The Safety of Regulated Consumer Products and MOAH

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The Article

- On May 26, 2015, the German consumer organization, Stiftung Warentest, published an article on its web site test.de called “Mineralöle in Kosmetika: Kritische Stoffe in Cremes, Lippenpflegeprodukten und Vaseline“.
  - Analyzed 25 personal care products including creams, baby care and lip care products, body oils, hair waxes and vaselines
  - Found up to 9% Mineral Oil Aromatic Hydrocarbon (MOAH)
    - A C24 molecule with one aromatic ring is 25% aromatic carbon content but it considered 100% MOAH in this article
  - Also reported finding Mineral Oil Saturated Hydrocarbon (MOSH) in C16 – C35 range in lip care products.

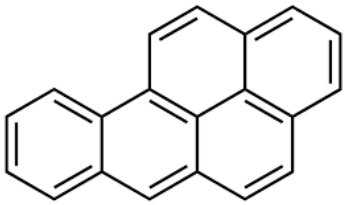
What is MOAH?

- A hydrocarbon compound with a single, substituted aromatic ring in a much larger molecule is considered 100% MOAH
  - Base oils (any molecule with C_a is classified as MOAH)
  - Linear Alkylbenzenes that are precursors for many detergents (20-25% of a typical laundry detergent)
- Other common single-ring, substituted aromatic compounds
  - Vanillin – the compound that makes vanilla taste the way it does
  - Aromatic Amino Acids (essential for human nutrition)
    - Phenylalanine
    - Tryptophan
  - Vitamins B12, E and K (essential for human health)
  - Melanin – the pigmentation in human skin

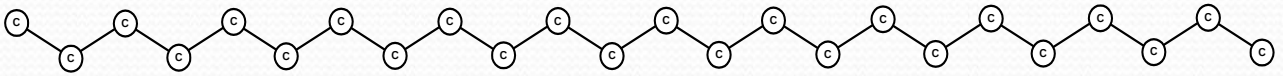
Two very different structures of “MOAH”

- Single Ring – Isolated, highly substituted, sterically hindered and unreactive mono-aromatic compounds having carbon numbers ranging from ~C_{16} to C_{100+}

- Conjugated Rings – also known as Polycyclic Aromatic Hydrocarbons (PAH’s) or two or more conjugated (fused) aromatic rings



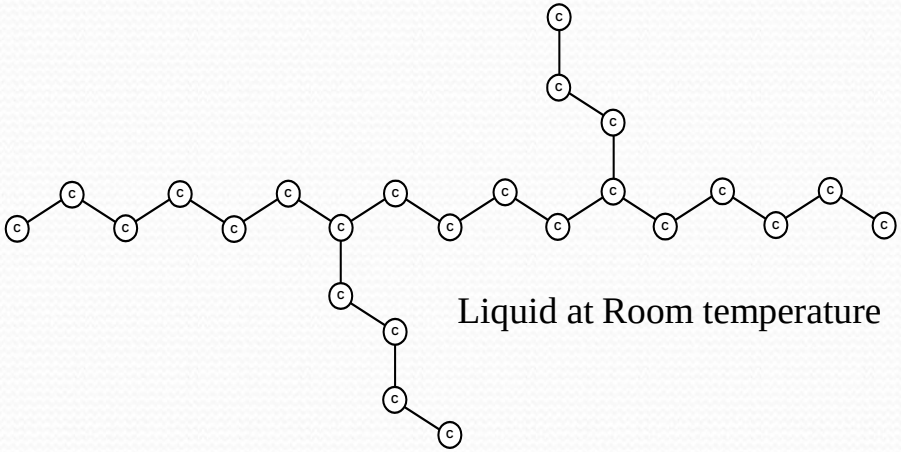
What is MOSH?



$C_{24}H_{50}$

M.P. =54°C (crystalline, solid at room temperature)

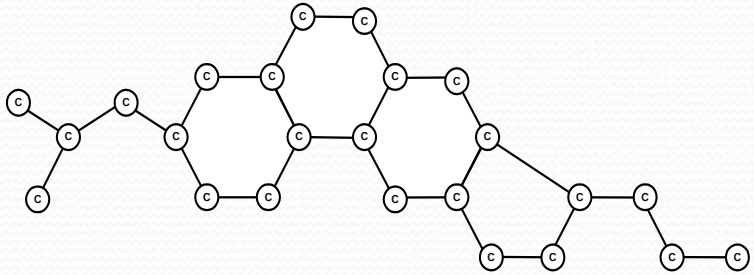
Normal Paraffin or n-alkane



Iso-Paraffin or isoalkane

$C_{24}H_{50}$

Liquid at Room temperature



Cyclo-Paraffin, cycloalkane or naphthene

$C_{24}H_{42}$

Liquid at Room temperature

Petroleum Refining

- Physical separations
  - Fractional distillation
    - Atmospheric
    - Vacuum
  - Deasphalting
    - PDA or propane deasphalting
  - Deoiling or dewaxing (fractional crystallization)
    - MEK
    - Propane
    - Wax sweating

Petroleum Refining cont'd.

