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HelioNews

News about In Vitro Sun Protection Testing by HelioScreen

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The surface treatment of oxides of $Ti0_2$ and Zn0 (to be continued)

An innovative method of quality control for the production of sunscreens products.

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Updated version
Few modifications have been performed (highlighted with *) in order to avoid misleading in comparison with original version in French.

Edito of the month....

The latest European recommendations, the position of health authorities and even now the «industrial» lead to in vitro methods now much more recognized than a few years ago when in fact few things have changed, just a recommendation from Colipa for the UVA method. No other method has been accepted or subject of a consensus and especially nothing is really controlled.

In recent years, some in vitro tests were offered and performed in such conditions that leads to a significant loss of confidence in vitro methods. The future of the confidence which can be placed in the in vitro methods can be serene if we become aware of the great difficulty of controlling such tests despite their apparent simplicity.

Except some companies involved longstanding in vitro methods, no institute had till now neither proposed nor worked on such methods. Nevertheless, we see here and there proposals for the realization of In Vitro tests! Nobody really cares about what to ask to a tester and even, moreover, he is not worried to propose what seems good to him... Often the conditions for carrying out tests are unclear and far from what seems to be a consensus yet... even in such cases the laboratory was non-existent and performed tests on the corner of a university lab bench...
It is time to define precise rules and conditions for the implementation for the realization of in vitro tests if we do not want after this new momentum for this type of tests, there is again a loss of credibility of this tool however so reliable:
- Who performs the tests, according to which protocol(s), with what appliances and what experience?
- A quality policy is followed to ensure the necessary rigor for test?
- How reliability of the results with In vivo tests has been assured? Internal correlation studies have been performed?

The methods themselves appear to be proposed without sometimes the necessary hindsight. For example, for the «critical wavelength» whih is now compulsory, the method is not really defined yet and the results can vary greatly depending on the substrate.

So, should we trust in vitro methods? Our opinion is of course yes but we must remain humble, there is still much to do and we must be very careful. We wish controls and criteria for performing or proposing in vitro tests otherwise, it is clear that we will do «everything and anything» instead of contributing to the proper development of a tool so essential for the development of products, but also the safety of the consumer.

Dominique Lutz, CEO Scientist Manager

A new In Vitro method for Water Resistance!!

The water resistance of a sunscreen is determined by the assessment of the evolution of the SPF of a sunscreen after immersion of the plate (In Vitro) or human volunteer (In Vivo) under certain conditions.

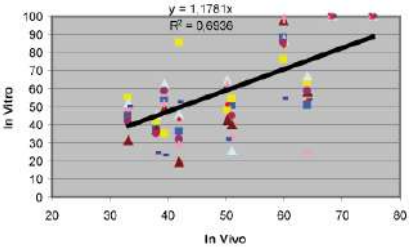
The new method proposed by a group of laboratories including HelioScreen Labs and published[1], provides an alternative to the proposal reviewed by the In Vivo Colipa in 2005[2] defining the conditions of realization (see details in our website www.helioscreen.fr) for a good inter-laboratory reproducibility on a representative range of products. The process conditions of the measurement of SPF were performed in accordance with a previous publication of the same working group[3].
In broad terms, the products are spread on Helioplates then subjected to immersion with constant stirring and in a bath whose temperature is maintained at 30°C. A large container (5L) is used to prevent re-deposition of product during the bath. The immersion time (5, 20 and 40 min) were chosen in order to correlate with the in vivo method including access to claims «water resistant» and «very water resistant».

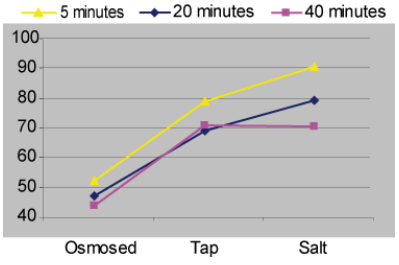
Although, the in vivo method reviewed by Colipa has low consideration of water quality, we decided to test several qualities expressed in conductivity using the following water:

Conclusion

Many of these values are consistent with the results of the same products tested according to the in vivo method. The variability of results within laboratories is about 15% and seems to be quite acceptable.

