The Safety of Regulated Consumer Products and MOAH

Tim Yasika
Regulatory Manager
Sonneborn, LLC
Petrolia, PA
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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 \( \sim C_{16} \) to \( C_{100+} \)

![Single Ring Structure](image1)

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

![Conjugated Rings Structure](image2)
What is MOSH?

Normal Paraffin or n-alkane

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

Iso-Paraffin or isoalkane

Cyclo-Paraffin, cycloalkane or naphthene

Liquid at Room temperature

Normal Paraffin or n-alkane

C<sub>24</sub>H<sub>50</sub>

Iso-Paraffin or isoalkane

C<sub>24</sub>H<sub>50</sub>

Cyclo-Paraffin, cycloalkane or naphthene

C<sub>24</sub>H<sub>42</sub>
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
  - SO₃ 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
  - For C16 and C21 - No absorption of beyond the epidermis

- 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

<table>
<thead>
<tr>
<th>Group</th>
<th>Carcinogenicity to Humans</th>
<th>Human Evidence</th>
<th>Experimental Animals Evidence</th>
<th>Relevant Mechanism Evidence</th>
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</thead>
<tbody>
<tr>
<td><strong>Group 1</strong></td>
<td>Carcinogenic to humans</td>
<td>Sufficient</td>
<td>Sufficient</td>
<td>Sufficient</td>
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<tr>
<td><strong>Group 2A</strong></td>
<td>Probably carcinogenic to humans</td>
<td>Limited</td>
<td>Sufficient</td>
<td>Sufficient</td>
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<tr>
<td><strong>Group 2B</strong></td>
<td>Possibly carcinogenic to humans</td>
<td>Limited</td>
<td>Limited</td>
<td>Limited</td>
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<tr>
<td><strong>Group 3</strong></td>
<td>Not classifiable as to its carcinogenicity to humans</td>
<td>None</td>
<td>Limited</td>
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<tr>
<td><strong>Group 4</strong></td>
<td>Probably not carcinogenic to humans</td>
<td>Sufficient</td>
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## Results

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

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<th>BUI Report Number</th>
<th>SON 1506</th>
<th>SON 1511</th>
<th>SON 1514</th>
<th>SON 1003D</th>
<th>SON 1519</th>
<th>SON 1512</th>
<th>SON 1513</th>
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<td>0.053</td>
<td>0.000</td>
<td>0.127</td>
<td>0.000</td>
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<td>SonneNatural</td>
<td>1.459</td>
<td>4.406</td>
<td>0.280</td>
<td>0.031</td>
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<td>13.377</td>
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<td>Multiwax W-445</td>
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<td>1.731</td>
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<td>Coconut Oil</td>
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</table>

Group 1

Group 2A

Group 2B

Group 3

Total PAH
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.
Contributors

Paul Raymond
Luther Jones
Tony Banaszewski
Clay Rozic
Jing Humphreys
Nicole Bozzell
THANK YOU!

sonneborn