Review of the current understanding of the effect of ultraviolet and visible radiation on hair structure and options for photoprotection

VITTORIA SIGNORI, BASF Corporation, 1705 Route 46 West, Ledgewood, NJ 07852.

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Synopsis

This article describes the current understanding of the effect of ultraviolet (UV) radiation and visible light on the structure and integrity of human hair fibers; furthermore, it discusses current and past approaches to the protection of hair from UV rays. Relevant literature is reviewed.

INTRODUCTION

Personal care products are formulated to deliver many benefits to the consumer. As the industry has become increasingly competitive, and the consumer has become more educated and at times rightfully skeptical of miracle-like claims printed on cosmetic products, the personal care scientific community has risen to the task of investigating the true cause of the effectiveness of some cosmetic treatments, and a great deal of understanding has been gained through these efforts. This knowledge is kept as a trade secret, patented, and delivered to the consumer in the form of innovative products, or shared openly in a scientific forum for the participating community to take part in the discussion. Either way, the whole personal care industry, some more enthusiastically than others, has embraced a more scrupulous way of looking at products and the scientific data in support of claims.

In the hair care discussion, hair damage has long been recognized to be an issue of great concern to most consumers. *Hair damage* is a generally recognized term that encompasses a variety of attributes, among which are dryness, ease to breakage, split ends, a coarse feel, lack of manageability, and lack of luster.

The following will give an overview of light and its interaction with organic compounds, solar simulators and their role in reproducing solar radiation, and the current understanding of the effect of ultraviolet (UV) radiation on the structure of human hair, as well as approaches aiming to limit these negative effects.

LIGHT, RADIATION, AND ENERGY

Exposure to radiation is a cause of concern to the personal care chemist, and in particular the radiation that has a great amount of energy, like UV, is known to cause many undesirable effects. For example, dyes, fragrances and carbomer-type thickeners exhibit varying degrees of instability upon exposure to light.

This article explores the potential for structural damage caused by UV radiation to human hair. Appendix I shows a number of basic equations that define the relationship of quantities and units of measures commonly used to describe light, radiation, and wavelength; Appendix II is a summary table of more complex functions like irradiance, radiant power, and radiant energy.

The following discussion will consider, light and its energy, chemical bonds and the energy required to break them, and the radiant energy coming from the sun that reaches the earth's surface and the spectral distribution of such energy. Table I shows the wavelength, frequency, and energy of different radiation.

Table II shows the energy required to break chemical bonds (bond dissociation energy); it is evident that the energy associated with UV is sufficient to break chemical bonds within the organic substrates (proteins, keratin, hair); in addition, the radiation of such energy as UV is capable of inducing free radical reactions that would have a lower activation energy and be even more likely than bond cleavage. The generally accepted mechanism for photo-oxidation is well presented by Robbins (2).

Figure 1 shows the actual values of the radiation power reaching the earth's surface at a specific point in time and geographical area. A large variation in the spectral power distribution is to be expected between times of the year, hours of the day, and the geographic location at which the measurements are taken (3).

The unit of measure of radiant power received per unit surface area is *irradiance* (W m⁻²). Irradiance is often associated with a wavelength or wavelength range (W m⁻² nm⁻¹); for instance, an average 1.5 W m⁻² nm⁻¹ over a wavelength range of 200 nm would give a total 300 W m⁻² total irradiance. The summation of irradiance over a period of time is called *irradiation energy* (or radiant exposure); e.g., irradiance of 1.5 W m⁻² over a period of five hours (= 18,000 s) is equal to 27,000 J m⁻². A radiant exposure of 3–6 KWh m⁻² day⁻¹ (= 10.8 × 10⁶ – 21.6 × 10⁶ J m⁻² day⁻¹) is the average for the US during the months of July and August (6). In comparison, in Australia, the global solar exposure in August is between 13 and 22 × 10⁶ J m⁻² day⁻¹ (6). The values reported above refer to the total solar radiation intensity, visible (VIS), and UV and infrared (IR) rays. Table III gives a breakdown of the ratio between VIS and UV radiation.

As seen in Table III, the irradiance ratio between UV and VIS radiation is approximately 1 to 10. Generally speaking, when the measurement of the solar radiation is referred to as *total*, that means that it includes visible, ultraviolet, and infrared (VIS, UV, IR) rays; when it is referred to as *global*, it means that the measurement was carried out in such a way as to capture the radiation from the sky, avoiding the radiation resulting from reflection on the ground. When the total radiation is considered, the relative proportions of UV, VIS, and IR, respectively, are 4–6%, up to 52%, and up to 42%.

 Table I

 Radiation's Frequency and Wavelength (1): Planck's Equation* Applies, and It Describes the Indirect Proportionality Between the Wavelength of the Radiation** and the Energy That Is Associated With It (the longer the wavelength, the lower the energy)

Wavelength, λ (m)	Radiation	Frequency, ν (Hz or s ⁻¹)	Energy of 1 mol of photons* (KJ mol^{-1})
$\overline{\begin{array}{c}10^{-12} - 10^{-10}\\10^{-10} - 10^{-8} (= 10 \text{ nm})\\10^{-8} (10 \text{ nm}) - 3.8 \times 10^{-7} (380 \text{ nm})\\3.8 \times 10^{-7} (380 \text{ nm}) - 7.8 \times 10^{-7} (780 \text{ nm})\\7.8 \times 10^{-7} - 10^{-4}\\10^{-4} - 10^{-2}\\10^{-2} - \dots\end{array}}$	γ-rays X-rays UV VIS Infrared Microwaves Radio waves	$3 \times 10^{20} - 3 \times 10^{18}$ $3 \times 10^{18} - 3 \times 10^{16}$ $3 \times 10^{16} - 7.8 \times 10^{14}$ $7.8 \times 10^{14} - 3.8 \times 10^{14}$ $3 \times 10^{12} - 3 \times 10^{10}$ $3 \times 10^{10} - \dots$	$11.95 \times 10^{7} - 11.95 \times 10^{5}$ $11.95 \times 10^{5} - 11.95 \times 10^{3}$ $11.95 \times 10^{3} - 314$ 314 - 153 153 - 1.19 $1.19 - 1.19 \times 10^{-2}$ $1.19 \times 10^{-2} - \dots$

* See Appendix I.

