Sunscreen Photostability: What it is and how to make it better

by Craig Bonda

taken in part from papers co-authored by Anna Pavlovic, Kerry Hanson, Chris Bardeen

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Preview

- Brief review of international sunscreen regulations as related to UVA
- A brief look at the photophysics of organic UV filters
- Introduction to a new photostabilizer for broad spectrum (UVB/UVA) sunscreens
- Results of *in vivo* studies
- Conclusions
≈95% of the solar UV spectrum is UVA
Commonly used abbreviations

- **SPF** = Sun Protection Factor
  - The ratio of erythemal response (reddening) of protected skin to erythemal response of unprotected skin

- **PPD** = Persistent Pigment Darkening
  - The biological response of skin to UVA exposure
  - The test method used to test for protection against UVA

- **PFA** = Protection Factor UVA
  - The ratio of PPD of protected skin to PPD of unprotected skin
  - Also called UVA-PF for UVA Protection Factor

- **CW** = Critical Wavelength
  \[
  \int_{290}^{400} A(\lambda) d\lambda = 0.9 \int_{290}^{400} A(\lambda) d\lambda
  \]
  
  Where \( \lambda_c \) = critical wavelength
  \( A(\lambda) \) = mean absorbance at each wavelength
  \( d\lambda \) = wavelength interval between measurements
International Sunscreen Regulations relating to UVA protection
Four Examples of Regulatory Venues

- U.S.
  - Sunscreens regulated as Over-The-Counter drugs
- Japan
  - Sunscreens regulated as cosmetics
- Europe (EU)
  - Sunscreens regulated as cosmetics
- Australia
  - Sunscreens regulated as Therapeutic Goods
June 17, 2011: FDA published its Final Rule (not Final Monograph)...

- Creates two sunscreen categories: Sunscreens that are “broad spectrum” and sunscreens that are not “broad spectrum”
  - To qualify as broad spectrum, a sunscreen must have a minimum critical wavelength of 370
    - “The critical wavelength is identified as the wavelength at which the integral of spectral absorbance curve reaches 90 percent of the integral over the UV spectrum from 290 to 400 nm.”
  - All other sunscreens are not broad spectrum
June 17, 2011: FDA published its Final Rule (not Final Monograph)...

- **Testing** -- clinical test required for SPF and *In vitro* test required for CW
  - Primary change to SPF test is reduction of valid tests from 20 to 10 (up to three may be rejected)
  - Critical Wavelength determined on PMMA plate (roughness 2-7 micron) following 4 MED exposure with solar simulator.
    Application rate -- .75 mg/cm² (no pre-saturated finger cot)

- Critical Wavelength calculation

\[
\lambda_c \int_{290}^{400} A(\lambda) d\lambda = 0.9 \int_{290}^{400} A(\lambda) d\lambda
\]

Where

- \( \lambda_c \) = critical wavelength
- \( A(\lambda) \) = mean absorbance at each wavelength
- \( d\lambda \) = wavelength interval between measurements
UV absorbance of a sunscreen that passes the broad spectrum test

- Absorbance
- Wavelength (nm)
- 376 nm Critical Wavelength

90% 10%
A sunscreen that does not pass the broad spectrum test

- Critical Wavelength: 369 nm
- Absorbance:
  - 90% for wavelengths less than 369 nm
  - 10% for wavelengths greater than 369 nm

Wavelength (nm)

Absorbance

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June 17, 2011: FDA published its Final Rule (not Final Monograph)...

- Labeling – new ways of communicating protection
  - Sunscreens that pass the broad spectrum test are labeled as Broad Spectrum SPF (value) on principal display panel. Broad spectrum products with an SPF value of 15 or greater can claim to protect against sunburn, and decrease the risk of skin cancer and early skin aging when used as directed with other sun protection measures.
  - Sunscreens that do not qualify as broad spectrum or have SPF values less than 15 may only claim to protect against sunburn and must carry a warning on the label that the product does not decrease the risk of skin cancer or early skin aging.
  - Sunscreens previously qualified as water resistant now labeled as “water resistant (40 minutes).” Those previously qualified as very water resistant now labeled as “water resistant (80 minutes).”
  - Terms such as “waterproof,” “sweatproof,” and “sunblock” not allowed and prohibition will be enforced!
  - Must conform to OTC Drug Facts labeling format
Sunscreen that helps prevent sunburn and decreases risk of skin cancer and early skin aging

Sunscreen Labeling
According to 2011 Final Rule

If used as directed with other sun protection measures, this product reduces the risk of skin cancer and early skin aging, as well as helps prevent sunburn.

