



The European voice of the
adhesive and sealant industry

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SAFE ADHESIVES FOR SAFE FOOD



Mineral oil hydrocarbons - toxicological
and regulatory background

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Nynas

Agenda

Mineral oil hydrocarbons

- What is it?
- Why is it used?
 - Different perspectives
- Toxicity
- Regulations

What is Mineral Oil Hydrocarbons?

- A term invented by EFSA*:
 - “Mineral oil hydrocarbons (**MOH**) comprise a diverse group of mixtures of hydrocarbons containing **thousands of chemical compounds of different structures and size, derived mainly from crude oil but also produced synthetically from coal, natural gas and biomass. ...**”

*<https://www.efsa.europa.eu/en/topics/topic/mineraloilhydrocarbons>

Why is the terminology MOH used?

- To assess the safety of the food and food contact materials
 - Migration analysis incl impurities should be performed
- Old (>20 yrs) issue of contamination/fraud
 - Edible oils e.g. olive and sunflower oils (Ukraine)
 - Chocolate, coffee and nuts from batching oils in jute sacks
 - Dry food from packaging material
 - Group of Dr Grob at Official Food Control Authority of the Canton of Zurich, Switzerland have published numerous peer-reviewed papers including GC-MS-FID

Why is the terminology MOH used?

Z Lebensm Unters Forsch (1993) 197:370–374

Originalarbeit

Verunreinigung von Haselnüssen und Schokolade durch Mineralöl aus Jute- und Sisalsäcken

Konrad Grob¹, Anna Artho¹, Maurus Biedermann¹, Heinz Mikle²

¹ Kantonales Labor, Fehrenstrasse 15, CH-8032 Zürich, Schweiz

² Halba AG, Alte Winterthurerstrasse 1, CH-8304 Wallisellen, Schweiz

Eingegangen am 30. April 1993

Contamination of hazelnuts and chocolate by mineral oil from jute and sisal bags

Abstract. Before spinning, jute and sisal fibres are treated

beträgt der Mineralöl
50–80 kg Haselnüsse
also 50–75 g Öl darat
siert (Säcke werden

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Eur Food Res Technol (2009) 229:679–688

DOI 10.1007/s00217-009-1099-8

ORIGINAL PAPER

Originalarbeit

**Verunreinigung
durch Mineralöl**

Konrad Grob¹, Anna Art

¹ Kantonales Labor, Fehrens

² Halba AG, Alte Winterthur

**Determination of mineral oil paraffins in foods by on-line
HPLC–GC–FID: lowered detection limit; contamination
of sunflower seeds and oils**

Katell Fiselier · Koni Grob

Eingegangen am 30. April 1993

**Contamination of hazelnuts and chocolate
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Eur Food Res Technol (2002) 215:51–54
DOI 10.1007/s00217-002-0538-6

SHORT COMMUNICATION

Adrian Covaci · Koni Grob

Mineral oil and PCB/dioxin analysis in some European food contamination episodes

y on-line
mination

² Halba AG, Alte Winterthur

Katell Fiselier · Koni Grob

Eingegangen am 30. April 1993

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Why is the terminology MOH used?

- The analytical technique LC-GC-FID cannot separate individual hydrocarbons
- Sort by hydrocarbon types: aromatics & saturates
 - MOAH: mineral oil **aromatic** hydrocarbons
 - MOSH: mineral oil **saturated** hydrocarbons

Why is the terminology MOH used?

- Limitations of chemically determining origin of hydrocarbons in “articles” like food, paper, cardboard etc
- In combination with the “old” focus on mineral oils (=petroleum derived products)
- The chemist named the **detected hydrocarbon fractions**
 - MOSH
 - MOAH

MOH

Why is the terminology MOH used?

- Yet, the last years it has become apparent that the fractions contain so much more than just “mineral oil”
- Numerous industries work on improving analytical methods to detect or deduct their chemicals in/from the MOH fraction
- So why is MOH in focus?
 - Because it can be measured in food and materials
 - Clean food
- Hazard potential?