** Very often, the UV radiation is referred to as "UV light"; this is strictly speaking inaccurate, as the definition of light implies that it is visible to the human eye. UV radiation is not visible; therefore, it is a radiation rather than a light.

bolid Dissociation Energies (BDE) (4,3)			
Bond	Bond dissociation energy (KJ mol ⁻¹)		
C–H	413		
CN	293		
C=O	707		
C–O	335		
S–S	213		
O-H	463		
S–H	364		
C–C	348		
C=C	619		
C–S	259		

Table IIBond Dissociation Energies (BDE) (4,5)

It is important to note that although the BDE gives a good idea of the strength of a chemical bond, in practice, solvation can weaken bonds and cause great deviation from the value reported in this table. Solvation occurs when the "bonds" (molecules) are in a chemical environment where secondary chemical bonds are formed, e.g., H-bonds.

As for substrate degradation, the IR portion of the energy contributes to increase the temperature of the substrate.^a The energy associated with IR radiation is low compared to UV radiation. When the hair structure is considered, both melanin and the proteins compete for the absorption of light between 254 and 345 nm (7).

As this article will review some of the most recently published papers on this subject, it will become clear that although it is not immediately perceived, UV damage to hair fibers plays an integral role in the overall aspects of hair damage.

UV-RADIATION SOURCES, SOLAR SIMULATOR SYSTEMS

Solar simulators are standard equipment for weathering studies. Although natural light is, in most part, readily available, the seasonal variability and the fact that it is available for only half of the day is a drawback. In addition, solar simulators can be set up to expose the sample to light of greater intensity than natural light.

Two major factors need to be considered when using an artificial light source:

- 1. Correlation between natural solar radiation (visible and non-visible) and the artificial light source. Does the exposure to the artificial radiation produce the same effects on the test material as the exposure to natural radiation does?
- 2. Acceleration factor (if applicable): How many hours in natural light are equivalent to one hour of radiation exposure in the instrument (or vice versa)?

A publication by Q-Panel (3) clearly describes the many aspects of establishing the correlation of real sunlight to artificially generated light and UV radiation.

^a Q-Panel, private communication.



Wavelength (nanometers)

Figure 1. Solar spectral power distribution (Cleveland, OH, at noon, June 1986). Reproduced by permission of Q-Panel. The UVC, UVB, and UVA ranges were added by the author.

Some important factors in weathering tests are:

- 1. Moisture, condensation, and humidity. They have a great influence on the overall effect of solar radiation on different substrates.
- 2. *Temperature and temperature changes.* Photodamage is accelerated and influenced by the temperature of the substrate under scrutiny (also related to the amount of infrared radiation that the sample is exposed to).
- 3. Spectral distribution of the radiation. Some wavelengths are very crucial for specific materials (capable of breaking specific chemical bonds). The shorter the wavelength the greater the energy of the radiation; even small portions of very energetic radiation can have dramatic effects (Table I, Table II).
- 4. Sun angle. The higher the sun angle the shorter the pathlength of the radiation through the atmosphere. Shorter wavelength radiations are preferentially absorbed by the atmosphere; therefore, the higher the sun angle the greater the quantity of shorter wavelengths reaching the earth's surface (3).

Table III Spectral Global Solar Irradiance (ASTM G151)			
Wavelength range (nm)	Irradiance (W m ⁻²)	Percent of total	
300–400 UV	74.6	11%	
400–800 VIS	604.2	89%	

5. There is no rule to predict what the acceleration factor is for one instrument (solar simulator or UV source) and one substrate in a specific application and testing protocol. There is no value in taking studies that report acceleration factors obtained on paints and applying them to plastics or textiles or other substrates (e.g., hair).

In accelerated stability tests it is often tempting to do unrealistic extrapolations; the researcher needs to keep in mind that if the test involves personal care formulations that are intended for hair care, for instance, the protocol should include reasonable cycles of application of the formulation and cleaning of the hair by shampoo.

A good reference paper, although not developed for personal care products, is Crump's work on correlation study between different solar simulators and Florida sunlight as it applies to gel coatings (8). This type of paper will give the reader an example of how to set up a study to correlate an artificial radiation source to natural sun radiation.^b

The four points of developing a testing protocol can be summarized as follows:

- Choice of the hair substrate (pigmented, unpigmented, untreated, chemically treated, etc.),
- Choice of the type of formulations to be tested (shampoo, conditioner, hairspray, hair gel, etc.),
- Choice of the irradiation procedure, time, and light intensity (light sources, total energy delivered over the time set for the experiment, frequency of re-application of the formulations to the hair, relative humidity, temperature, etc.)
- Choice of analytical methods for the determination of the physical/chemical damage or changes occurring during exposure (tensile strength, amino acid analysis, IR spectroscopy, etc.).

LITERATURE REVIEW

EFFECT OF IRRADIATION ON THE STRUCTURE OF HUMAN HAIR

This section is dedicated to an in-depth understanding of the effect of visible and UV radiation on human hair as reported by a variety of authors. It is clear that there is no standard protocol on how to expose human hair to light and/or UV radiation, and there is no standard test for assessing the damage that UV radiation causes. The findings reported in the following mentioned papers confirm that both UV and VIS radiation can have a very significant effect on hair. Among the literature available on this and related topics, the following papers were chosen because of the relevance of the work presented to the way photoprotection for human hair is often considered from the formulation point of view.