Only products labeled with both “Broad Spectrum” AND SPF15 or higher have been shown to provide all these benefits.

Drug Facts

Active Ingredients
Avobenzone 3%
Homosalate 10%
Octyl methoxycinnamate 7.5%

Uses
• helps prevent sunburn
• if used as directed with other sun protection measures (see Directions), decreases the risk of skin cancer and early skin aging caused by the sun

Warnings
For external use only
Do not use on damaged or broken skin
When using this product keep out of eyes. Rinse with water to remove.
Stop use and ask a doctor if rash occurs
Keep out of reach of children. If product is swallowed, get medical help or contact a Poison Control Center right away.

Directions
• apply liberally 15 minutes before sun exposure
• reapply:
  • after 40 minutes of swimming or sweating
  • immediately after towel drying
  • at least every 2 hours
• Sun Protection Measures. Spending time in the sun increases your risk of skin cancer and early skin aging. To decrease this risk, regularly use a sunscreen with a broad spectrum SPF of 15 or higher and other sun protection measures including:
  • limit time in the sun, especially from 10 a.m. – 2 p.m.
  • wear long-sleeve shirts, pants, hats, and sunglasses
  • children under 6 months: Ask a doctor

Inactive Ingredients
aloe extract, barium sulfate, benzyl alcohol, carboxer, dimethicone, disodium EDTA, jojoba oil, methylparaben, octodecenoic acid
polymer, polyglyceryl-3 distearate, phenethyl alcohol, propylparaben, sorbitan isostearate, sorbitol, stearic acid, tocopheryl (vitamin E), triethanolamine, water

Other information
• protect this product from excessive heat and direct sun

Questions or comments?
Call toll free 1-800-XXX-XXXX

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Sunscreens that only help prevent sunburn and require Skin Cancer/Skin Aging Alert

Sunscreen Labeling According to 2011 Final Rule
These products have not been shown to protect against skin cancer and early skin aging. They have been shown only to help prevent sunburn.

Drug Facts

Active Ingredients
Avobenzone 3%
Homosalate 10%
Octyl methoxycinnamate 7.5%

Uses
• helps prevent sunburn

Warnings
Skin Cancer/Skin Aging Alert: Spending time in the sun increases your risk of skin cancer and early skin aging. This product has been shown only to prevent sunburn, not skin cancer or early skin aging.
For external use only
Do not use on damaged or broken skin
When using this product keep out of eyes. Rinse with water to remove.
Stop use and ask a doctor if rash occurs
Keep out of reach of children. If product is swallowed, get medical help or contact a Poison Control Center right away.

Directions
• apply liberally 15 minutes before sun exposure
• reapply:
  • after 40 minutes of swimming or sweating
  • immediately after towel drying
  • at least every 2 hours
  • children under 6 months: Ask a doctor

Inactive ingredients
aloe extract, butyln sulfite, benzyl alcohol, carbenor, dimethicone, diocidum EDTA, jojoba oil, methylparaben, octodecene/MA copolymer, polyglyceryl-3 distearate, phenethyl alcohol, parfum, propylene glycol, sorbitan isostearate, sorbitol, steearo acid, tocopherol (vitamin E), triethanolamine, water

Other Information
• protect this product from excessive heat and direct sun

Questions or comments?
Call toll free 1-800-XXX-XXX

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Japan

- UVA-PF determined clinically \((in \ vivo)\) by PPD* and communicated via a “+” system
  - PA+ (2-4)
  - PA++ (4-8)
  - PA+++ (highest level of UVA protection – PPD score of 8 or greater)

*Persistent Pigment Darkening
Japanese Sunscreen Labeling

Note PA++ below SPF 25
Ratio of labeled SPF to PFA should be no greater than 3
Critical wavelength should be at least 370 nm
PPD is PFA “gold standard” (mod. JCIA); *In vitro* UVA method proposed by Colipa includes pre-irradiation

SPF scores are grouped; for example:
- SPF 30 – 49.9 is SPF 30 (PFA 10)
- SPF 50 – 59.9 is SPF 50 (PFA 17)
- SPF > 59.9 is SPF 50+ (PFA 20?)
Note color-coded category ratings. These are “Hoch” for “High.” Also note “EU Konform” meaning it meets the 3:1 SPF to PFA standard.
Australia

