

Comparative Evaluation of Commercial SPF 100+ Sunscreen Products

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MORE THAN three years ago, the FDA introduced a proposed rule that includes testing of sunscreen efficacy in vivo (SPF and UVA-PF) and in vitro (UVAI/UV ratio after pre-irradiation).¹ The FDA requires U.S. sunscreen manufacturers to declare, in addition to SPF, the level of UVA protection provided by sunscreen product, based on the lowest result obtained using in vivo and in vitro UVA testing.

The FDA's vision is to ensure and reward balanced and photostable UVA/UVB protection; according to the agency, both UVB and UVA radiation protection are equally important and more protection against UVA radiation damage is beneficial for consumers' health. Others, however, have questioned the use of high SPF products.²

FDA also indicates its position regarding sunscreens with high SPF values. Data submitted to FDA show that the SPF test is accurate and reproducible for sunscreens with SPF up to 50. Thus, the agency proposes to allow labeled SPF values up to 50+ for the following reasons: to satisfy consumers who desire or need high levels of UV protection; help to compensate for inadequate application and/or re-application; provide additional sunburn protection during intense UV radiation conditions; help reduce cumulative UV radiation exposure; and generally provide consumers with incremental increases in sunburn protection.

FDA recognizes that future data may

Star Rating	★☆☆☆☆ Low	★★★☆☆ Medium	★★★★☆ High	★★★★★ Highest
UVAI/UV Ratio	0.2-0.39	0.40-0.69	0.70-0.95	> 0.95
UVA-PF	2 to under 4	4 to under 8	8 to under 12	12 or more

demonstrate that test variability may not be a problem for sunscreen products over SPF 50. It states that it will consider specific SPF values greater than 50 upon receipt of data demonstrating that accurate and reproducible results can be obtained from the SPF test for sunscreen products with SPF values over 50. According to FDA, allowing manufacturers to label sunscreens as "SPF 50+" may encourage further research into skin photobiology and the development of effective and safe sunscreen drug products with specific SPF values over 50.

Apparently, major U.S. sunscreen manufacturers followed this FDA encouragement by developing numerous commercial sunscreen products with SPF label values ranging from 100 to 110, which numerically are at least two times higher than the proposed limit of SPF 50+; all these products were introduced to the market in 2010 with description "new" on the packages.

From the technical point of view, the development of sunscreen products with 100+ SPF values using sunscreen actives selected from the current FDA approved list is a challenging task that requires creativity

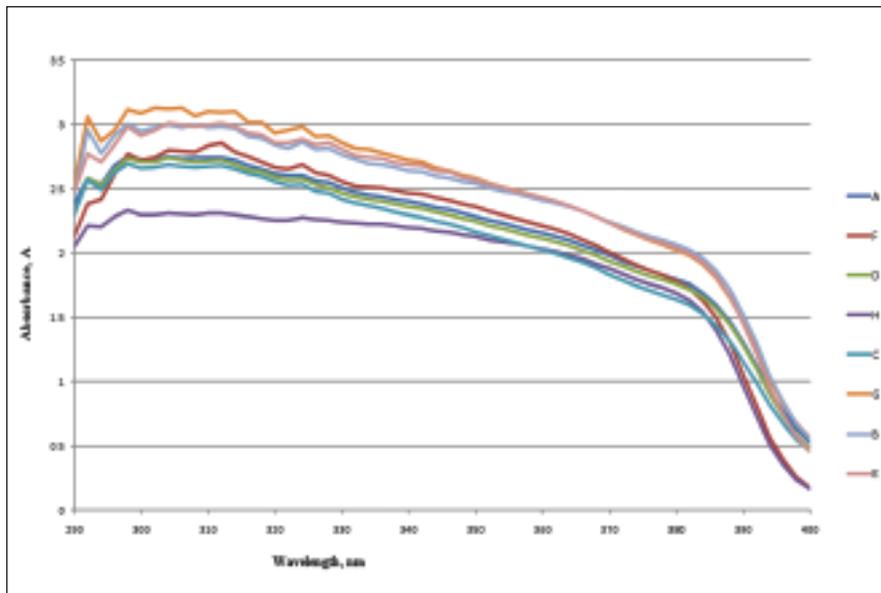
and utilization of optimized delivery systems in conjunction with:

- Photostabilizing technologies and ingredients, for example Helioplex,³ Avotriplex,⁴ triplet combination of avobenzone, octocrylene and oxybenzone,⁵ and the use of sufficient levels of octocrylene to photostabilize avobenzone, etc.;

- SPF boosting technologies and ingredients, diethylhexyl syringylidenemalonate,⁶ styrene/acrylates copolymer microspheres,⁷ Triplet-Triplet and Singlet-Singlet quenchers⁸ and UV attenuating emollient butyloctyl salicylate; and

- Utilization of effective film-forming polymers, antioxidants, plant-derived ingredients and additional particulates (silica, modified silica) that help to improve overall product efficacy, sensorial profile and generate additional skin benefits.