The paper by Dubief (9) reported data obtained by exposing human hair to natural sunlight (with and without the UV portion of the radiation) as well as to artificial light; no UV absorbers were tested in these experiments. This is one of the few papers that

 $^{^{\}rm b}$ For background information, the reader may find useful consulting two ASTM publications: G155 and G151.

systematically compares the results from solar simulator to sunlight, and for this reason it is a valuable point of reference.

The findings refer to the effect of irradiation on hair structure:

- 1. Hair exposed to both sunlight and artificial light showed an increase in IR absorption bands characteristic of $C = O (1720 \text{ cm}^{-1})$ and $RSO_3H (1041 \text{ cm}^{-1})$ bonds. This indicates a change in the chemical "composition" of the hair; the hair is photo-oxidized.
- 2. Hair exposed to natural sunlight showed a decrease in tensile strength and was more prone to alkaline attack (alkaline solubility). Visible sunlight (no UV) increased the alkaline solubility and more than doubled the cysteic acid content of the hair (compared to unirradiated hair). The complete VIS + UV (sun) radiation further promoted an increase in alkaline solubility (almost quadrupling it from the unirradiated hair) and in cysteic acid content (more than quadrupling it with respect to the unirradiated hair).
- 3. The UV portion of the solar radiation promoted the changes in the fibers that lead to less protein being extracted (three months, 127,000 J cm⁻² (= 1.27×10^9 J m⁻²)). This was interpreted as possible evidence of protein cross-linking.
- 4. The main factor in photobleaching brown hair appeared to be the amount of VIS light. Only after approximately 100,000 J cm⁻² (= 10^9 J m⁻²), the samples exposed to VIS + UV radiation showed a greater photobleaching effect than with just visible light.
- 5. When brown hair was exposed to up to 150,000 J cm⁻² (= 1.5×10^9 J m⁻²) in the Xenon test at 88% RH, the fibers showed substantially more photobleaching than when they were exposed to the same radiation intensity in the Suntest at only 5% RH. The photobleaching obtained when the hair was exposed to natural sunlight, for the same radiant exposure, was distinctively greater than that obtained by artificial irradiation.

This study shows that there is some, but not perfect, correlation between the solar simulators used and the natural sun radiation. Some of the changes monitored, such as photobleaching, are more pronounced when the hair is exposed to natural light than to the solar simulators used. Relative humidity is shown to play a very important role in accelerating or increasing photobleaching. These findings are consistent with the work of other authors (as reported below). The magnitude of discrepancy between simulated light and natural light should be taken into account when interpreting data that was generated solely by sunlight simulators; such studies will also be reviewed in the following paragraphs.

A systematic study of the effect of UVB, UVA, VIS, and IR energies on human hair was carried out by Hoting *et al.* in a two-part paper (7,10). The authors investigated the effect of radiation on both chemically untreated and chemically treated human hair of different pigmentation levels (light to dark brown). The equipment used was especially designed to reproduce the different portions of the solar radiation, and the hair was exposed for a prolonged period of time, 1008 hr, at 25° -48°C, 70-94% R.H.

- 1. VIS radiation produces more photobleaching that UVA or UVB radiation, UVB being the feast effective. In all cases, to different extents, permed, dyed, and particularly bleached hair is more prone to photobleaching than hair that was not cosmetically treated.
- 2. Dark hair is more protected against photobleaching than light brown hair.
- 3. UVB radiation produces the most apparent changes in the chemical composition of

the cuticle of both dark or light brown hair (photo-oxidation). A high concentration of melanin pigments (dark brown hair) protects the whole fiber, but not the cuticle, against photo-oxidation (melanin granules are present in the cortex of the fiber, not in the cuticle).

4. Evidence of cross-linking of keratin was found when the hair was exposed by either UVA or UVB radiation.

Although the energy to which the samples were exposed was perhaps a little excessive (see Table IV), the results are consistent with the work of other authors, and this paper is particularly informative for differentiating the effect of UVA and UVB radiation on hair structure, which is a topic often discussed while choosing the appropriate UV absorber for photoprotection.

A study by Ruetsch, Kamath, and Weigmann (11) also studied hair photodamage under conditions of prolonged exposure to UV radiation, and hair has been found to undergo substantial changes, both chemical and morphological. These changes were more pronounced, as more humidity/moisture was available during exposure. The number of hours of exposure used in this study was up to 700 hr. Two artificial light sources were used in this study: the Accelerated Weathering Tester^c (QUV), simulating UV radiation and the Atlas Weather-Ometer^d (AW), simulating UV and VIS radiation. The humidity, the temperature, and humidification cycles were controlled throughout the experiments.

This comprehensive study confirmed findings from other authors (no UV absorbers were tested in these experiments):

- 1. Both UVB and UVA radiation caused photodegradation of hair involving both proteins (keratin) and pigments (melanin). Photo-oxidation occurs at the cystine C-S bond to yield 1 mole of cysteic acid among the products of reaction, and the mechanism is thought to be free radical in nature (12). This mechanism is different from chemical oxidation that follows the S-S scission pathway yielding 2 moles of cysteic acid.
- 2. Photodegradation of hair proteins was more pronounced in unpigmented/blonde hair, the highest level of photodegradation occurring in the cuticular region, where cystine is present at its highest concentration.
- 3. Prolonged (700 hr) UV irradiation (290–400 nm, with QUV, 95% RH at 42°C) produced the thinning and the fusion of cuticular cells; the proposed theory is that the outer proteic layers would photodegrade to smaller, lower-molecular-weight peptides, which would then diffuse into the hair structure when enough humidity would allow for the fiber's swelling.
- 4. In prolonged exposure to UV radiation (700 hr) and also to humidification cycles (but no water immersion or shampoo cycles) using the QUV simulator, the authors found that melanin was not degraded, the pigmented hair retained its color, and the

^c Simulates sunlight in the range of 290–400 nm. The irradiance at 340 nm is equal to 0.97 W m⁻²; the total irradiance between 300 and 400 nm was equal to 5.06 mW cm⁻².