- All sunscreens must be SPF 15 and have minimum Critical Wavelength of 360 as determined by *in vitro* test that includes pre-irradiation
- Expected soon to adopt a version of the 2006 EU Recommendations (SPF:PFA ≤ 3:1)
Australia

AS/NZ 2604

- Revised draft open for public consultation — deadline July 18, 2011
- Expected to be published end 2011/early 2012
- Waiting for ISO 24443 in vitro UVA to be published before can finalise
- Includes ISO 24444 in vivo determination of SPF
- Maximum SPF will be raised from 30+ to 50+
- Specifies permitted SPF numbers (more than EU; 4, 8 + 40) for mandatory labeling.
- Broad spectrum:
  - currently optional unless making anti-ageing claims
  - proposal to make obligatory if SPF >30 (primary + secondary)
  - proposal for optional ‘Extra broad spectrum’ for SPF 50+ primary sunscreens

Credit: Debra Redbourn, dR Cosmetic Regulations, UK
Presented at Sun Protection Conference, June 8-9, 2011, London
Australian Sunscreen Labeling

SPF 30+ is the highest allowed
The Photophysics of Organic UV Filters
The Paradigm of Photophysics and Photochemistry

**Photophysical**

- **R** = Chromophore in ground state
- **R** = Chromophore in excited state
- **I** = Reactive intermediate
- **P** = Reaction product
- **hν** = UV photon

**Photochemical**

- (Electronic isomer)
- (Change in structure or geometry)
- (Chemical reaction)

**Thermal**

- (No change in structure or geometry)

Visualizing Photon Absorption

Photon Absorption to Form a Hydrogen Excited State
© BlackLight Power, Inc
Excited State

**Resonance Condition:** $\Delta E = h\nu$

$(\lambda=122 \text{ nm}, \Delta E=234 \text{ kcal mol}^{-1})$

Ground State

- $1S$
- $2P$

Ground State

- $1S$

Photon Absorption to Form a Hydrogen Excited State

© Black Light Power, Inc
Resonance Condition: \( \Delta E = h\nu \)

\( (\lambda=290-400 \text{ nm, } \Delta E=98.6-71.5 \text{ kcal mol}^{-1}) \)
DEXSTER

SINGLET EXCITED STATE

IC F SQ

GROUND STATE

TRIPLET EXCITED STATE

ST P TS TQ

PCR
Deactivation of Excited States by Emissions and Radiationless Pathways
The energy in UV radiation “pumps” molecules from the ground state to the singlet excited state.
Physical processes "drain" the molecules to the triplet excited state, and directly to the ground state.
The faucet “leaks” all the molecules destroyed by photochemical reactions.
Chromophores, including the UV filters used in sunscreens, convert the energy in ultraviolet radiation (UVR) and light into electronic excitation energy...
Electronic: \( \psi_0 \) (Orbital motion)
(computed from quantum numbers \( n,l,m \))*

Shown:
1s0 to 2p1 to 1s0
amu = 1

*principal, orbital,(s,p,d,f etc.) angular momentum

Rendered with Orbital Viewer, available on www.orbitals.com
Chromophores, including the UV filters used in sunscreens, convert the energy in ultraviolet radiation (UVR) and light into electronic excitation energy...

...then convert electronic excitation energy into nuclear vibrational energy.
Hooke’s law: $PE = \frac{1}{2} kx^2$

Potential energy equals one half the spring constant (bond strength) times the square of the displacement from equilibrium.
When graphed, the motion of an harmonic oscillator describes a parabola: y axis is energy; x axis is internuclear separation.

\[ PE = \frac{1}{2} kx^2 \]
Vibrational: $\chi$ (Nuclear Motion)

Classical Potential Energy Curve

Each point on the surface represents a specific energy and geometry
Vibrational: $\chi$ (Nuclear Motion)

The 3D molecular motions take the form of an energy surface where each point on the surface corresponds to a potential energy and specific nuclear geometry. A potential energy curve is a cross-section of a 3D energy surface.
Vibrational: $\chi$ (Nuclear Motion)

The 3D molecular motions take the form of an **energy surface** where each point on the surface corresponds to a potential energy and specific nuclear geometry. A **potential energy curve** is a cross-section of a 3D energy surface.