Toxicity & Mineral Oil Hydrocarbons

- A term invented by EFSA*:
 - “Mineral oil hydrocarbons (MOH) comprise a diverse group of mixtures of hydrocarbons containing thousands of chemical compounds of different structures and size, derived mainly from crude oil but also produced synthetically from coal, natural gas and biomass. ...”
 - “The potential human health impact of MOH varies widely; so-called **‘aromatic’ MOH** may act as genotoxic carcinogens (that is they may damage DNA, the genetic material of cells, as well as cause cancer), while some ‘saturated’ MOH can accumulate in human tissue and may cause adverse effects in the liver. In the European Union, some low- and medium-viscosity MOH are authorised for use as food additives.”

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Toxicity of Mineral Oil Hydrocarbons

- By definition, MOH is the analytical fraction using a non-standardised method
 - No toxicity data available on the analytical fractions
 - Worth performing?
 - Results would be on a spot sample/article that could possibly never be repeated or reproduced due to complexity in supply chain
- EFSA wording proves misunderstandings
- Instead, assess the raw materials and possible contaminants (NIAS) in the supply chain

MOH = Mineral oil?

- No!
- Mineral oil = petroleum **substances** sold by petroleum industry
- Petroleum industry define mineral oil as
 - Lubricant Base Oils (LBO)
 - incl process oils, transformer oils, base oils
 - Highly Refined Base Oils (HRBO)
 - equals white oils
 - (Waxes are not oils! Yet, part of MOH if analysed)