^d This instrument emitted UV as well as visible light; the irradiance at 340 nm was kept constant at 0.3 W m⁻²; the irradiance between 300 and 400 nm was equal to 4.46 mW cm⁻². The total irradiance of this source was 41.272 mW cm⁻².

Table IV

Summary of Solar Light Irradiation Energy and Power, and Exposure Time and Humidity Used by Several Authors in Their Studies (some quantities were derived to SI units from the quantities reported in the articles).

Wavelength	Spectral Irradiance		
range	or	Reference	
(nm)	Irradiation Energy		
300-315	< 0.7 W m ⁻² nm ⁻¹	Solar radiation	
315-380	0.5 - 1.2 W m ⁻² nm ⁻¹	Cleveland , OH, June 1986	
380-700	1.2 - 1.9 W m ⁻² nm ⁻¹	(Q-Panel)	
300-400	74.6 W m ⁻²	Spectral Global Solar Irradiance	
400-800	604.2 W m ⁻²	ASTM G151	
UV-VIS-IR	10 106 – 20 106 J m-2 day-1	Renewable Resource Data Center, National Renewable Energy Laboratory and Bureau of Meteorology of Australia (Data available on the internet)	
UV-VIS-IR	6,330 x 10 ⁶ J m ⁻² year ⁻¹ = 520 x 10 ⁶ J m ⁻² month ⁻¹ = 17.3 x 10 ⁶ J m ⁻² day ⁻¹	Q-Panel	
UV	= 300 x 10 ⁶ J m ⁻² year ⁻¹ = 25 x 10 ⁶ J m ⁻² month ⁻¹ = 0.82 x 10 ⁶ J m ⁻² day ⁻¹	(Actual data for Florida, an average of 3 years)	
VIS	52 % of the total energy is VIS: = 3,300 x 10 ⁶ J m ⁻² year ⁻¹ = 270 10 ⁶ J m ⁻² month ⁻¹ = 8.9 10 ⁶ J m ⁻² day ⁻¹	(Personal Communication)	

IRRADIATION PARAMETERS USED BY THE DIFFERENT AUTHORS

Wavelength	Spectral	Irradiation	Source of	
range	Irradiance	Energy	radiation	Comments
(nm)	(W m ⁻²)			
		8 x 104 –	Solar	(Dubief) Up to 3 months (natural light).
		18 x 104 J cm-2	radiations,	Up to 360 hr (15 days, 1.3 x 10 ⁶ s) of
UV- VIS	615 –		Suntest and	exposure to artificial light.
	1,384	(8 x 10 ⁸ –	Xenontest	Suntest: 40° C, 3-7 % RH
		1.8 x 10 ⁹ J m ⁻²)		Xenotest : 25° C , 88% RH
280-350 UVB	2.5	9 x 10 ⁶ J m ⁻²		
320-400 UVA	48	1.8 x 10 ⁸ J m ⁻²		(Hoting) Total irradiation time 1,008 hr
370-780 VIS	463	1.6 x 10 ⁹ J m ⁻²	Lamp + filters	(= 3.62 x 10 ⁶ s), 25-48° C at 22-94 %
750-2,800 IR	440	1.6 x 10 ⁹ J m ⁻²		R.H.
280-1,100	1,037	3.7 x 10 ⁹ J m ⁻²		
Global				
300-400	50.6	= 127 x 10 ⁶	QUV solar	(Rutsch) Up to 700 hr exposure (2.52 x
UV		J m ⁻²	simulator	10 ⁶ s), 10-95 % RH, 40°-50° C.
300-400	44.6	= 112 x 10 ⁶	AW solar	Oxidative post treatments and water
UV		J m ⁻²	simulator	immersion post-treatments.
300-700	412.7	= 104 x 10 ⁷	(UV+VIS)	Accelerated weather testing
UV + VIS		J m-2		Atlas weather-Ometer
280-320 UVB	1.4	2.42 x 10 ⁶		(Gao) 20 days (1.73 x 10 ⁶ sec), 27° C, 65
		J m ⁻²	Different lamps	% RH, treatment repeated every 24 hr.
320-400 UVA	4.9	8.47 x 10 ⁶	were combined	
		J m ⁻²		
Daylight		139 x 106-	Atlas Ci35A	(Pande) 96 hr-226 hr (=9 days), 50° C,
simulator	178-401	312 x 10 ⁶ J m ⁻²		50% RH.
UV +VIS				(up to 0.813 x 10 ⁶ sec)
Daylight			Heraeus	(Bernhard) Up to 30 days, 50% RH, 25°-
simulator	41.3	107 x 10 ⁶ J m ⁻²	Xenon Test	45° C. 5% Solids of different UV filters.
UV+VIS				(Up to2.59 x 10 ⁶ sec)
UVB	2.77	10 ⁷ J m ⁻²	UVB lamp	(Inove) 100 hr irradiation time

It is important to note that an equivalence in the energy that the sun is radiating and that of a solar simulator does not necessarily reflect a true correspondence in terms of the effect on the substrate (hair) properties.

pigment granules appeared intact. However, when the same pigmented (and previously UV-exposed) hair fibers were treated with alkaline hydrogen peroxide, melanin was instantaneously disintegrated, revealing that severe damage was produced by the UV irradiation to both keratin and melanin.

5. Water and humidity are believed to have a very crucial role in the decomposition of the protein structure and in the mechanism of photobleaching. High RH accelerates photochemical oxidation of hair and is the primary contributing factor to accelerated loss in hair color (melanin).

The findings in this paper indicate that prolonged UV irradiation can have a devastating effect on human hair. Also, it is crucial to introduce high-humidity or better shampoo/cleansing/water immersion cycles into the protocol of exposure of hair to UV/VIS radiation to induce some of the changes that would not otherwise been observed.