Vibrational: $\chi$ (Nuclear Motion)

Vibrational motion is both quantum and anharmonic.
\[ \Delta E = h\nu \]

Radiative transitions (Absorption and Fluorescence?)

...because, the oscillations are actually anharmonic, and may lead to reactive inter-mediates and products.

\[ R + h\nu \rightarrow \ast R \]
\[ \ast R \rightarrow R + h\nu \]
Avobenzone Unimolecular Photoreactions
Experimentally, it was discovered that silver atoms, having lone electrons with no orbital angular momentum \((l = s \text{ or } 0)\) in their outer shell, are deflected by a non-uniform magnetic field (Stern-Gerlach Experiment, 1921) into two distinct parts indicating that they have a magnetic moment with two possible orientations. Classically, a charged particle such as an electron with a magnetic moment \textbf{must} have angular momentum; i.e. be a spinning ball of charge.
Rotational motion and orientation of a free electron in a magnetic field

Clockwise spin in the direction of the vector
Rotational and precessional motion and orientation of a free “up” electron in a magnetic field

Z Axis
Free electron $\alpha \ (s = \frac{1}{2}, m_s = +\frac{1}{2})$
Rotational and precessional motion and orientation of a free “down” electron in a magnetic field

Free electron $\beta$ ($s = \frac{1}{2}, m_s = -\frac{1}{2}$)
The Singlet State: “coupled”* electrons rotating on opposite vectors; precessing $180^\circ$ out of phase (anti-parallel)

Singlet state $\alpha_1 \beta_2 - \beta_1 \alpha_2$ ($S = 0, M_s = 0$)

*“coupled” means their vectors are added together

Either orbitally paired or unpaired
The Triplet State: “coupled”* electrons rotating on like or opposite vectors; precessing in phase (parallel)

Always orbitally unpaired

Triplet state sublevels \( T_{+1}, T_0, T_{-1} \)

*“coupled” means their vectors are added together
Photochemistry

Photoaddition/substitution

2+2 Cycloaddition

cis-trans Isomerization

Photofragmentation
Avobenzone—Octyl Methoxycinnamate Photoreaction

**Energy transfer**

*(also called Excited State Quenching)*

- General Description
  - Let “D” be the Donor (the molecule in the excited state)
  - Let “A” be the Acceptor (starting out in the ground state)

\[
D^* + A \rightarrow D + A^*
\]
Energy transfer

- Two important mechanisms
  - Dipole-Dipole (aka Coulombic or Förster quenching; also see FRET)
    - “action at a distance” though diminishing with the inverse sixth power of the distance between donor and acceptor
    - Primary mechanism for singlet quenching
Energy transfer

- Two important mechanisms
  - Dipole-Dipole (aka Coulombic or Förster quenching; also see FRET)
    - “action at a distance” though diminishing with the inverse sixth power of the distance between donor and acceptor
    - Primary mechanism for singlet quenching
Energy transfer

- Two important mechanisms
  - Dipole-Dipole (aka Coulombic or Förster quenching; also see FRET)
  - **Electron Exchange (aka Dexter exchange)**
    - Requires proximity (electron cloud overlap)
    - Dominant mechanism for triplet quenching
**Energy transfer**

- **Two important mechanisms**
  - Dipole-Dipole (aka Coulombic or Förster quenching; also see FRET)
  - **Electron Exchange** (aka Dexter exchange)
    - Requires proximity (electron cloud overlap)
    - Dominant mechanism for triplet quenching
Energy transfer

Comparison of Coulombic (dipole-dipole) mechanism with Dexter Exchange

Hypothetical plot of ET efficiency by separation of Donor and Acceptor, $R_{DA}$

- Coulombic ($\propto 6 \ln R_{DA}$)
- Dexter exchange ($\propto 2R_{DA}/R_{DA}^0$)

Size of aromatic hydrocarbons

Effect of “Triplet Quenching”

- Octocrylene
- Polyester-8
- Diethylhexyl 2,6 naphthalate
- Methylbenzylidene camphor
Effect of “Singlet Quenching”
Some molecules in the Singlet Excited State deactivate by emitting another photon in a process called *Fluorescence (F)*.
Fluorescence Spot Demonstrations

U.S. Patent 7,776,614
Visible fluorescence of Avobenzone and Octyl Methoxycinnamate (OMC)
**Introduction to a new photostabilizer for broad spectrum (UVB/UVA) sunscreens**