- Chemical transformation and separation
  - Liquid:Liquid separation, aka solvent extraction
    - Furfural or nMP
  - Hydrogenation
    - Hydrofinishing – lower pressure; S and N removal
    - High pressure hydrogenation – saturation of aromatics
  - Catalytic Dewaxing (isomerization) – turning wax into oil
  - SO_3 or Oleum sulfonation (acid treatment)
  - Adsorption – bauxite or clay filtration
  - 21 CFR Compliance - chemical processes, positive controls, testing, and procedures in the case of high purity, food and pharmaceutical compliant oils, waxes and petrolatum
  - **Confirmed by FDA audits for 21 CFR compliance**

White Mineral Oil USP

- FDA - **21 CFR 172.878** and **178.3620 (a)** for food
  - Release agent
  - Grain de-dusting
  - Plasticizer in food packaging
- Global standards….. Similar regulations worldwide
- Personal Care - **USP/NF**
  - Emollient
- Pharmaceutical - **USP/NF**
  - Active Ingredient
  - Excipient
- **No test or epidemiological evidence of mutagenicity or carcinogenicity in over a century of widespread use**

Petrolatum USP

- FDA - **21 CFR 172.880** for food
- FDA - **21 CFR 347.10 (m)** skin protectant monograph for OTC drugs
- **USP Grade** excipient in drug products
  - USP established chemical purity standards in 1920's
- Global standards….. Similar regulations worldwide
- Petrolatum was patented in 1872 by Robert Chesebrough ("Improvement in Products from Petroleum," US Patent 127,568 June 4, 1872)
- Petrolatum is known by several additional names including Petroleum Jelly and Vaseline® (a registered trademark of Unilever Corporation)
- **Over 150 years of demonstrated safe use…no laboratory or epidemiological evidence of mutagenicity or carcinogenicity**

Microcrystalline Wax

- FDA **21 CFR 172.886** – Petroleum Wax …Microcrystalline Wax NF
- Higher carbon numbers form micro as opposed to macro crystals
- Developed circa 1926 by separating wax from petrolatum
- Need for protective coatings during WWII drove demand
- Today's uses
  - Viscosity Modifier for hot melt adhesive
  - Chewing Gum Base – FDA **21 CFR 172.615**
  - Crystal modifier in candle formulations
  - Forms occlusive moisturizing barrier, water wash-off resistance and adds body in skin lotions and creams
- **No laboratory or epidemiological evidence of mutagenicity or carcinogenicity in nearly a century of widespread use**

Natural Fats, Oils, Fatty Acids and derivatives

- Triglycerides – animal and vegetable
  - Palm
  - Soy
  - Canola
  - Sunflower
  - Coconut
  - Olive
  - Tallow
  - Lard
- Grade Range
  - Extra Virgin (meaning no refining)
  - Refined, Bleached and Deodorized (RBD)
- Regulated? For insects, microbes, rodent hair and feces, but not for chemical composition….
- **No US regulatory limits or controls for PAH's**

Natural Products Processing

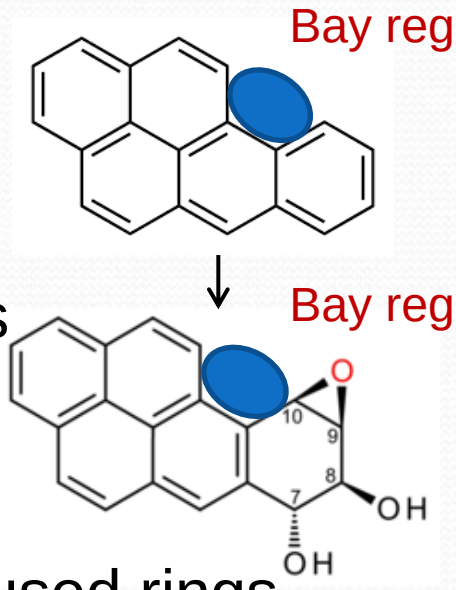
- Separations
  - Pressing
  - Expelling
  - Solvent extraction
- Chemical refining and processing…..parallel to treatment of petroleum
  - Hydrolysis
  - Dewaxing
  - Hydrogenation
  - Amidization
  - Ethoxylation
  - Sulfation
  - Sulfonation
  - Reduction to alcohols
  - Bleaching
  - Deodorizing

Natural Products Processing cont'd.