In 1993 Pande and Jachowicz published a paper in which the amino acid tryptophan (Trp) is identified as an early indicator of photodamage in human hair (13). Trp is an integral part of keratin and it absorbs UV rays at a maximum wavelength of 280 nm. The study shows that both simulated light (irradiation wavelength 295 nm) and sunlight (summer in Connecticut, total exposure length 72 hr) can damage Trp, resulting in the depletion of its fluorescence emission. The effect of water versus mineral oil was also explored; the experimental procedure employed appears to give more accurate results when the fibers are soaked in a medium. While no great difference was found between wet or dry fibers^e exposed to UV radiation, a big difference was found between water-soaked fibers and fibers soaked in mineral oil. The rate of destruction of Trp was found to be much lower in non-polar media (mineral oil) than in water.

The study hypothesizes on the kinetics of photodegradation, proposing that the photodegradation of Trp precedes that of the disulphide bond in keratin, where significant loss in Trp is detected before any increase in photo-oxidation products is detected. UVweathered hair appears to be characterized by a lower Trp, but by a higher cysteic acid concentration. This paper describes a unique approach to the investigation of photodamage, very specific to one amino acid. Some effort was made to correlate natural light to the radiation emitted by the solar simulator; however, this comparison was not very comprehensive.

More recently, Inoue *et al.* (14) reported that a type of protein, classified as S1003A (high cystein content protein) and found predominantly in the cuticular region (endocuticle), is thought to be intimately involved in the disulphide bond cross-links that determine the structural integrity of hair fibers. This study shows that irradiation of hair with UV radiation induces damage to the S1003A disulphide bonds that link the protein to the rest of the hair matrix, resulting in the ability to elute the protein from the hair fiber. UV irradiation was performed using a UVB lamp (100 hr, 10 J cm⁻² hr). A four-stage model was proposed where the elution of S100A3 is the major cause of hair damage. The authors conclude that UV radiation, as

^c Dry hair fibers gave more background noise and less contact area with the sample holder cell. Possibly because of lesser accuracy, no significant difference was found between irradiated dry and irradiated wet hair fibers, in terms of Trp content.

well as daily shampooing and grooming practices, contributes to what is defined as hair damage.

Although different irradiation methodologies were used, as well as different analytical tests, the results of the studies herein reviewed indicate very similar findings. All results are summarized in the Conclusion section of this paper.

OPTIONS FOR PHOTOPROTECTION ON HUMAN HAIR

In the previous section the effect of radiation on the structure of human hair was discussed in detail. It is apparent that there is unanimous consensus on the fact that UV or VIS radiation is capable of altering the chemical composition, morphology, and appearance of human hair. The following discussion will describe a few options for the photoprotection of human hair through the use of UV absorbers formulated in hair care products.

Pande and Jachowicz (13) proposed two approaches to photoprotection of hair: (i) reducing the amount of rays reaching the hair structure (via use of UV filters) and (ii) changing the chemical environment that favors the photodegradation of Trp to one that quenches photochemical intermediates or retards the excited-state decomposition. The authors agree with the model according to which Try sensitizes the decomposition of other amino acids.

In their studies it was found that a leave-on styling formulation containing 0.2% w/w of octylmethoxycinnamate (OMC) was successful at reducing the extent of Trp photodegradation up to 40%.^f Also, the problem of delivering the UV filter to the hair from rinse-off formulations was discussed. The oil-soluble UV filters do not normally have affinity for the hair, and the deposition of oily ingredients or of oil-soluble ingredients from rinse-off products is very formulation-dependent. This paper concluded that in many cases UV filters^g will only deposit in minimum amounts from cleansing or conditioning rinse-off products, mainly due to their poor affinity for the substrate and the short contact time (e.g., hair-to-shampoo). This topic is of much importance since it is one of the determining factors in whether or not a formulation is capable of providing photoprotection to the hair. Other aspects of this discussion will be explored in the next few paragraphs.

Bernhard *et al.* (15) described their work that involved five UV absorbers and two cosmetic formulations (hair-setting lotion and hairshine spray). The irradiation energy used was up to 29,880 Whm⁻² (Heraeus, Xenon test) (29,880 Whm⁻² = 107×10^6 J m⁻²), and the total irradiation time was up to 30 days (RH 50%, 25°–45°C). Before these authors tested the efficacy of the sunscreens as applied to hair from a cosmetic formulation, they tested the stability of the sunscreens themselves as they were exposed to the radiation. The results indicate that after ten days of irradiation Benzophenone-3 was the most stable (90%), Benzophenone-4 was less stable (60%), and octyl dimethyl PABA and phenylbenzimidazole sulphonic acid were even less stable. The photostability

^f The protocol followed for the irradiation was 10 hr, followed by a shampoo. This was repeated three times to give 30 hr total irradiation time.

 $^{^{}s}$ No cationically modified sunscreens were tested in this study; these compounds are now widely available in the market and are designed for hair care, rinse-off application.

of UV absorbers is another determining factor in providing photoprotection. The concentration of the sunscreens tested in this work was 5% solids, and the formulations were applied by immersing the hair in the formulations, to aid in the uniformity of application. The test protocol included application of the formulation, drying, irradiation for three days, washing with 1% SLS, rinsing, and drying. This cycle was repeated ten times during the duration of the experiment. Benzophenone-3 and -4 were shown to provide better protection than the other UV absorbers tested in terms of protection from melanin photobleaching and retention of tensile properties.

The ability of UV absorbers to penetrate the hair shaft was investigated. Although none of the UV absorbers tested were shown to have diffused through the hair fiber, the distribution of the UV filters on the hair fiber surface was even greater in the case of the oily-shine spray formulations. Two different formulations, carrying the same UV absorber, showed different overall effectiveness towards protection of the hair from the radiation. A number of mechanisms may be responsible for that, including H-bonding, interaction of the UV absorber with PVP, and other possibilities that are discussed in the article.