However, the test was performed with different water qualities and it is clear from this study that this factor is predominant and can completely transform a result. Figure 3 shows clearly that no water resistant product can still have a persistence of more than 50% if the water presents too high conductivity. The conclusion of this study is firstly need to choose a low water conductivity and that under these conditions, the results well correlate with the In Vivo values but also, on the other hand, it would be recommended to validate this parameter for in vivo methods. However, this study demonstrates the overall relevance of the method.





(1) Journal of Cosmetic Science, 2007, 29, 451-460 In vitro: assessment of water resistance of sun care products: a reproducible and optimized in vitro test method. M Pissavini. V allard . U Heinrich D Lutz et col.
(2) COLIPA Guidelines for evaluating Sun Product W)ater Resistance 2005,
(3) Cosmetic & toilettries 2003 118,63-71 Determination of the in vitro SPF. Pissavini Ferrero Allard Lutz et col...

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We will be at booth FI93

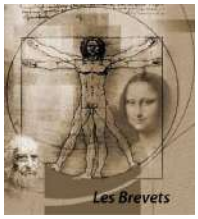
Review of patents in solar

B1 - Patent EP1837053 published on 26/09/07 by Procter and Gamble (also published as WO2007107914) concerning a cosmetic composition comprising an extract of Gingko biloba, an alkyl beta, beta-diphenylacrylate and / or alpha-cyano derivative beta, beta-diphenylacrylate and a dibenzoylmethane derivative. This invention prevents damage due to excessive sun exposure and aging.

B2 - Patent EP1829583 published on 05.09.07 by Beierdorf (also published as EP1277460) relates to cosmetic formulations, which contain 2,2 '-methylene-bis-(6 - (2Hbenzotriazol-2-yl) -4 - (1, 1,3,3-tetramethylbutyl)-phenol) and at least one self-tanning substance.

B3 - Patent EP1832272 published on 12/09/07 by Shiseido (also published as WO2006064821) A cosmetic product containing a powder whose surface is coated with a hydrophobic material and a cationic surfactant. The powder is preferably an oxide of titanium, zinc, cerium, iron, bismuth, zirconium, chromium.

B4- Patent WO2007073909 published on 07/05/07 by Unilever relates to a cosmetic composition of water-in-oil emulsifier comprising a surfactant silicone water-in-oil, ultrafine titanium dioxide and conjugated linoleic acid . The presence of the conjugated linoleic acid composition stabilized against the degradation of colors and also maintains an approximately uniform viscosity.



B5 - Patent EP1870077 published on 26/12/07 by L'Oréal. The invention relates to the use of annular concave or particles of silicone material, especially in the form of portions of hollow spheres in a composition comprising at least one aqueous phase and at least one organic UV and / or inorganic UV filter a filter in the to increase the sun protection factor (SPF).

B6 - Patent WO2007147785 published 27/12/07 by BASF. The invention relates to a method for increasing the sun protection factor of a cosmetic preparation and / or dermatological composition, the use of UVA filters to increase the coefficient of such a sun protection preparation, and preparations cosmetic and / or dermatological activity with special sunscreen.

B7 - Patent WO2008022970 published on 28/02/08 by Unilever offers photostable sun composition comprising: an organic complex of a filter and a paramagnetic metal ion coupled to a second organic filter.

B8 - Patent US2008008669 published on 10/01/08 by L'Oréal (also published under the numbers: EP1-815885, JP2007204477, FR2896988). This patent proposes a photostable composition by the combination of a cinnamic acid ester (UVB) and a particular S-triazine compound having a high efficiency in the UVB.

What happens in the solar...

- International Journal of Cosmetic Science, 2007, 29, 451-460. In vitro: assessment of water resistance of sun care products: a reproducible and optimized in vitro test method. M Pissavini. V allard. U Heinrich D Lutz et col. The aim is to provide an in vitro method for assessing the water resistance correlated with the in vivo method recently reviewed by Colipa in 2005. This article highlights in particular the importance of water quality on the level of result, a point which had not been explained well with the in vivo method. Could it challenge the in vivo method. (Ed)

- International Journal of Cosmetic Science, 2007, 29, 443-449. In vivo persistent pigment darkening method: proposal of a new standard product for UVA protection factor determination. D Moyal M Pissavini F Boyer V Perrier. The proposal for a new standard index (10) more compatible with the current level of protection than existing with validation in six different centers. This new standard is really consistent with current products and will also serve as a reference to in vitro tests. (Ed)

- Cosmetics and Toiletries – february 2008 (page 49) under title: Research Pathways to Photostable Sunscreens, Craig Bonda, The HallStar Company examines the mechanisms of degradation of sunscreens under UV irradiation. A fluorescence technique identifies photostable filters. In a document dated 27/08/07, the FDA highlighted the importance of the photostability of sunscreens.