Typical integrated Refinery

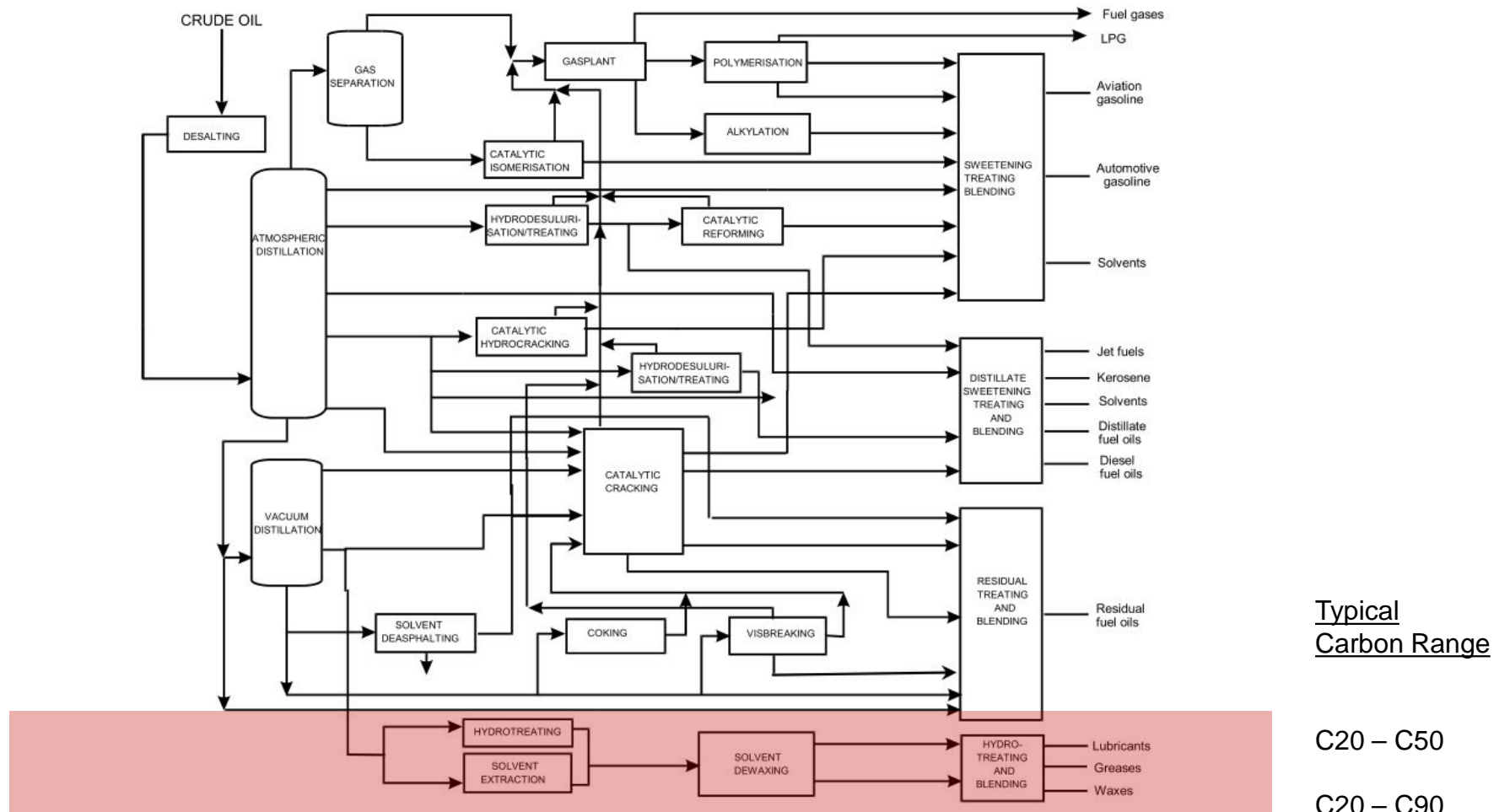