One may conclude that when different formulations are used as vehicles for UV absorbers for the protection of hair, overall efficacy does not solely depend on the UV absorber used and on its concentration, but is the result of complex interactions between the active material, the vehicle used, and the substrate. A very good point was made in this study, to investigate the stability of UV absorbers under UV irradiation. This factor could be a determining one when prolonged irradiation times are used and the test formulation is not reapplied to the hair samples.

The impact of the choice of UV absorber on the formulation's appearance and performance (other than photoprotection) is eloquently presented by Georgalas (16). This author comments on the challenges of formulating with sunscreens in hair care. The paper covers a variety of chemical classes of sunscreen and discusses a few points that are very relevant to formulation strategy:

- 1. In rinse-off formulations (shampoos and conditioners), oil-soluble sunscreens can be treated as if they were fragrances (need to be solubilized/emulsified). Water-soluble sunscreens can sometimes be more easily incorporated, although incompatibilities and pH-dependent solubility may be very important.
- 2. In styling aids (carbomer gels), some water-soluble sunscreens may have a saltthinning effect and the oil-soluble sunscreens may require solubilizers/emulsifiers, which may have a sharp impact on the thickness of the gel and its clarity (causing a haze or imparting a yellow coloration to the gel).
- 3. With hairsprays, the large amount of solvent, ethanol, makes it easy to incorporate sunscreens into these formulations; however, during application, hairsprays deposit droplets onto the hair shaft. A large portion of these droplets stay as such and dry at the intersection of the hair fibers, and consequently a very small portion of the hair shaft surface is covered by the hairspray formulation. In summary, hairsprays do not form a continuous film onto the hair fibers; therefore, they do not offer uniform surface protection.
- 4. Some sunscreens, Benzophenone-3 and -4, for instance, are beige, powdery substances; there is a need to make sure that the sunscreen active does not recrystallize once the solvent from which they were deposited onto the hair (e.g., ethanol or water) has evaporated.

All of what has been written so far indicates that oil-soluble sunscreens present some challenges from the formulation point of view. The formulations need to be cosmetically acceptable, the sunscreen needs to be delivered to the hair in a more or less uniform manner, and it should be deposited onto the hair and retained by the substrate to provide protection for a period of hours or maybe a couple of days (until reapplication). Also, as has been reported so far, there is little learning that is transferable from one formulation to another; all the data reviewed appears to be very formulationdependent.

In summary, traditional water-insoluble UV absorbers are difficult to deliver to the hair, and traditional water-soluble UV absorbers can be easily washed off from the hair during the rinsing steps of hair care product application. The term *traditional* is used here to describe sunscreens that have been mainly used for skin protection and sun care formulations and that have also been investigated for the protection of human hair. A different class of sunscreens, cationically modified, is discussed in the next paragraphs. Zulli (17) describes the delivery of lipophilic UV absorbers (isoamyl p-methoxycinnamate and avobenzone) to the hair via preparation of cationically charged nanovesicles. The nanoparticles described were prepared by high-pressure homogenization of a phospholipid dispersion. With this mechanism the particles can be designed to be positively charged or even negatively charged. The positively charged particles, unlike the negatively charged ones, show affinity for the hair, even from rinse-off treatments. A different class of UV filters was investigated by Gao and Bedell (18). In this case, affinity was achieved by cationically modifying the UV-absorbing molecule. The authors investigated the effectiveness of cinnamidopropyltrimonium chloride (CATC, a cationically modified UV absorber) as it compared to octylmethoxycinnamate (OMC) on natural grey hair.

The paper describes a shampoo formulation based on sodium lauryl sulphate (10%) and 2% sunscreen (CATC or OMC). Under these conditions, OMC, an oil-soluble compound, was solubilized by the surfactant. CATC was thought to form a complex with the surfactant, subsequently to be solubilized by it. The application of the formulation to the hair was by immersion and it was followed by a rinsing step. The application (and rinse) was performed after every 24 hours of irradiation; the total irradiation time was 20 days (27°C and 65% RH). The distribution of the UV irradiation was given by combining the following two sources (no VIS light source was added): 280–320 nm (UVB), 0.14 mW cm⁻² (= 1.4 W m⁻²), and 320–400 nm (UVA), 0.49 mW cm⁻² (= 4.9 W m⁻²).

The irradiated and non-irradiated hair was analyzed for color change (CIE L*a*b*, DL, Db, and DYI, yellowing index), fiber diameter and cross-sectional area, tensile strength, wet combing force, dynamic contact angle, and transverse swelling. The substantivity (19) of CATC, under the conditions employed, was found to be 4.5 g of material deposited per 100 g of hair. Only trace amounts of OMC deposited under the same conditions; this is not surprising since the formulation was not optimized to deposit OMC. On the other hand, CATC, being cationically charged, has an intrinsic affinity for the hair fiber. Although the paper does not go into detail on the interactions between the cationically modified UV absorber and the anionic surfactant, it is plausible to expect that the two oppositely charged moieties will form some sort of complex, and perhaps it is the complex that is depositing onto the hair as well as, or instead of, the free cationic UV absorber molecule.