- Cosmetics and Toiletries – february 2008 (page 73) under title: A Sunscreen Formulation for Acne-prone Skin, P. Morganti, Mavi Sud Srl; E. Ruocco, University of Naples Federico II; F. Guarneri, University of Messina; A. Cardillo, R&D ISCD; C. Pagliarello, IRCCS; et G. Fabrizi, University of Molise describe the use of a formula containing TiO2 solar and the ethylhexyl methoxycinnamate and filters as phosphatidylcholine and azelaic acid for the treatment of acne.

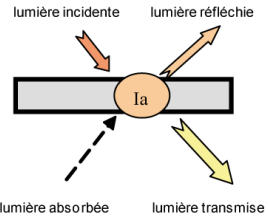
- Gunther et al - Variability of UV Irradiance in Europe - Photochemistry and Photobiology 84 (1), 172–179. Variations in the intensity of UV irradiation depends mainly on time, absorption by ozone plays a minor role and the clouds are an important factor. Erythematous daily dose varies between 2.2 kJ m-2 at 70 ° N and 5.2 kJ m-2 at 35 ° N, these values are reduced to 1.5-4.5 kJ m-2 in the presence of clouds.

TiO2 - ZnO :

The zinc and titanium oxides are interesting filters. They are stable, inexpensive, effective and relatively little dangerous because there is no degradation product. The use of metal oxides is however often limited by its implementation.

The effectiveness of protection will depend. mainly including the physical quality of the particle size. Indeed, an oxide particle subjected to UV radiation plays a role screen (transmitted radiation lower than the incident radiation) (Fig. 1).

However, sometimes it may also play the role of filter when a portion of the radiation may be absorbed by the particle. The exact use to describe zinc oxide or titanium term is therefore: filters / screens mineral not just: mineral screens.



The oxides which can be used for protection against ultraviolet radiation come from the family of transition metals and four metals could be used: iron, cerium, titanium and zinc.

The photoreactivity of the titanium

We have seen that, under UV irradiation, electron movement causes a reaction of:

$TiO_2 + h\nu \rightarrow TiO_2 (e_{-CB} + h_{+VB})$

The return of the electron to its initial state or its reaction with a hole in a few millionths of a second, the reaction of a titanium atom of crystalline TiO_2 network with mobile electrons lead to the reaction:

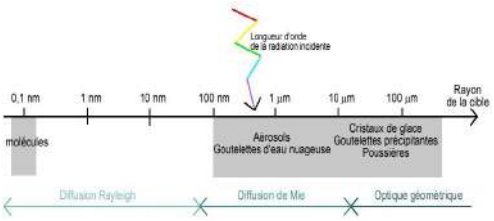
$$Ti^{4+} + e^- \longrightarrow Ti^{3+}$$

It is this reaction which causes graying / blueness of the titanium oxide. Return to the initial state (bleaching) takes place some time after the end of irradiation (a few tens of minutes to several hours); this is a manifestation of the photoreactivity of titanium oxide.

This reaction does not affect the efficiency of absorption / reflection of UV radiation, but, in order to avoid it, a titanium oxide coated silica or by either of the alumina is frequently used which hides the phenomenon.

chemical or mineral filter? *1st part*

Typically zinc oxide and titanium return light in the Rayleigh criterion: the intensity of the scattered energy is inversely proportional to the factor 4 of the incident wavelength: it means they refer to wavelengths after the visible field. Due to the presence of «large» particles, the Mie theory is also applied.



When the particle size allows it, a portion of the radiation may be absorbed by the particle. The titanium oxide and zinc oxide then act as semiconductor (absorb energy at one wavelength and restore it at a higher wavelength): they produce free radicals in the light, and they can form hydroxyl radicals or superoxides, which can initiate oxidation reactions.

Titanium ANATASE form is more reactive than RUTILE form.

It is clearly demonstrated that zinc oxide and titanium uncoated generate free radicals. So there is a danger to the application on the skin. If this occurs in the stratum corneum, it is conceivable that, if species are highly reactive hydroxides, they combine and disappear quickly. However, there is a danger in the case of penetration of the inorganic material or the development of more stable radical, it can induce oxidation reactions!