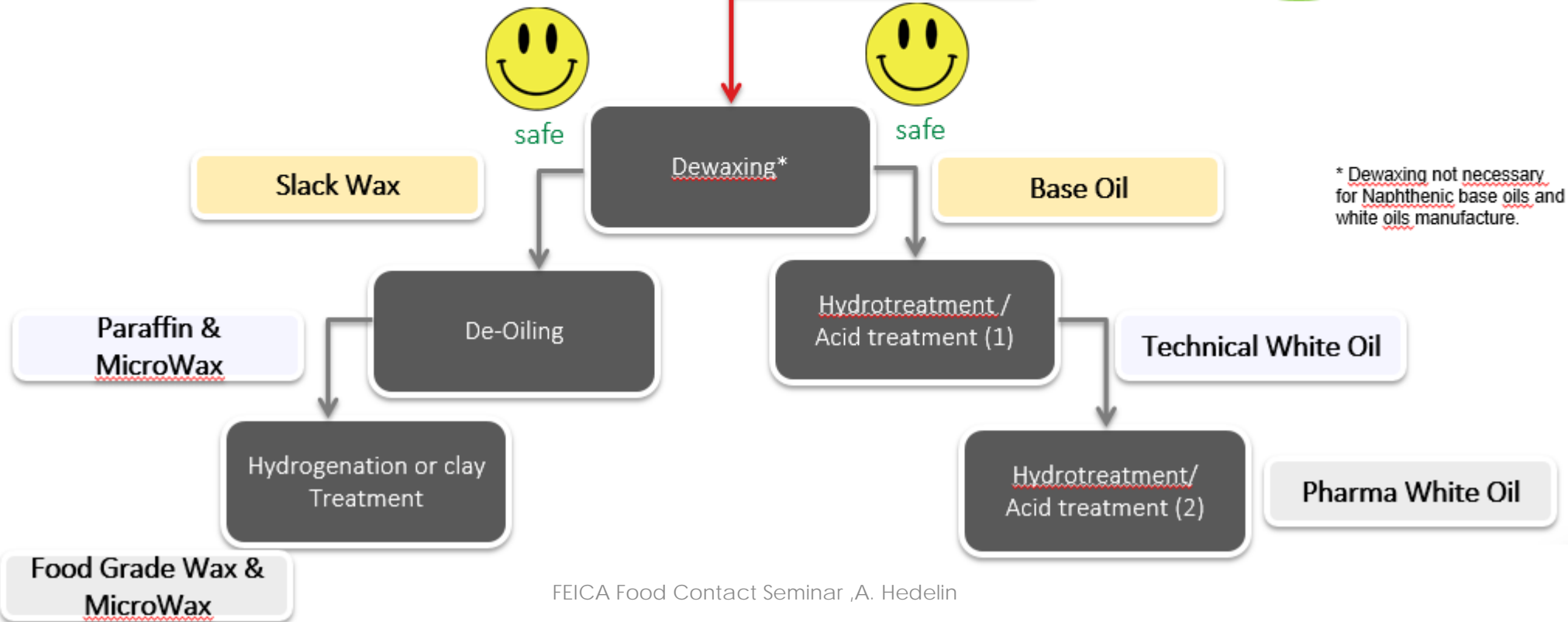
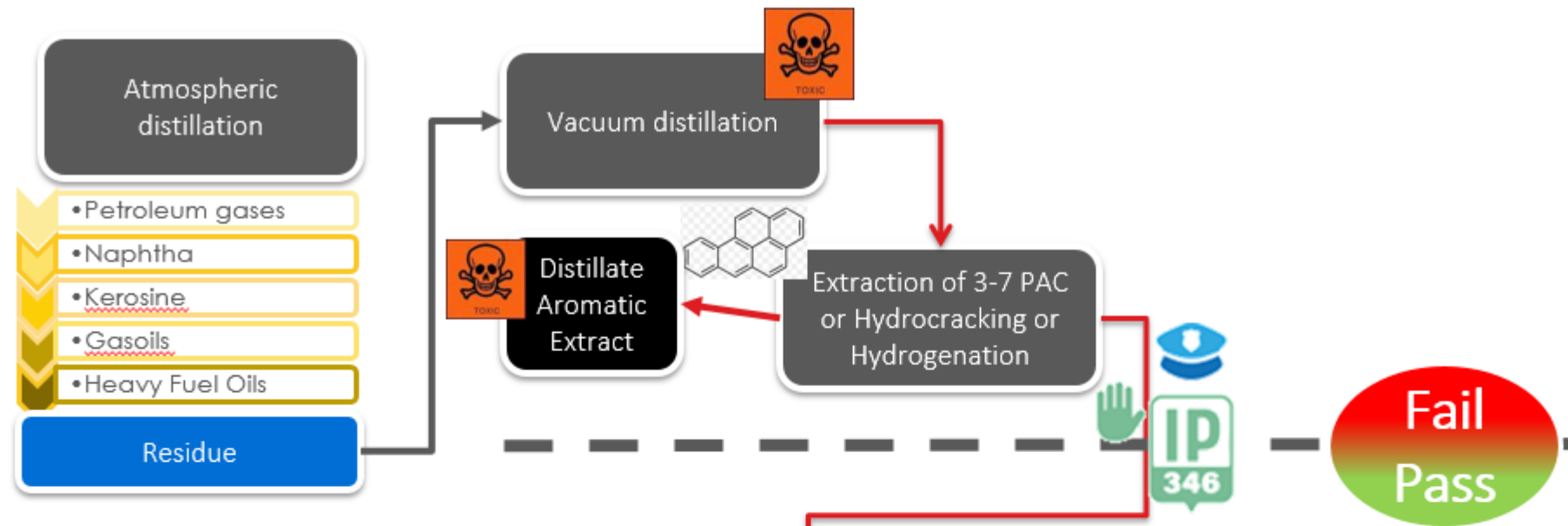