- **INCI:** Ethylhexyl methoxycrylene
- Oil soluble
- High solvency (w/w)
  - Avobenzone 25%
  - Oxybenzone 30%
  - Octyl triazone 25%
  - Bemotrizinol 25%
- **U.S. Patents 7,588,702; 7,597,825; 7,713,519; 7,754,191, 7,959,834**
Avobenzone Fluorescence
Quenched by Ethylhexyl Methoxycrylene
OMC Fluorescence Quenched by Ethylhexyl methoxycrylene
Streak Scope Measurements

© 2008 Hamamatsu Photonics
Streak Scope Measurement of Avobenzone
Fluorescence Lifetime: $1.3 \times 10^{-11}$ sec.

Fluorescence Lifetime Raw Data

- **Avobenzone in EtOH**
- **EtOH**

1. The decay for Avo is slightly broadened relative to the raman of EtOH
2. Can convolve Et with Avo data to distinguish $\tau_{(Avo)}$

Convolution of Avobenzone in EtOH

- **Avobenzone in EtOH**
- **$\tau = 13$ ps**
Streak Scope Data Showing no Quenching by Octocrylene at 75:1

Figure 3: Streak scope data shows that OC does not quench the singlet excited state of BMDM (avo above), even when the ratio of OC to BMDM is 75:1.
Streak Scope Data showing EHMC Quenching of Avobenzone Fluorescence

Figure 2: Streak scope data shows that EHMC (EC above) quenches the singlet excited state of BMDM in a concentration-related manner, though not in a linear one.
Streak Scope Data Showing Concentration-related EHMC Quenching of Avobenzone Fluorescence

Experimental and Calculated Stern-Volmer Data for EC and Avo

- $\tau_0/\tau$ vs. EC Concentration (mM)

- $\circ$ Expected Stern-Volmer data for diffusoanl quenching
- $\blacksquare$ Experimental Stern-Volmer data is non-linear at high EC concentration

Here that data become non-linear. This indicates some form of quenching, but it is not diffusion controlled.
**EHMC photostabilizes OMC and Avobenzone together**

EHMC is superior to Octocrylene in preserving UVA absorbance of a formulation containing 7.5% OMC and 3% Avobenzone after 25 MED.
Retinol Photolability

UVA-induced Retinol Photoproducts

EHMC Photostabilizes Retinol and Retinyl palmitate

% Retinoid Peak Absorbance Retained after 5 MED by UV Transmittance Analyzer

- Retinol @ 325nm
- Retinyl palmitate @ 329nm

0% EHMC  4% EHMC
Clinical Test Results

1. SPF determined *in vivo* by FDA Final Monograph method, 5 subjects static
2. PFA determined *in vivo* by JCIA method (PPD), 5 subjects static
# Avobenzone and OMC Formulations

**Base:** Glyceryl Stearate, PEG-100 Stearate, Potassium Cetyl Phosphate

<table>
<thead>
<tr>
<th>Key Oil Phase Ingredients</th>
<th>Formula One (JZ3-20)</th>
<th>Formula Two (JZ2-302C)</th>
<th>Formula Three (JZ3-43)</th>
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</thead>
<tbody>
<tr>
<td>Avobenzone (BMDM)</td>
<td>3%</td>
<td>3%</td>
<td>3%</td>
</tr>
<tr>
<td>Ethylhexyl Methoxycinnamate (OMC)</td>
<td>2.5%</td>
<td>7.5%</td>
<td>7.5%</td>
</tr>
<tr>
<td>Octocrylene</td>
<td>2.8%</td>
<td>2.8%</td>
<td>2.8%</td>
</tr>
<tr>
<td>Oxybenzone (Benzophenone-3)</td>
<td>-----</td>
<td>-----</td>
<td>6%</td>
</tr>
<tr>
<td>Solvent/Emollient</td>
<td>7%*</td>
<td>7%*</td>
<td>15%**</td>
</tr>
<tr>
<td>Ethylhexyl Methoxycrylene</td>
<td>4%</td>
<td>4%</td>
<td>4%</td>
</tr>
</tbody>
</table>

*in vivo SPF (FDA)*§: 15*** 36 50
*in vivo PFA (JCIA)*§: 8*** 11 20

* C12-15 Alkyl Benzoate
** 5% each Caprylic/Capric Triglyceride, Diisobutyl Adipate and Phenethyl Benzoate
§ *in vivo* studies are five subject static
*** *in vitro*
## Avobenzone and ZnO Formulations