In a study performed for the FDA, it was demonstrated that the titanium oxide photocatalytic a significant number of functional changes in cells with alteration of the cell membrane permeation of the potassium and calcium ion. It has been shown that the coating is efficient enough to avoid the generation of radical species.

The principal oxides used

Iron oxides

They are widely used for wood preservation (wood tint) but are rarely used in cosmetics by the sharp color they bring.

Cerium oxide

Is used in a minority and especially in Asian countries, it is a yellow powder that is more protective UVA qu'UVB.

Titanium dioxide

Most used is the oxide; this is mainly a protective against UVB.

Zinc oxyde

Is increasingly used, but it suffers from not being accepted as sunscreen in Europe; it protects mainly against UVA.

Parameters affecting the ability of UV absorption by an oxide particle

The particle size

A primary particle of a few tens of nanometers has a short shelf life, it is just after its synthesis and moves very quickly by grouping particles; we distinguish three sets of particles:

- Aggregates: primary particles sticking together by their major faces.

- Agglomerates: primary particles or aggregates stick from the corner of the particles.

- The flocs are arrangements in the form of agglomerates of hollow spheres that enclose air.

The primary particle shape is variable and depends on the material and its synthesis method and: they can be hexahedral, spherical, elongated, irregular shapes. In the case of titanium oxide or zinc rather it will elongate or spherical shapes. The size of these different sets is quite variable:

Primary particle	5 - 100 nm
Aggregates	50 - 300 nm
Agglomerates	300 nm - 1µ
Flocs	few micrometers

However, the necessary energy to break these sets is very variable:

- Flocs break quite easily by simple agitation (type rotor / stator) in a liquid. It should be noted that if they disaggregate easily, they also tend to re-form, that is why dispersions nanofines particles must be stabilized.

- The agglomerates require a greater energy (microbead crusher) and dependent of the environment (presence of surfactants).

- Aggregates are almost impossible to reduce. Only the biggest can be disaggregate with very powerful crushers in wet phase.

Crystallinity

The energy jump is different depending on the crystalline titanium oxide state. Brookite is a rare condition.
In rutile form, the primary particles are more elongated in the anatase form more regular, spherical.

Particle charge

It is given by the zeta potential, which is a quantity related to the surface charge of the particle. We will not go into the details of this parameter but we will just say that it depends on:

From the polarity of the environment in which the particle is dispersed.

Additives present in the middle thereof may have an affinity for the particles, in particular polymers and surfactants which are loads carriers.
It is important to know the charge of the individual particles when they are combined in a formula.

The coating of the particles:

There are two basic types of surface treatment:
Coating a thin oxide layer (mainly aluminum and silicon but also zirconium) whose role is to change the zeta potential of the particle and hide the photoreactivity of the particle which we will discuss later.

Coating an organic substance whose role is essentially to improve compatibility with various cosmetic media (hydrophilic, lipophilic, silicones).

The particularities of each oxide

Titanium Titanium oxide is mainly a UVB filter, it absorbs only slightly in the UVA. The graph below shows that the absorption of small particles (nanoparticles) is predominantly in the UV when the particulate titanium oxide leads to absorption over the entire spectrum from which its effect on whitening the skin.

This statement, however, must be weighted according to the size of the primary particles (*) because the smaller they are, the more they absorb UVB and the more they are «large» (up to 100 nm), the more they absorb UVA, which shows the following curves here below.

(*) M. SAKAMOTO et col. - Importance of particle size of titanium dioxide on UV-ray shielding property – J. Japan. Soc. Colour Mater. (SHIKISAI) 68 (4), 203-210 (1995)

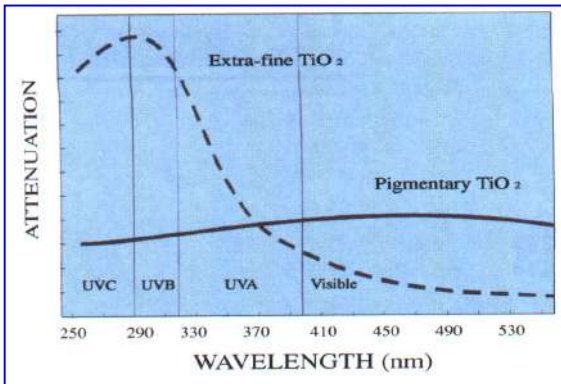
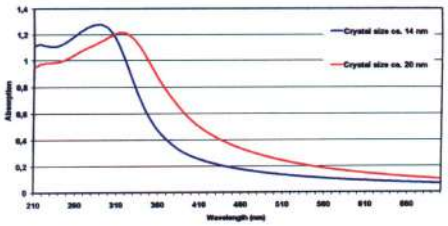