Figure 4: Schematic flow diagram of a typical integrated oil refinery.

Lubricant Base Oils, White Oils, Wax < 10% of total refinery production



Toxicity of mineral oil

- Depends on the degree of refinement
- Petroleum industry have performed hundreds of animals studies the last 30 years to understand the hazard profile of different grades of petroleum products
- Skin tumors is the critical effect due to content of PACs*

*Polycyclic aromatic compounds



Chimney sweeper 1850

Carcinogenicity screening

- For carcinogenicity assessment, skin painting studies in mice is golden standard
 - Worst case scenario and cover oral route
 - Time consuming
 - Animal and cost intense
- A rapid and reliable method required
 - No use of animals
- Reflect toxicity hypothesis, i.e. 3-7 PAC
- Highly correlated to in vivo skin painting data

Toxicity of mineral oil

- Use of DMSO extract to analyse PAC content according to IP346



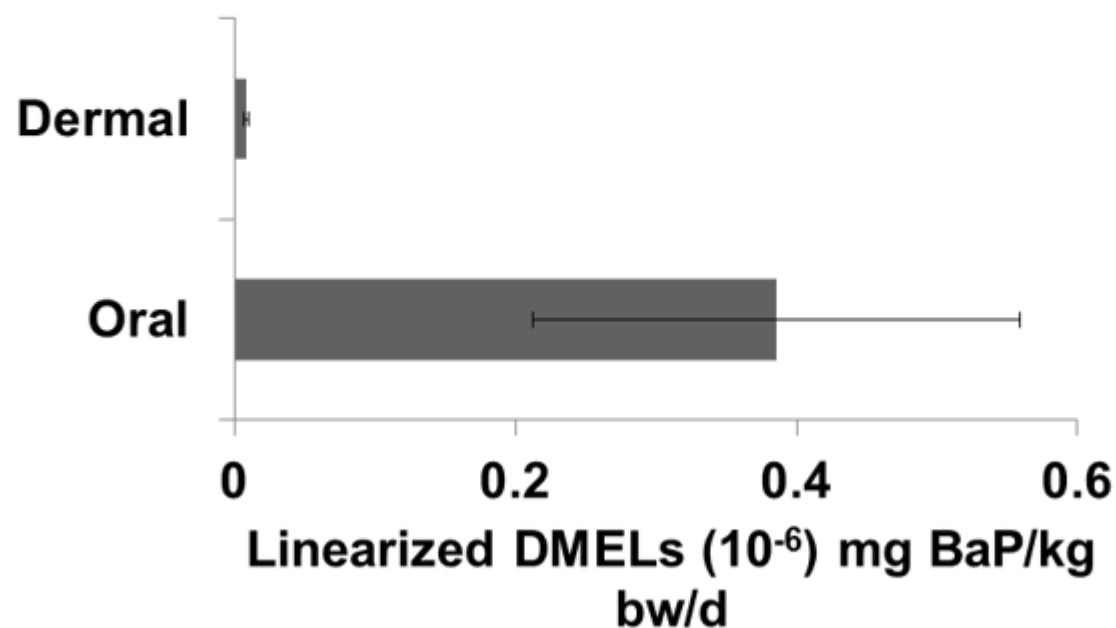
IP346 & skin carcinogenicity

- Oils with both DMSO extract and mouse skin painting data (n=133) are used to determine a carcinogenicity cut-off with an accuracy = 92%. (*CONCAWE report 06/16*)
- Cut-off is hazard based and binary: **pass/fail**
- No discrimination between malignant or benign tumors.
- Tumor incidence above 4% used as evidence of carcinogenicity.
- DMSO extract $\geq 3\%$ → oil is **carcinogenic**
- DMSO extract $< 3\%$ → oil is **safe**
- This relationship is the basis for the industry standard and EU legal requirement: **IP346**

Dermal vs oral route

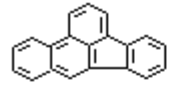
Tissue sensitivity to B[a]P-induced tumors is reflected in average rodent DMEL values

Dermal route is the worst case scenario for PAH mediated carcinogenicity.

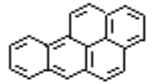


Polycyclic aromatic hydrocarbons (PAHs)

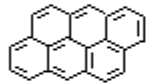
- Composed of multiple aromatic rings
- Abundant in universe
 - incl crude oils & some petroleum products*
 - *Contains Polycyclic Aromatic Compounds (PAC)
 - PAC= PAH incl heteroatoms (N, S, O)
- Formed in incomplete combustion of organic matter
- Alkylated or non-alkylated PAHs