Currently, the FDA is still finalizing new regulations. In the event the FDA rules in the near future and confirms the allowed limit of SPF 50+, manufacturers will have substantial time to comply with new regulations. In the meantime, commercial SPF



Absorbance Spectra of Commercial SPF 100+ sunscreen products after pre-Irradiation

100+ products will continue to be marketed. If the FDA abandons the proposed SPF 50+ limit, this will likely lead to the continuation of the development of SPF 100+ sunscreens, or so-called sunscreen race. In any scenario, the comparative evaluation of SPF 100+ commercial products using relevant in vitro test methods will help sunscreen consumers to better differentiate these products and provide formulators with useful information and data regarding commercial benchmarks.

Materials and Methods

Eight commercially available sunscreen products with label SPF waterproof (very water resistant) values ranging from SPF 100 to 110 are shown in the photo below. These products were evaluated in vitro according to the FDA proposed rule using

Commercially available SPF 100+ sunscreen products



Vitro Skin (N-19)⁹ as alternative substrate instead of roughened quartz plates, which FDA proposed for the in vitro portion of its UVA test method while requesting comments regarding the suitability of other possible substrates. The suitability of Vitro Skin (N-19) as an alternative substrate for evaluation of UVAI/UV ratio was demonstrated by Dueva-Koganov et al.¹⁰

The required pre-irradiation step used a Solar Simulator 16S-300-002 with full spectrum sunlight (Air Mass 1.5) in conjunction with XPS 400—a precision current source, PMA2100 Radiometer with PMA2101 Detector (all from SolarLight Company, PA)¹¹ and Peltier-cooled surface provided by SC25 Orbital Mixing Chilling / Heating Plate from Torrey Pines Scientific.¹²

The diffuse transmittance/absorbance measurements were conducted on the transmittance analyzer with integrated sphere Labsphere UV 2000S with Version 1.2 software to measure FDA proposed UVAI/UV ratio.¹³ Pre-irradiation dose for each test product was calculated based on its actual SPF label value according to the

2/3, where 1 MED = 200 J/m²-erythemally effective dose. Absorbance spectra of all test articles were within the dynamic range for Labsphere UV 2000S.¹³

Measurements of the contact angle of water to quantify the effects of test products on the surface properties of a skin-substitute substrate Vitro Skin (N-19) were conducted according to the test methodology described in a paper by Dueva-Koganov et al.¹⁴ where it was demonstrated that products producing relatively low contact angles tend to make more “light” and “non-greasy” sensory claims, while products that produce relatively high contact angles make more claims related to long-term moisturization. Contact angles were measured according to sessile drop method using Krüss EasyDrop analysis system with attached computer running Krüss DSA1 software for device control, image acquisition and analysis of drop shape images.¹⁵ In addition, it was previously shown that water resistant properties of sunscreen products correlate with the respective water contact angles (wettability) after their application in vitro on Vitro Skin (N-19)¹⁶ and in vivo on human skin—according to Hagens et al.¹⁷

In preparing the substrate and applying the product, Vitro Skin (N-19), Lot#0231 was pre-cut and pre-hydrated as described. The application dose of the test product in all in vitro tests was 2mg/sq. cm—similar to the application density used in the in vivo tests.

Results/Discussion

Detailed description of the test products, their UVAI/UV ratios, measured contact angles and absorbance spectra after pre-irradiation are presented in the graph above and the table on p. 52. Seven test products A, B, C, D, E, F and G contain identical composition of five sunscreen actives: avobenzene, 3.0%; homosalate, 15.0%; octisalate, 5.0%; octocrylene, 10.0%; and oxybenzone, 6.0%. Products A, B, C, D and F utilize Helioplex photostabilizing patented technology in conjunction with maximum allowed concentration of UVB sunscreen active octocrylene to further photostabilize avobenzene. Product G employs diethylhexyl syringylidenemalonate, a photostabilizer

and SPF booster and maximum allowed concentration of octocrylene to further stabilize avobenzone.