Base: Glyceryl Stearate, Polyglyceryl-3 Methylglucose Distearate, TEA-Oleth-3 Phosphate

<table>
<thead>
<tr>
<th>Key Oil Phase Ingredients</th>
<th>Formula One (JZ2-194F)</th>
<th>Formula Two (JZ2-222B)</th>
<th>Formula Three (JZ2-237)</th>
<th>Formula Four (JZ2-239)</th>
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<tr>
<td>Avobenzone (BMDM)</td>
<td>2%</td>
<td>2%</td>
<td>3%</td>
<td>3%</td>
</tr>
<tr>
<td>Zinc Oxide (ZnO)</td>
<td>6.2% (uc)</td>
<td>10% (sc)</td>
<td>10% (sc)</td>
<td>10% (sc)</td>
</tr>
<tr>
<td>Octocrylene</td>
<td>-----</td>
<td>5%</td>
<td>5%</td>
<td>10%</td>
</tr>
<tr>
<td>Solvent/Emollient*</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>Ethylhexyl Methoxycrylene</td>
<td>3.4%</td>
<td>3.4%</td>
<td>3.4%</td>
<td>3.4%</td>
</tr>
<tr>
<td>* In vivo SPF (FDA)</td>
<td>19</td>
<td>37</td>
<td>42</td>
<td>65</td>
</tr>
<tr>
<td>* In vivo PFA (JCIA)</td>
<td>25</td>
<td>27</td>
<td>32</td>
<td>25+§</td>
</tr>
</tbody>
</table>

uc = uncoated  
sc = silane coated  
* C12-15 Alkyl Benzoate  
§ in vitro
## Avobenzone and TiO₂ Formulations

**Base:** Glyceryl Stearate, PEG-100 Stearate, Potassium Cetyl Phosphate

<table>
<thead>
<tr>
<th>Key Oil phase Ingredients</th>
<th>Formula One (JZ2-275T3)</th>
<th>Formula Two (JZ3-15B)</th>
<th>Formula Three (JZ3-15A)</th>
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</thead>
<tbody>
<tr>
<td>Avobenzone (BMDM)</td>
<td>3%</td>
<td>3%</td>
<td>3%</td>
</tr>
<tr>
<td>Titanium Dioxide (TiO₂)</td>
<td>4% (uc)</td>
<td>4% (uc)</td>
<td>4% (uc)</td>
</tr>
<tr>
<td>Octocrylene</td>
<td>-----</td>
<td>2.8%</td>
<td>10%</td>
</tr>
<tr>
<td>Solvent/Emollient</td>
<td>5.6%*</td>
<td>10%**</td>
<td>5%**</td>
</tr>
<tr>
<td>Ethylhexyl Methoxycrylene</td>
<td>3.4%</td>
<td>3.4%</td>
<td>3.4%</td>
</tr>
<tr>
<td>* In vivo SPF (FDA)</td>
<td>25</td>
<td>40</td>
<td>54</td>
</tr>
<tr>
<td>* In vivo PFA (JCIA)</td>
<td>32</td>
<td>24</td>
<td>27</td>
</tr>
</tbody>
</table>

uc= uncoated  
* Caprylic/Capric Triglyceride  
** C12-15 Alkyl Benzoate
Conclusions

1. Regulatory

Regulators (and consumers) around the world increasingly demand that sunscreens meet minimum standards of protection against UVA radiation.

2. Photophysical

After photonic excitation, a chromophore’s ultimate fate is determined by competing photophysical and photochemical processes, which may preserve it in its original form or lead to its destruction.
3. New Photostabilizer

Avobenzone’s singlet excited state is extremely short-lived at 13 picoseconds. Even so, Ethylhexyl methoxycrylene (EHMC) quenches the singlet excited state of Avobenzone (and other UV filters) and greatly improves sunscreen photostability in a new, more efficient way.

4. Results of *in vivo* studies

Avobenzone can be used successfully with OMC, Zinc oxide, and Titanium oxide to create sunscreens with superior UVA protection at all SPF levels when formulated with EHMC.
Acknowledgements

- **Co-authors**
  - Anna Pavlovic
  - Kerry Hanson
  - Chris Bardeen

- **HallStar Colleagues**
  - John Paro
  - Gary Wentworth
  - Jean Zhang
  - Steve Semlow
  - Gary Neudahl
Thank you very much!