERAL OIL HYDROCARBONS IN FOODSTUFFS



#### MINERAL OIL IN PAPER-BASED FOOD PACKAGING: AN ANALYTICAL CHALLENGE



On-line coupled HPLC-GC-FID chromatography



Lorenzini et al., Food Add Contam 2010

# Mineral oil saturated hydrocarbons **MOSH**

Mineral oil aromatic hydrocarbons **MOAH** 



#### MOH MIGRATION FROM PACKAGING TO FOOD

Lorenzini et al., *Food Add Contam* 2013

Food Additives & Contaminants: Part A 769



Figure 7. MOSH migration to muesli as a function of carbon numbers at different storage temperatures. At higher temperature and prolonged storage, higher molecular mass hydrocarbons migrate.

EFSA Scientific Opinion on Mineral Oil Hydrocarbons in Food Mineral oil hydrocarbons (MOH), alkanes, aromatic hydrocarbons, analysis, sources of MOH, human dietary exposure, toxicokinetics, toxicity, risk assessment, margin of exposure (MOE), acceptable daily intake (ADI), food contact materials First published in the EFSA Journal: 6 june 2012; Adopted: 3 may 2012; Last Updated: 28 august 2013.

#### CURRENTLY AVAILABLE TECHNOLOGIES TO CONTROL MOH MIGRATION TO FOODSTAFFS



#### Multilayer components of cellulose-based food packaging

- virgin fiber
- recycled fiber
- aliminum foil (barrier)
- plastic layer (sorbent or barrier)
- activated carbon layer (sorbent)

## THE EXPERIMENTAL EVIDENCE

- Recycled tissue does not contain significant MOH amount
- MOH are removed with inorganic fillers (calcium carbonate, kaolin etc...)
- MOH should not be firmly retained by cellulose in the presence of MOH high affinity/high surface sorbents



PAPER DECONTAMINATION - A POSSIBLE SOLUTION



#### FIRST STEP: POWDER SORBENT FOR MOH STABILIZAZION IN PAPER

Scheme 1 Sketch of the process adopted for the production of recycled paper sheet with an indication of the main production steps: pulping unit for pulp production, washing unit for pulp cleaning, and forming unit for paper sheet production. Particles <105 µm diameter: pigments, inorganic particles, and soluble substances



Stabilization of mineral oil hydrocarbons in recycled paper pulp by organofunctionalized mesoporous silicas and evaluation of migration to food

Enrico Buscaroli, Daniele Bussini, Chiara Bisio, Daniela Montecchio, Graziano Elegir, Davide Garbini, Leonardo Marchese, et al.

> European Food Research &

#### FIRST STEP: POWDER SORBENT FOR MOH STABILIZAZION IN PAPER

Sorbent materials	Source or synthesis method	Particle size (µm)	Pore size (nm)	$SSA~(m^2~g^{-1})$	MOH adsorption (% dw)
SiO <sub>2</sub> -Davisil	Sigma-Aldrich	150-250	6.0	605	<1
Porous Al <sub>2</sub> O <sub>3</sub>	[41]	5-10	3-8	450	<1
SAP-20	[42]	<2	0.10-10	216	2.0
SAP-110	[42]	<2	0.1-10	369	$\geq 1$
SAP-150	[42]	<2	0.1-10	314	$\geq 1$
SBA-15	[37]	0.5-0.6	8	757	<1
Platelet SBA-15	[43]	0.2-0.3	~8.5	733	$\geq 1$
SBA-15-isobuty1	[36]	<1	8.1	659	137
SBA-15-Si(CH <sub>3</sub> ) <sub>3</sub>	[38]	<1	6.5-15	690-1040	318
MCM-41-Si(CH <sub>3</sub> ) <sub>3</sub>	[38]	<1	2.5	729	184

SSA specific surface area, dw dry weight



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#### FIRST STEP: POWDER SORBENT FOR MOH STABILIZAZION IN PAPER



Analytical error <25%

#### FIRST STEP: POWDER SORBENT FOR MOH STABILIZAZION IN PAPER

Mesoporus silicas:

- high affinity for MOH
- thermally recyclable



15 days at 40°C





■ Flour ■ Treated paperboard ■ Unrecovered fraction

#### SECOND STEP: RECOVERABLE MONOLITHS AT HIGH AFFINITY FOR MOH



# MONOLITHS CHARACTERISTICS

- Floating material
- Easily recoverable
- Adaptable shape
- High superficial surface area
- Good mechanical resistance
- Good hydrothermal resistance
- Fully thermally regenerable
- High affinity to hydrocarbons





## FUTURE PERSPECTIVES

MOH removal as a function of

- cellulose/water ratio (2% better than 1%)
- extraction temperature  $(T > 40^{\circ}C)$
- contact time
- water pH

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• production systems







0.6±0.15 ppm MOH in treated paper



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https://www.unibo.it/en/research/business-and-research/patents/2016/use-of-mesoporous-silica

#### PCT PATENT

Braschi I, Bisio C, Buscaroli E, Bussini D, Elegir G, Marchese L (2016) Application No. 102016000072535. Use of mesoporous silica 12/07/2016 Italy Patent 12/07/2017 PCT extension