THE EVOLUTION OF SUN CARE: ANTIOXIDANT PROTECTION

Sun care products have evolved extensively during the past four decades. In the 1970s and 1980s, an effective sunscreen was one that blocked burning UVB rays and permitted so-called healthy UVA rays to go through the skin. The emphasis was on protection from the then-perceived harmful UVB rays. In fact, UVA rays were termed friendly and beneficial tanning rays. A tan was considered healthy and a sign of wealth and wellbeing. This misperception resulted in increased damage to the skin since we now know that a tan represents an injury to the skin. More importantly, sunscreens gave sunbathers a false sense of security and allowed them to stay longer in the sun without the uncomfortable sensation of burning. The outcome was more damaging UVA rays were penetrating the skin!

In the 1990s and the 2000s, products focused on protection from the now-documented harmful UVA rays. These rays penetrate the skin much more deeply and are still sufficiently energetic to cause major damage to cellular material. Products created during this period resulted in a major increase in the use of UVA filters with more claims of broad-spectrum protection. While more documentation was presented regarding the damage caused by UVA rays from tanning booths, the practice continued unabated. The recent statistic from the 2012 Mayo Clinic study revealed that the rate of skin cancer among young female adults has increased an eightfold in the past two decades.[1] This increase may have a number of causes, yet it clearly implicates the unchecked use of the tanning parlors by young women seeking a tan.

This leads to the question, "Why are skin cancer rates still rising dramatically despite the improvement of sun care products with more efficient filters that provide protection from both the UVA and UVB rays?" The answer, of course, is not simple or satisfactory. The emphasis here is neither to describe past efforts nor to address the regulations, or lack thereof in the field of broad spectrum and is definitely not to address the efficacy and stability of UVA filters. Rather, it is to emphasize that contributing factors for this skin cancer epidemic may be in play. Suggestions that other factors are the main culprit for this epidemic are obviously premature, as new research on the mechanism of damage to the skin and human wellbeing is emerging. Future protocols for protection will undoubtedly be introduced, and ultimately we will prevail in significantly reducing the incidence of skin cancer worldwide.