Products A, B, C, D, E and G are oil-in-water emulsions; all contain styrene/acrylates copolymer microspheres, an effective SPF booster that also imparts smooth skin feel, additional particulates and polymers that contribute to product's efficacy and performance. Products A and B both contain plant-derived natural ingredients glycine soja (soybean) seed extract, dipotassium glycyrrhizate and chrysanthemum parthenium (feverfew) leaf/flower/stem juice. Product E contains similar ingredients as product C, but listed in different order, with additional tocopheryl acetate, butylene glycol, ascorbyl palmitate and glycine soja (soybean) protein. Product H contains only three sunscreen actives: avobenzone, 2.5%; octocrylene, 8.0%; and oxybenzone 3.5%. These concentrations are lower than those in the other seven test products; it is a water

in oil system and utilizes at least two patented photostabilizing/SPF boosting technologies, AvoTriplex and a triplet combination of avobenzone, octocrylene and oxybenzone together with particulates, polymers and emollients (including UV-attenuating butyloctyl salicylate), which likely contribute to the product's high efficacy.

Experimental data show that UVAI/UV ratios of SPF 100+ sunscreen products launched in the U.S. in 2010 are in the narrow range of 0.8-0.85; all are photostable and belong to the proposed "High UVA Protection" category (three stars) while failing to fulfill the "Highest UVA Protection" criterion (four stars). Product H has highest UVAI/UV Ratio of 0.85 and product C the lowest at 0.80.

Products A and B generated similar contact angles of about 40 degrees, suggesting that their sensory properties are similar; products C, D and E are in the range of 52-57 degrees, indicating their possible sensor-

ial similarities as well. Products A, B, C, D and E have combinations of "light" and/or "lightweight and/or non-greasy" claims, which are consistent with correlations, established earlier. Product G related contact angle value of 62.9 degrees predicts its good moisturizing potential that is actually confirmed by moisturization claim on its label. Product H generates contact angle value of 33.9 degrees; this is the lowest value ever found among more than 50 products evaluated so far under these test conditions and may indicate good sensory properties of this product, which currently does not have any relevant claims on the package. It was previously found that the majority of lotions with "non-greasy" and/or "lightweight" claims contain a certain particulate(s) or their combination: aluminum starch octenylsuccinate, silica, etc.;¹⁴ these findings are in agreement with current data—where seven SPF 100+ products that produce relatively low water contact angles contain spherical micro par-

● Evaluating Sunscreens

ticles⁷ and other particulates, which are simultaneously contributing to achieving SPF 100+ and beneficial sensory profiles of these products. Test product F is an alcohol containing spray that generates a contact angle of 81.1 degrees; however, this is not a prohibitive value from having “non-greasy” and

“lightweight” sensorial properties claimed for this product; it may also suggest its long term moisturization potential.¹⁴ Manufacturers also describe additional skin benefits for certain SPF 100+ products: their ability to counter skin damage on cellular level, prevent deep oxidative damage, prevent the

appearance of discoloration and fine lines, protect collagen and elastin from breaking down (A and B); shields skin six layers deep from skin-aging UVA rays, combats free radicals that accelerate signs of aging (C); helps shield skin from environmental damage (E); moisturizing (H).

Table: Commercially available SPF 100+ products, their UVAI/UV ratios after pre-irradiation and contact angles of water on Vitro Skin (N-19) after product application.