The following points summarize the results presented in this paper:

- 1. Gray hair changes color, turning yellow upon exposure to UV radiation. CATC effectively prevents gray hair from changing color when compared to the untreated samples.
- 2. Brown hair treated with CATC changes less in color (photobleaching) than the untreated, UV-exposed sample.
- 3. The OMC-treated hair was substantially less protected from UV radiation, with results more similar to the untreated hair than to the CATC-treated hair (OMC deposited on the hair in much lower concentration than CATC from the test formulation studied). The test hair samples were analyzed for changes in color, wet combing force, tryptophan concentration, cuticle abrasion, and change in contact angle.
- 4. When the treated hair tresses were tested for tensile strength (Young's modulus and stress-to-break), all four hair tresses tested (not exposed to UV, CATC + SLS, OMC + SLS, and SLS alone) scored with approximately the same difference, from one to the other. The most damaged was the SLS-treated hair, and the least was the unexposed; CATC + SLS gave more protection than OMC + SLS. A similar trend was observed when transverse swelling was measured.
- 5. Hair tresses pretreated with SLS + CATC, and irradiated with UV, showed improved wet compatibility when compared to the unirradiated samples.
- 6. Gray hair is more sensitive to UV-induced damage than dark brown hair.

This study investigates the properties of two UV absorbers that have different solubility and intrinsic charges; it is not surprising that OMC performed quite differently from CATC in the tests described. The mechanism of deposition of the UV absorbers onto the hair was not described by the paper, but it is reasonable to assume that the mechanism would involve both hydrophobic forces (OMC, CATC) as well as ionic interactions (CATC). It is interesting that although OMC was solubilized by the surfactant system, it did show some degree of efficacy in some of the experiments.

A totally different approach to photoprotection was investigated by Pande et al. (20). They investigated the role of hair dyes (oxidation, as well as direct dyes for hair color) in the photoprotection of human hair (as monitored by tensile strength measurements). The total irradiation time was between 96 hr and nine days (13.9 kJ cm⁻², 31.2 kJ cm⁻²), depending on the dye product investigated. The instrument used was an Atlas Fadeometer Ci35A, 50°C, 50% RH. The data presented in this article showed that natural unpigmented hair (Piedmont) is more damaged by irradiation than naturally pigmented hair (brown). In addition, hair color (artificial) does provide protection from UV-VIS irradiation; in all cases, the darker the color shade, the more the protection. A distinct difference was also identified between oxidation hair color and direct hair color. The testing protocol used involved subsequent cycles of hair dying and shampooing, which is very appropriate when studying the fading behavior of artificially colored hair, even if the dyes used are oxidation colors (oxidation dyes are usually considered to be less prone to fading by shampoo; however, red shades are more sensitive to it than dark shades). Another aspect to keep in mind is that while oxidation colors have the ability to penetrate completely though the hair fiber, direct dyes do not always penetrate much into the fiber. Depending on the depth of the shade, this may have a substantial impact on the results of irradiation. A direct dye that has heavily deposited on the surface of the hair fiber may act as an effective screen for any radiation to penetrate into the fiber, thereby protecting it.

SUMMARY AND CONCLUSIONS

From the discussion presented it is clear that there is no real doubt as to the undesirable effect of visible and/or UV radiation on hair structure and physical integrity. Surprisingly, there is very little data to show the correlation between natural radiation and artificial radiation. In any case, a number of findings are consistent among all reports. The following is a summary of the commonly shared results:

- 1. For the most part, photobleaching, the attack to the melanin granules, is caused by visible light; the UV portion of the radiation promotes/accelerates it. UVA radiation is more effective than UVB radiation in inducing photobleaching. Humidity and moisture contribute significantly, enhancing this phenomenon.
- 2. Photo-oxidation of the hair fiber follows a different mechanistic pathway than chemical oxidation; water is a crucial medium in which free radicals diffuse, thereby enhancing the chemical reactions taking place during photodegradation.
- 3. Damage to protein and lipids in the cuticle of the hair fiber are caused by UVA and UVB irradiation, but only marginally by VIS rays.
- 4. It was shown that irradiation of hair with UVB light induces damage to the S1003A disulphide bonds that link this protein to the rest of the hair matrix, resulting in the ability to elute the protein from the hair fiber and indicating structural damage produced by irradiation.
- 5. Both VIS and UV radiation can, independently, promote the conversion of cystine to cysteic acid (photo-oxidation); UV radiation is more effective at promoting this degradation.
- 6. The amino acid tryptophan can be used as an early indicator of photodegradation of human hair.
- 7. Unpigmented (gray or Piedmont) and lightly pigmented (light brown) hair fibers are substantially more prone to photo-induced damage than pigmented fibers (dark brown and black). Melanin does not protect the cuticle layer (which is free from melanin granules) against the damage induced by UV radiation, but it does protect the whole fiber (cortex, where the melanin is present).
- 8. Eumelanins are less prone to be degraded by irradiation than pheomelanins; on the contrary, eumelanins are more prone to chemical oxidation (bleaching) than pheomelanin.
- 9. UV radiation has clear effects on the physical measurements correlated to the strength and integrity of the hair fiber: it decreases the stress-to-break, the Young's modulus (fiber strength), and dynamic contact angle (hydrophobicity), and it increases the wet-combing force (coarser, difficult to manage hair), copper uptake (negative sites in the fiber), and the transverse swelling of the hair fiber (index of the level of unaffected cross-linking of the proteic matrix constituent, the hair cortex).
- 10. Prolonged exposure to UV radiation can cause dramatic changes to the physical properties of human hair; in extreme cases irradiation can cause the whole cuticular layer to disintegrate, exposing the cortex.

The studies that report on the effectiveness of UV absorbers in reducing the damage present a rather more complex picture; the underlying problem that every author was faced with was the one of choosing an appropriate formulation in which to incorporate the UV absorber. Even more challenging was the choice of one or more formulations that would be suitable to compare different UV absorbers (some are hydrophobic, some are water-soluble, some are oily substances, some are powders!). While a number of authors made a considerable effort in the comparison of two or more UV filters, there was no straightforward solution to the problem: a system that would work with some UV absorbers would not work for others, making the comparison difficult. It is clear, though, that a number of UV absorbers were shown to "protect" the hair fiber from physical degradation as well as from color degradation. UV absorbers that were specifically developed for hair care applications (cationically modified), as well as vehicles that would impart affinity to the hair to oil-soluble sunscreens, showed effectiveness and ease of application. A different approach to photoprotection is offered by the evidence that shows that artificial hair color (permanent or not) protects the hair's mechanical integrity from the damaging effect of light (VIS or UV).