Those at Risk

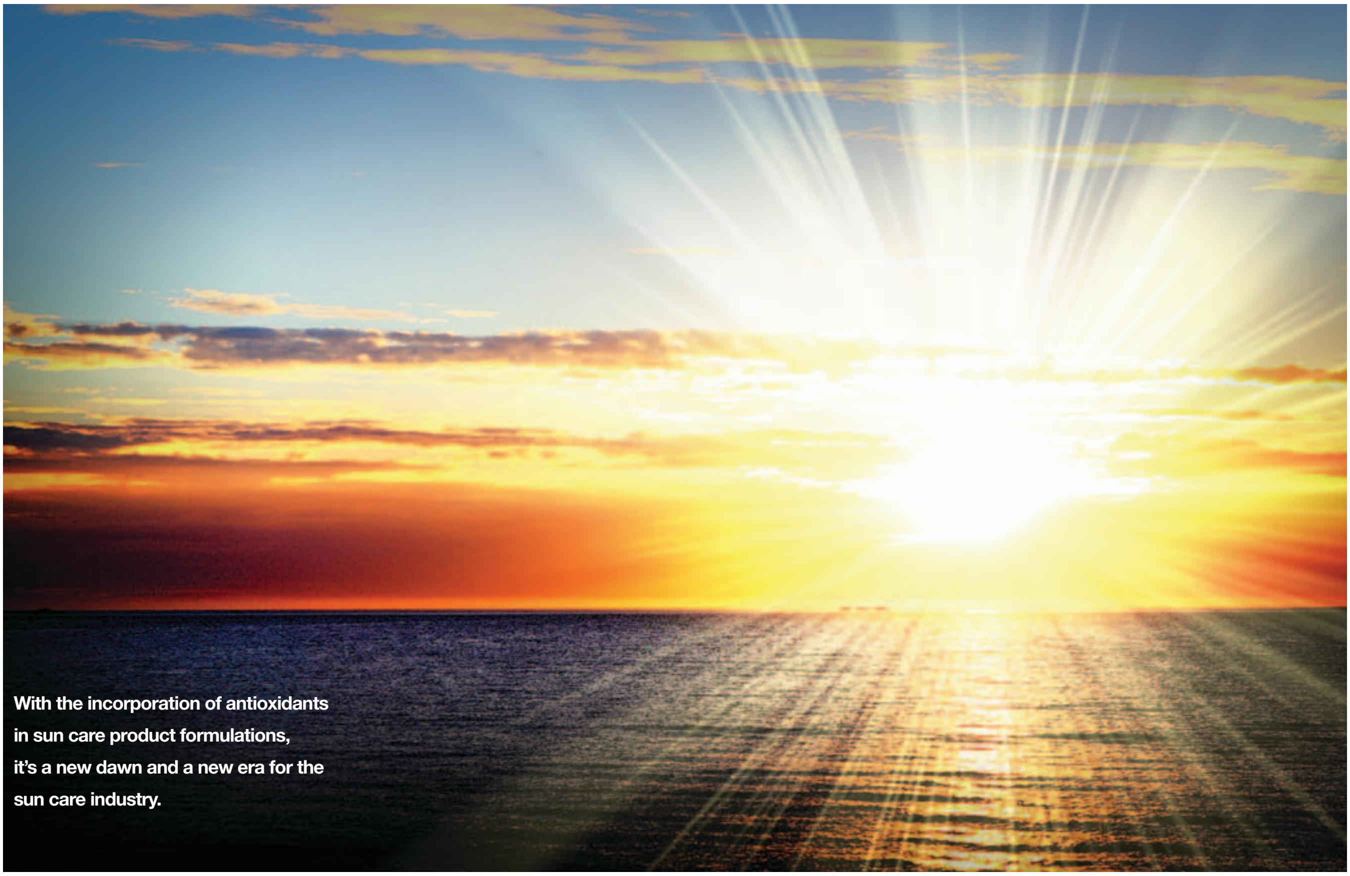
An examination of skin cancer pathology clearly points to a major increase among fair-skinned individuals who bask in the sun without adequate sun care protection or proper clothing or necessary protective skin characteristics such as melanin, proper genetic makeup or adequate internal repair mechanisms. It also implicates irresponsible behavior of excessive exposure to the sun and its elements, be it a noon sun or a tanning booth. Clearly, the main culprit is the sun's overall radiation and the resulting increase in damaging free radicals on the skin.

The solar spectrum extends from the ultraviolet, through the visible region and into the infrared radiation. Only 7% of the solar spectrum is the ultraviolet rays (280-400nm), as the majority of UVC radiation is blocked by the variable ozone layer. The visible rays (400-740nm) represent another 39% of the solar spectrum with the infrared rays (750-1,000,000nm) constituting the majority of the sun's rays (54%). Of the 7% UV rays, only 1% of the sun's total output is the damaging UVA rays, yet they are the major villains responsible for this epidemic. It is true that these rays have sufficient energy and long wavelengths capable of penetrating the skin's epidermal layers, and they are bound to cause a major portion of the damage. Yet, Haywood reported that the best broad-spectrum sunscreen on the market only blocks 55% of the free radicals formed on the skin due to exposure to the UV rays.[2] What happens to the remaining 45% of free radicals on the skin? What happens to the free radicals that are formed as a result of the vast majority (93%) of the sun's rays, namely the visible and the infrared rays? In the future, protection must include regimens that adequately deal with damaging free radicals that are active on our skin today from overexposure to the full spectrum of solar radiation.

Before delving into the free radical damage caused by solar radiation, it is important to understand the energies, frequencies and wavelengths of the different components of the sun's rays, as

Nadim Shaath
Alpha Research & Development Ltd
Email: alpharnd@aol.com

Dr. Nadim Shaath is the president of Alpha Research & Development, Ltd. in White Plains, NY. He has over 30 years of experience as chairman of the chemistry department at SUNY-Purchase and the CEO of Kato Worldwide. Recently he formed a consulting company serving the cosmetic industry called ShaathMeadows Corporation (SMC) with laboratories in New York, New Jersey, Texas, Florida and Egypt.