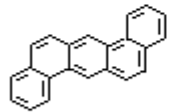
Benzo[Δ]fluoranthene



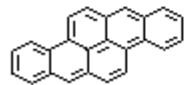
Benzo[a]pyrene



Anthanthrene



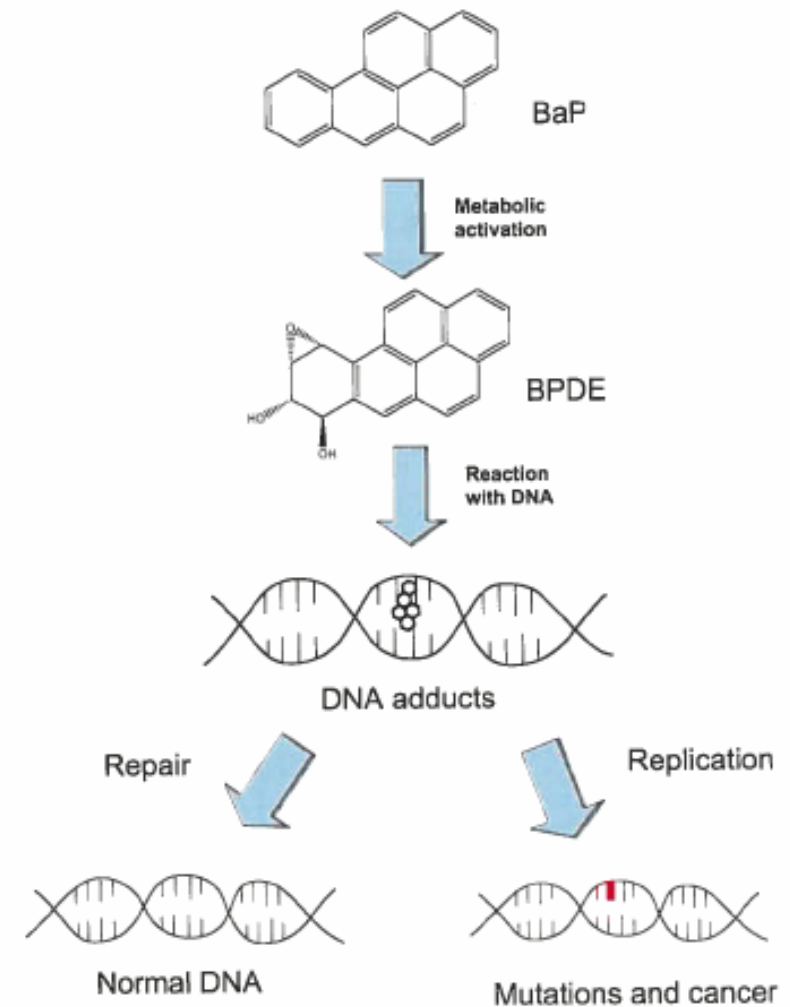
Dibenz[a,h]anthracene



Dibenzo[a,h]pyrene

Polycyclic aromatic hydrocarbons (PAHs)

- Critical effect is cancer
 - Could bind to Ah-receptor and metabolised by CYP450
 - Could form DNA-adducts if planar molecules
 - Some individual 3-7 ring PAHs listed by many agencies as carcinogenic and/or mutagenic



PAH	CAS-NO	BOILING POINT (°C)	LISTS				CANCER CLASSIFICATION / CATEGORY							
			Limitations Directive	EPA list	Grimmer list MAK proposal	EPCRA list	EU	IARC	ACGIH	MAK	EPA	OSHA	WHO	
1-Nitropyrene	5522-43-0	n.d.				x		2B					Carc.	
3-Methylcholanthrene	56-49-5	n.d.				x								
5-Methylchrysene	3697-24-3	n.d.				x		3					Carc.	
7,12-Dimethylbenz[a]-anthracene	57-97-6	n.d.				x							Carc.	
7H-Dibenzo[c,g]carbazole	-	-				x		2B					Carc.	
Acenaphthene	83-32-9	279		x										
Acenaphthylene	208-96-8	265-75		x										
Anthanthrene	-	-			x									
Anthracene	120-12-7	340		x				3						
Benzo[a]anthracene	56-55-3	433	x	x	x	x	Cat 2 (R45)	2B						
Benzo[a]pyrene	50-32-8	495	x	x	x	x	Cat 2 (R45)	1	A2	2	Carc.	Carc.	Carc.	Positive
Benzo[e]pyrene	192-97-2	n.d.	x	x	x	x	Cat 2 (R45)	3						
Benzo[b]fluoranthene	205-99-2	n.d.	x	x	x	x	Cat 2 (R45)	2B	A2	2	Carc.	Carc.	Carc.	Positive
Benzo[b]naphtho[2,1-d]-thiophene	-	-			x									
Benzo[g,h,i]perylene	191-24-2	n.d.		x		x		3						Positive
Benzo[j]fluoranthene	205-82-3	n.d.	x		x	x	Cat 2 (R45)	2B		2			Carc.	Positive
Benzo[k]fluoranthene	207-08-9	480	x	x	x	x	Cat 2 (R45)	2B		2	Carc.	Carc.	Carc.	Positive
Benzo[r,s,t]pentaphene	189-55-9	n.d.				x							Carc.	
Chrysene	218-01-9	448	x	x	x	x	Cat 2 (R45)	2B	A3	2	Carc.			
Cyclopenta[cd]pyrene	27208-37-3	n.d.			x			2A						
Dibenz[a,h]acridine	226-36-8	n.d.				x		2B					Carc.	
Dibenz[a,j]acridine	224-42-0	n.d.				x		2B					Carc.	
Dibenz[a,h]anthracene	53-70-3	524	x	x	x	x	Cat 2 (R45)	2A		2	Carc.	Carc.		
Dibenzo[a,e]fluoranthene	5385-75-1	n.d.				x								
Dibenzo[a,e]pyrene	192-65-4	n.d.			x	x		2B			2		Carc.	
Dibenzo[a,h]pyrene	189-64-0	n.d.			x	x		2B			2		Carc.	
Dibenzo[a,l]pyrene	191-30-0	n.d.			x	x		2A			2		Carc.	
Fluoranthene	206-44-0	375		x		x		3						
Fluorene	86-73-7	293-5		x				3						
Indeno[1,2,3-cd]pyrene	193-39-5	n.d.		x	x	x		2B			2	Carc.	Carc.	Positive
Naphtalene	91-20-3	218		x	x		Cat 3 (R40)		A4	3			Carc.	
Phenanthrene	85-01-8	340		x	x			3					Carc.	
Pyrene	129-00-0	393		x	x			3						