Another note of considerable importance is the possible, and in many cases probable, lack of correlation between the radiation emitted by the sun and that emitted by the solar simulator. More importantly, it is known that even small differences, at very high energy frequencies (UV), can result in big differences in results when comparing the effect of natural light exposure to that of artificial light. A comparison between the irradiance or irradiation energy used by the different authors whose articles are reviewed is shown in Table IV. The values were converted into SI units and, where it was not reported by the authors, the irradiance was transformed into irradiation energy and vice versa, thus simplifying the task of comparing different exposure conditions. It is important to note that although it may appear that some of the exposure conditions for solar simulators are similar to the irradiation energy coming from the sun for a period of a few days or a few months, this table does not mean to imply that equal radiant energy of exposure is a guarantee of realistic results (i.e., in vitro = in vivo).

Since it is useful to present some hypothetical cases of exposure to sunlight, the following cases are rough approximations of possible exposures and are all the result of calculation and not actual measurements:

- Spending all day outdoors in a sunny week of summer: between 70 × 10⁶ and 140 × 10⁶ J m⁻² week⁻¹ (UV-VIS-IR) and 6 × 10⁶ J m⁻² week⁻¹ (UV only).
 Spending half a day outdoors: approximately 60 × 10⁶ J m⁻² week⁻¹ (UV-VIS-IR)
- and 3×10^6 J m⁻² week⁻¹ (UV only).
- 3. Spending only a few hours per day outdoors, probably in the later afternoon and evening: approximately 20×10^6 J m⁻² week⁻¹ (UV-VIS-IR) and 1.15×10^6 J m⁻² week⁻¹ (UV only).

Most of the authors used reasonable exposure conditions, although the only real way to know would have been to carry out a parallel test using natural sunlight. Most of the irradiation energies used in the studies reviewed were in the same order of magnitude as the exposure for a whole year (case 1 calculated above).

For future experiments involving hair photoprotection, it would be advisable to carefully balance the steps in the testing protocol to reflect a reasonable amount of UV-VIS radiation and moisture and to allow for the hair to be washed with shampoo and perhaps treated with a rinse-off conditioner, in order to achieve a higher degree of confidence for the correlation of laboratory versus real-life conditions. Despite the many differences in approach that the different authors chose to adopt, there is an overall agreement on what the most important factors are in hair photodamage.

APPENDIX I

Planck's equation:

 $\mathbf{E} = \mathbf{h} \mathbf{v}$

E = energy of one photon (J)

h = Planck's constant (6.62 x 10^{-34} J s)

v = frequency of radiation (s⁻¹ also Hz)

Also:

 $v = c/\lambda$

 λ = wavelength of radiation (m)

 $c = speed of light (3 \times 10^8 m/s)$

Therefore:

 $E = (h c)/\lambda$ energy per molecule

Also:

 $E' = N_A (h c) / \lambda$ energy per mole

Where NA is Avogadro's number (6.022 x 1023 mol-1) and E' is expressed in J mol-1

The relationship between wavelength (nm) and E' (kJ mol⁻¹) can be summarized:

 λ (nm) = 11.96 10⁴ / E' (kj/mol)

N.B.: 1 cal = 4.184 joule

Prefixes for units

106	mega	10-3	milli (m)
10 ³	kilo (k)	10-6	micro (µ)
10-2	centi (c)	10-9	nano (n)

Some conversion factors

 $1 \text{ KJ cm}^{-2} = 10^7 \text{ Jm}^{-2}$ $1 \text{ Jcm}^{-2} = 10^4 \text{ Jm}^{-2}$ $1 \text{ mW cm}^{-2} = 10 \text{ Wm}^{-2}$ 1 day = 86400 sec

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APPENDIX	Π
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Term	Symbol/s	Units	Luminous energy term (21)	Units	Equation/ description
Wavelength	λ	m			
Frequency	ν	s ⁻¹ , Hz (hertz)			$v = c/\lambda$
Wavenumber	m	m -1			<i>m</i> = 1/ν
Force	N (newton)	kg m s ⁻²			Force = (mass) x (acceleration)
Energy	J (Joule)	N m			
Power	W (watt)	J s -1			
		J (joule),			
Radiant Energy		kg m² s⁻²			
Radiant exposure		J m ^{.2}	Light exposure	lux s	
Radiant Power					
	Pe	W (watt),	Luminous flux	lm	
(Radiant energy		J s ⁻¹,		(lumen)	
per unit time)		kg m-2 s-3			
Radiant exitance					$M_{e} = dP_{e}/dA_{1}$
	Me	W m-2			where dA ₁ is the
(Radiant power					surface of the
emitted per unit					element of source
surface)					
Irradiance					$E_e = dP_e/dA_2;$
	Ee	W m-2	Illuminance	lm m-2	where dA ₂ is the
(Radiant power				(lux)	surface of the
received per unit					element receiver
surface)					
Radiant intensity					
	Ie	W sr-1	Luminous	cđ	
(Radiant power			intensity	(candela)	
per unit of solid					
angle)					
Radiance					
	Le	W m ⁻² sr ⁻¹	Luminance	cd m ⁻²	$L_e = dP_e/steradian$
(Radiant intensity					
per unit area)					
Spectral radiant	P _{eλ}	W m-1			$P_{e\lambda} = dP_e/d\lambda$
power distribution					<u> </u>
Spectral					
irradiance	Eeλ	W m ⁻² m ⁻¹			$E_{e\lambda} = dE_e/d\lambda$
distribution					

Steradian is a unit of measure equal to the solid angle subtended at the center of a sphere by an area on the surface of the sphere that is equal to the radius squared. The total solid angle of a sphere is 4 π steradians.

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