With the incorporation of antioxidants in sun care product formulations, it's a new dawn and a new era for the sun care industry.

well as the amounts emitted from the sun. Clearly the UV portion (7%) represents the most energetic rays, and every sun care regimen must include effective UVB and UVA filters as the primary mode of protection. The visible region generally represents healthy moderate radiation that causes a number of biological transformations and, of course, they emit the positive color portion of the spectrum—imagine life without rainbows! These energies are obviously less than those of UV, but they penetrate skin more deeply, and their natural abundance in the solar spectrum is significantly (39%) greater.

The energy from the infrared portion of the spectrum is clearly much less than the ultraviolet and visible portions. However, IRA rays penetrate most deeply into the dermis (65%). In addition, IRA alone represents a third of the solar rays and the full IR region represents a whopping 54% of the total solar radiation.

This massive amount of IR radiation that we receive daily from sun exposure, along with the many gadgets that we use today that emit infrared radiation; i.e., hair dryers, saunas and ovens, would have remained unnoticed if not for two important considerations. First, free radicals have been clearly identified and studied when dermal fibroblasts and human skin were irradiated with pure IRA.[3-6] Free radicals were implicated in a number of biological processes including an increase in the enzyme matrix metalloproteinase (MMP-1) that results in damage to the underlying collagen leading to skin damage. Second, IRB and IRC radiation is mostly heat waves that impart the warm sensation when we are exposed to the sun. This heat is due to the absorption of the IRB/C radiation by the water molecules present in skin, hence the need for effective moisturization. Water absorbs around the wavelength of the IRB/C rays that cause the oxygen-hydrogen bonds in the water molecules of the skin to stretch and vibrate resulting in friction that is perceived as heat on the skin. In chemical reactions, heat is a major catalyst making it an accelerator of the normally lower frequency and energy IRA radiation. The formation of these damaging free radicals, exacerbated by the increased heat perceived on the skin due to excessive solar radiation exposure, makes it crucial to include effective antioxidants in every sun care regimen.

Popular Antioxidants

As I was writing this column, I received a copy of Roger McMullen's "Antioxidants and the Skin."[7] This treatise has made the need to fully review antioxidants and skin so much easier. I was planning to write two articles on topical antioxidants, but with this publication that is no longer necessary. I will comment on some of the crucial aspects of the efficacy of antioxidants in topical cosmetic applications.

First, some of the most important antioxidants for topical cosmetic use include the vitamins which are listed

Citrus fruits such as lemons and limes are loaded with vitamin C.

in their order of discovery: Vitamin A (retinyl/retinal), vitamin C (ascorbic acid), vitamin D, vitamin E (tocopherols) and vitamin F (essential fatty acids). In addition, a number of ingredients are important antioxidants including: Lycopene, ferulic acid, niacinamide (nicotinamide), coenzyme Q (ubiquinone), idebenone, silymarin, quercitin, genisten, phloretin, oryzanol, curcumin, turmeric, oleuropein and resveratrol. Finally, a number of natural extracts have substantial antioxidant activity including pomegranate, coffeberry, grapeseed, rosemary, St. Johns Wort, feverfew, artichoke, jojoba, argan, pumpkin seed, kelp, papaya, watercress, pine bark, açai berry and green tea extracts.

A Review of Vitamin C

For illustrative purposes, and to demonstrate the effectiveness and drawbacks of antioxidants in sun care formulations, I will briefly review vitamin C, the gold standard of antioxidants.

Vitamin C is a weak sugar acid structurally similar to glucose. The body cannot synthesize it, and therefore it is an essential nutrient. In biological systems, vitamin C is found as the L-ascorbate enantiomer (the de-protonated form) as protonation to form the acid requires a pH of 4 or less. Vitamin C is a requisite cofactor in several enzyme reactions, especially those related to wound-healing and preventing easy bruising due to fragile capillary walls in animals and its role in many collagen synthesis reactions.