Table 1. A selection of PAH/PAC lists and cancer classifications.

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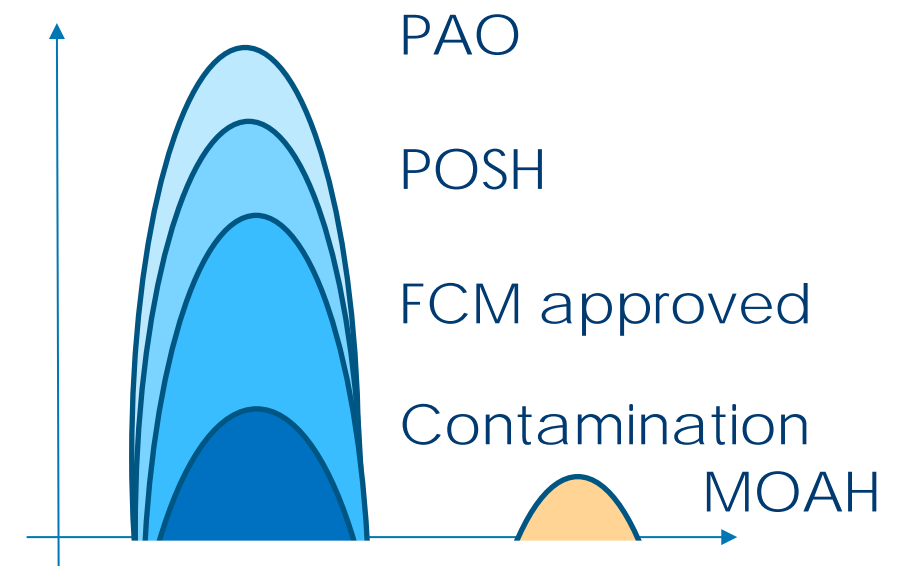
Analysis of hydrocarbons

Mineral oil

- 3-7 PAC analysis
 - DMSO extract → GC-FID → 3-7 ring polycyclic aromatic class → correlation to skin painting studies
 - *Fund. Applied Toxicol.*, **1988**, 10, 466
- UV/Vis
 - PAH in White Oils
 - UV absorbance at 260 to 420 nm should not exceed 1/3 of that of a standard reference sample → PAH content in food would be 1 ppb or less (maximum 1500 ppm mineral oil permitted in food)
 - *Journal A.O.A.C.*, **1962**, 45, 59
- NMR
 - Protons or carbons in an aromatic structure

Food / FCM

- HPLC-MS-FID
 - Possible composition:



Opinion(s) on MOH hazards

- MOSH – microgranulomas (accumulation) in F-344 rat liver in 90-day oral study
 - Performed on a “MOSH mix” – oils and waxes (Cravedi, 2017)
 - Very few toxicologist including EFSA believe “accumulation” is an adverse effect
 - A recovery period decreases the liver concentrations
- MOAH is often misinterpreted as carcinogenic
 - Only a subset of MOAH; the 3-7 ring PAC are possibly carcinogenic
 - Metabolic activation required for possible adverse effects of PAC
 - Competitive metabolism for PAH

Regulatory

- REACH
- Application regulation, e.g.
 - Food
 - Plastics
 - Adhesives
 - Printing inks etc
 - Pharma
 - Cosmetics
- Biocides