- Extra virgin is the least rigorous grade from a chemical standpoint
- No refining other than simple filtration
- **No regulatory control for PAH's in natural products in the United States**

Safety Considerations

- Why is limiting exposure to PAH important?
  - Cancer in Climbing Boys (chimney sweeps)….Potts…1775
  - Polycyclic Aromatic Hydrocarbons
  - Bay region theory – PAH metabolizes to diol expoxides in turn react with DNA to form mutagens
  - Bay region exists exclusively within fused rings
  - Potentially created anytime you burn a hydrocarbon
    - Product of incomplete combustion
  - Wood, coal, oils, peat and most famously, tobacco



Testing of Petroleum Products for PAH levels

- FDA Method - Haenni / Hall UV Absorbance
- DMSO Extractions to isolate all PAH compounds
- UV Spectroscopy for PAH's is very specific and quantitatively precise
  - Elegant, robust, low-cost test that is globally recognized
- No complicated million dollar instruments needed

Product Testing in Humans and Surrogates

- Skin Painting
  - Absorption Studies
    - For C16 and C22 - No absorption of beyond the epidermis
  - Carcinogenicity of petroleum products correlated to IP 346 limit of 3% DMSO extractables
    - IP 346 values compared to mouse skin painting results and Modified Ames Test results
- Feeding
  - Accumulation C16 - C35 in F344 Rats at 5% and 10% of diet (no inflammation)
  - Evidence of reversibility

PAH Levels in Refined Petroleum and Natural Products

- Concentration of 28 PAH's measured in Refined Petroleum and Natural Products (Grimmer GC/MS)
- Samples tested
  - Carnation® White Mineral Oil
  - Kaydol® White Mineral Oil
  - Super White Protopet® Petrolatum
  - Multiwax ® W-445 Microcrystalline Wax
  - SonneNatural® (100% vegetable-based emollient)
  - Canola Oil
  - Certified Organic Coconut Oil

IARC Groups

		SUPPORTING EVIDENCE		
		HUMAN	EXPERI-MENTAL ANIMALS	RELEVANT MECHANISM
Group 1	Carcinogenic to humans	Sufficient	Sufficient	Sufficient
Group 2A	Probably carcinogenic to humans	Limited	Sufficient	Sufficient
Group 2B	Possibly carcinogenic to humans	Limited	Limited	Limited
Group 3	Not classifiable as to its carcinogenicity to humans	None	Limited	Limited
Group 4	Probably not carcinogenic to humans	Sufficient	Sufficient	Sufficient

Results

Units = µg/kg or parts per billion (ppb)

BUI Report Number	SON 1506	SON 1511	SON 1514	SON 1003D	SON 1519	SON 1512	SON 1513
	Carnation S/N 29350	Kaydol S/N 29355	SonneNatural (100% Vegetable) S/N 29358	Multiwax W-445 S/N 15682	Superwhite Protopet S/N 29363	Canola Oil S/N 29356	Certified Organic Coconut Oil S/N 29357
Group 1	0.000	0.093	0.053	0.000	0.127	0.000	1.692
Group 2A	0.000	0.011	0.000	0.000	0.218	0.000	3.986
Group 2B	1.459	4.406	0.280	0.031	2.218	13.377	41.174
Group 3	1.116	3.099	1.291	1.700	31.792	70.133	77.361
Total PAH	2.575	7.609	1.624	1.731	34.355	83.510	124.213

Conclusions

- MOAH is a generic, non-specific classification of aromatic hydrocarbons that provides no information regarding mutagenicity or carcinogenicity
- There is no evidence to suggest that single-ring, highly substituted, sterically hindered, aromatic structures that exist in food and pharmaceutical grade refined petroleum products are problematic.
  - Supported by CONCAWE studies in establishing limits for IP-346
    - Safety factor on the order of at least 30,000 (3% ÷ 1 ppm)
- Topically applied, hydrocarbons >C16 will not penetrate the epidermis ….rather they form an occlusive barrier promoting retention of moisture in the skin (moisturization)
- Hydrocarbons >C35 show little to no accumulation

More Conclusions

- Current FDA standards for PAH levels in compliant white oils, petrolatum and waxes provides a wide margin of safety for the positive control to avoid dangerous levels of known carcinogens

- There are no US standards for control of PAH's in "natural" products

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THANK YOU!

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