Vitamin C deficiency results in scurvy due to collagen synthesis dysfunction.[8,9] Ascorbic acid is widely used as a food preservative because of its antioxidant properties. It acts as an antioxidant, keeping iron and copper atoms in their reduced states. Ascorbate acts as an antioxidant by initially donating a single electron to neutralize a free radical and itself becoming an ascorbyl radical (semidehydroascorbate) in the process.

Most studies have shown that a minimum amount of vitamin C is required to be effective in quenching free radicals. Vitamin C must penetrate the skin and remain stable. Several derivatives have been employed, but the ascorbic acid itself remains the most important form for exerting maximum mitrochondrial activity so long as certain conditions are met. These conditions include a minimum of 10% (preferably 15%), a pH environment of 2.5-3.5 and stabilization by other components. Pinnel and his group have published studies elucidating the effect of ferulic acid in stabilizing ascorbic acid and vitamin E formulations.[10]

Some cosmetic and sun care manufacturers use their topical applications, a plethora of antioxidants, at ineffectively low concentrations. Only targeted antioxidants that are effective, stabilized, in the correct environment (eg. pH), in substantial percentages in the formulations and more importantly effectively penetrating the skin, are effective free radical scavengers.

It's very difficult to imagine formulations with 15% vitamin C for example, as being included in sunscreen formulations that are generally already loaded with more than 20% of ultraviolet filters and have a neutral pH of 6-7. Delivery of effective antioxidants for sun care protection may require the use of separate product categories other than those that deliver ultraviolet filters. Any attempts at formulating vitamin C antioxidants in regular sunscreen products are futile and ineffective. Such effective antioxidants require a separate category of products for the reversal of sun damage.

The gradual evolution of sun care ingredients is the result of ongoing research in response to real life needs. The more we learn about solar radiation[11] in particular, the more we can effectively address the causes of sun damage and cancer. The latest research on antioxidants represents the next stage in this industry's development and greater hope for the protection of people contending with the enormous power of the sun. •

References:

1. http://www.mayoclinic.org/news 2012

2. R. Haywood et al., (2006) "Sunscreens Inadequately Protect Against Ultraviolet A-Induced Free Radicals in Skin: Implications for Skin Aging andMelanoma?" *J. Invest. Dermatol.*, 121:862-8.

3. C.Calles et al., (2010) "Infrared A Radiation Influences the Skin Fibroblast transcription: Mechanism and consequences" *J. Invest. Dermatol.*, 130:1524-36

4. P. Schroeder et al., (2008) "Infrared Radiation induced Matrix Metalloproteinase in Human skin: Implications for Protection" *J. Invest. Dermatol.*, p.2491.

5. C.Elmets et al., (2010) "The other side of the rainbow: Infrared and Skin", J.Invest.Dermatol., 130: 1496-9

6. For a review of IR damage consult "The Suncreen Filter," Happi, May 2012.

7. R. McMullen (2013), "Antioxidants and the Skin", Allured Books, Carol Stream, IL.

8. NHS choices (2011), "Vitamin C" Vitamins and minerals". National Health Service (NHS), London, UK, http://www.nhs.uk/Conditions/vitamins-minerals/Pages/Vitamin-C.aspx

9. A. Evert (2011), "Vitamin C–Overview". University of Maryland Medical Center, Baltimore, MD.http://www.umm.edu/ency/article//002404.htm

10. S. Pinnel et al., "A Topical Antioxidant Solution Containing Vitamins C and E with Ferulic Acid Protects Human Skin from Sunlight Damage and DNA Mutations Associated with Skin Cancer", AAD poster presentation, New Orleans, Feb. 17, 2005. See also article in Dermatol.Surg.(2001), 27:137.

11. For a review of solar radiation, consult The Sunscreen Filter, Happi, March 2012.