10/2011: Oils & waxes

- FCM substance **No. 95: White mineral oils, paraffinic**, derived from petroleum-based hydrocarbon feedstock. No specific migration limit (SML) is defined (i.e. its use is restricted only by the overall migration limit of 60 mg/kg food or 10 mg/dm² food contact surface). The product must comply with the following specifications:
 - hydrocarbons with carbon number less than 25, not more than 5% (w/w);
 - viscosity not less than 8.5 mm²/s at 100°C;
 - average molecular weight not less than 480 Da.
- FCM substance **No. 94: Waxes, refined**, derived from petroleum-based or synthetic hydrocarbon feedstock. No SML is specified (i.e. its use is restricted only by the overall migration limit). The product must comply with the following specifications:
 - hydrocarbons with carbon number less than 25, not more than 5% (w/w);
 - viscosity not less than 11 mm²/s at 100°C;
 - average molecular weight not less than 500 Da.
- FCM substance **No. 93: Waxes, paraffinic, refined**, derived from petroleum-based or synthetic hydrocarbon feedstock. **An SML of 0.05 mg/kg food is specified.** In addition, these oils are not to be used for articles in contact with fatty foods. The product must comply with the following specifications:
 - hydrocarbons with carbon number less than 25, not more than 40% w/w;
 - viscosity at 100°C min 2.5 mm²/s;
 - average molecular weight not less than 350 Da.

10/2011: Oils & waxes

- Approved to be used in plastics FCMs
- All contain MOSH (if analysed), not MOAH free
- No use in asking in MOSH-free substances
- Low SML for FCM 93; based on lack of data (lower-tier application) and NOT hazard profile

FCM substances:

No. 95: White mineral oils, paraffinic

No. 94: Waxes, refined

No. 93: Waxes, paraffinic, refined

Adhesives

- 1935/2004
 - Not endanger human health
- $RISK = EXPOSURE \text{ (migration)} \times HAZARD$
- No migration (with or without functional barrier) – no RISK
- Full hazard profile of substance; if no hazard – no RISK

EU COM: Monitoring of MOH

- European Union Reference Laboratory for Food Contact Materials (EU-RL)
 - Should provide further guidance methods of sampling and analysis
- Member States should perform food sampling
 - MOSH & MOAH in both food and FCM
 - Close to expiry date & warm storage conditions
 - Investigate source
 - By 28 Feb 2019

17.1.2017

EN

Official Journal of the European Union

L 12/95

RECOMMENDATIONS

COMMISSION RECOMMENDATION (EU) 2017/84

of 16 January 2017

on the monitoring of mineral oil hydrocarbons in food and in materials and articles intended to come into contact with food

(Text with EEA relevance)

<http://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:32017H0084&from=EN>

Use of mineral oil in FCMs adhesives from a regulatory perspective

- "Easy and simple":
 - Use/recommend use of functional barrier, or
 - Formulate using only substances listed in Plastics Regulation EC 10/2011
- Perform hazard assessment of mineral oil to understand risk if used in adhesive

Take-home message

MOH/MOSH/MOAH

- Invented terminology
 - Use with caution
 - Analytical fraction using non-standardised method (HPLC-GC-FID)
 - Contains hydrocarbons with numerous origins
- MOH ≠ mineral oil
- MOAH ≠ PAH
- Toxicity not investigated

Mineral oil

- Old-fashion nomenclature
 - Use with caution
- Petroleum products (b.p. ~ >300°C)
 - LBOs
 - HRBOs
- Mineral oil ≠ MOH
- PAC ≠ MOAH
 - Focus on 3-7 PAC (reduced when refined)
- Toxicity well investigated
- Use non-hazardous mineral oils for FCMs

More information

- MOCRINIS II <https://www.concawe.eu/event/mocrinis-ii-workshop/>
 - review manufacturing, toxicity, analytical methods and risk assessment of mineral oils and waxes
 - a special focus on personal care products and food contact (packaging)



- Concawe Q&A on MOSH/MOAH etc

Acknowledgement

- STF-33: Mineral oils and waxes
 - Dirk Danneels, chair
 - Juan-Carlos Carillo, chair MOCRINIS

“Don’t focus on what you can measure,
measure what you need to focus on”

- *Dr. Dirk Danneels*