Product	Name	Inactive Ingredients	UVAI/UV Ratio	Contact Angle +/- St Dev	Sensory / Other Benefits
A	Neutrogena Spectrum+ Advanced Sunblock Lotion SPF 100+ Helioplex 360 full spectrum uva uvb Waterproof	Water, styrene/acrylates copolymer, silica, beeswax, glycine soja (soybean) seed extract, cyclopentasiloxane, glyceryl stearate, PEG-100 stearate, ethylhexylglycerin, acrylates/dimethicone copolymer, tocopherol, caprylyl glycol, acrylates/C10-30 alkyl acrylate crosspolymer, chlorphenesin, triethanolamine, disodium EDTA, dipotassium glycyrrhizate, BHT, chrysanthemum parthenium (feverfew) leaf/flower/stem juice, methylisothiazolinone, diethylhexyl 2,6-naphthalate, fragrance	0.83	40.2 +/-3.66	Ultra sheer light non-greasy
B	Neutrogena Spectrum+ Face Advanced Sunblock Lotion SPF 100+ Helioplex 360 full spectrum uva uvb Waterproof	Same ingredients as listed in product A without fragrance	0.84	40.05 +/-2.31	Ultra sheer lightweight non-greasy
C	Neutrogena AgeShield Face Sunblock Lotion SPF 110 Helioplex broad spectrum uva uvb Waterproof	Water, styrene/acrylates copolymer, silica, beeswax, cyclopentasiloxane, glyceryl stearate, PEG-100 stearate, ethylhexylglycerin, acrylates/dimethicone copolymer, acrylates/C10-30 alkyl acrylate crosspolymer, chlorphenesin, triethanolamine, disodium EDTA, dipotassium glycyrrhizate BHT, methylisothiazolinone, diethylhexyl 2,6-naphthalate, fragrance	0.8	53.1 +/-0.82	Ultra light non-greasy
D	Neutrogena UltraSheer Dry-Touch Sunblock SPF 100+ Helioplex Broad spectrum uva uvb Waterproof	Same ingredients as listed in product C in different order than in C	0.82	52.2 +/-3.09	Lightweight ultra light
E	Aveeno Active Naturals Continuous Protection Sunblock Lotion SPF 100+ Face active photo-barrier complex Broad uva uvb protection Waterproof	Same ingredients as in product C listed in different order than in C with additional ingredients: tocopheryl acetate, butylene glycol, ascorbyl palmitate, glycine soja (soybean) protein	0.84	57.1 +/-2.41	Lightweight, non-greasy
F	Neutrogena Ultimate Sport Sunblock Spray SPF 100+ Helioplex broad spectrum uva uvb Waterproof	Alcohol denat., isobutane, butyloctyl salicylate, acrylates/octylacrylamide copolymer, water, cyclopentasiloxane, acrylates/dimethicone copolymer, diethylhexyl 2,6-naphthalate, glycerin, tocopheryl acetate, saccharomyces/zinc ferment, saccharomyces/magnesium ferment, saccharomyces/calcium ferment, saccharomyces/potassium ferment, saccharomyces/sea salt ferment, ascorbyl palmitate, retinyl palmitate, artemia extract, fragrance	0.81	81.1 +/-2.19	Lightweight non-greasy
G	Coppertone ultraguard Sunscreen Lotion SPF 100+ Broad Spectrum UVA/UVB Protection Photostable Waterproof	Water, styrene/acrylates copolymer, propylene glycol, behenyl alcohol, glyceryl stearate, microcrystalline cellulose, benzyl alcohol, diethylhexyl syringyldienemalonate, palmitic acid, myristyl alcohol, stearic acid, hydrolyzed wheat protein/PVP crosspolymer, lauryl alcohol, cetyl alcohol, retinyl palmitate (vitamin A palmitate), tocopherol (vitamin E), sodium ascorbyl phosphate, lecithin, cellulose gum, chlorphenesin, fragrance, butylated PVP, disodium EDTA	0.82	62.9 +/-2.11	Moisturization
H	Banana Boat Sport Performance ActiveMAX Protect Broad Spectrum Sunscreen SPF 100 AvoTriplex Very Water Resistant	Water, hydrogenated polyisobutene, lauryl PEG-8 dimethicone, butyloctyl salicylate, ethylhexyl palmitate, hydrated silica, cyclopentasiloxane, cyclohexasiloxane, retinyl palmitate (vitamin A), ascorbic acid (vitamin C), tocopheryl acetate (vitamin E), PEG-8 dimethicone, sodium propoxyhydroxypropyl thiosulfate silica, octyldodecanol, silica, aloe barbadensis leaf juice, beeswax, disodium EDTA, microcrystalline wax, acrylates/C12-22 alkyl methacrylate copolymer, sodium chloride, polyethylene, stearyoxy dimethicone, caprylyl glycol, benzyl alcohol, methylparaben, propylparaben	0.85	33.9 +/- 3.12	None

Conclusions

Comparative evaluation of eight SPF 100+ commercial products launched in the U.S. in 2010 using in vitro test methods was conducted; study demonstrated that their photostability, UVAI/UV ratios in the range of 0.80-0.85 and good sensorial attributes can be considered beneficial to the consumer. However, all these products belong to the FDA proposed "High UVA Protection" category (three stars) while failing to fulfill the "Highest UVA Protection" criterion (four stars). Reaching the highest UVAI/UV ratio (four star) for sunscreens with SPF 100+ cannot be achieved with the use of sunscreen actives currently approved in the U.S. Measurements of the contact angle of water to quantify the surface modifying effects of test products on a skin-substitute substrate suggested similarities in sensorial profiles for certain SPF 100+ products. This study helps sunscreen consumers to better differentiate SPF 100+ commercial products while providing formulators with a useful testing approach to conduct in vitro benchmarking studies and optimize development of effective sunscreen products with good sensorial profile, moisturizing and other benefits.

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