Figure 2. Attenuation of UV radiation and visible light by pigmentary and extra-fine titanium dioxide[5]



Zinc Zinc oxide is an amphoteric compound: it reacts with organic and inorganic acids and bases are dissolved to give zincates; it also combines with acid gases (CO2, SO2, H2S). In contact with water it reacts slowly to give Zn (OH) 2 with an increased pH of the mixture; so it is less easy to use than titanium oxide compound.

For a solar use, the primary particle size is generally between 20 and 100 nm; unlike titanium oxide particularly active in the UVB, zinc oxide is a UVA and UVB filter, but it absorbs / reflects more particularly in the UVA (**).

The zinc oxide must always be coated to prevent the formation, with water, zinc hydroxide and the increase of pH (up to 8-9) that accompanies the formation. Zinc oxide may also react with certain compounds (especially carbomers). The transparency of zinc oxide in the visible range is greater than that of titanium oxide (refractive index lower).

Zinc oxide can be used as the only sunscreen in a formula where a high SPF related to this contribution too low SPF is desired; Therefore we recommend to use either by coupling with titanium oxide when it is desired to be enhanced UVA protection with organic filters. In a particular article on the zinc oxide, Hewitt (***) shows the influence of the content of zinc oxide on the formulations containing octyl methoxycinnamate (OMC):

As TiO2, the figure shows that the absorption of small particles (nanoparticles) is predominantly in the UV when the particulate zinc oxide leads to absorption over the entire spectrum from which a whitening effect on the skin.

% OMC					5	5	5	5
% ZnO	2,5	5,0	7,5	10.0	2,5	5,0	7,5	10
SPF in vitro	3,1	3.1	6,5	9,2	19,7	21,8	28,8	33,8

(**) W. JOHNCOCK - Sunscreen interactions in formulations - Cosmet. Toilet. Vol.114(9), Sept. 1999, 75-82
(***) J.P. HEWITT – Novel formulation strategies for high SPF and broad spectrum sunscreen products - European UV sunfilters, Conference Proceedings Paris 17-18 november 1998, 111-120.

.....In our next issue find the rest of this article.....

Technological intelligence

Unusual eye blink In Cosmetics and Toiletries - february 2008 under the title: «Are Killing the Coral Reefs Sunscreens?» scientific reported that four chemicals (octinoxate, oxybenzone, 4-methylbenzylidene camphor and butylparaben) promote the development of viruses that kill algae feeding corals through photosynthesis. These substances would come from 4-6000 tons of solar products that would be eliminated from water by swimmers. This could be solved by the use of mineral filters (titanium oxide and zinc) of the biodegradable and sunscreens. (Full article available)

Scientificts articles Safety: A. Perez, D. A. Basketter, I. R. White, J. McFadden (2008) Positive rates to propyl gallate on patch testing: a change in trend- Contact Dermatitis 58 (1), 47–48. Comparative studies between the periods 1988-1996 and 1997-2005 showed a significant increase in contact allergy to this antioxidant.

M Norval, P McLoone, A Lesiak, J Narbutt (2008). The Effect of Chronic Ultraviolet Radiation on the Human Immune System - Photochemistry and Photobiology 84 (1),19–28. The effect of repeated UV exposure on the immune system was studied. The various parameters (DNA damage, urocanic acid, Langerhans cells and dendritic...) show photoadaptation or photoprotection of the skin under high UV dose.

Environment

Tego Galanga is a natural extract of root kaempferia galangal (Thai ginger). Besides a good absorption of UV radiation, the extract, a natural source of ethyl-p-methoxycinnamate minimum content of 98%, offers similar advantages to the OMC. It is particularly suitable for the protection of the hair fibers and protects the color from fading by ultraviolet rays.

Regulation Cosmetics Directive - 02/05/08 Brussels - The European Commission has proposed to simplify the law on cosmetics to transpose the 3500 pages into one coherent text. The new law also seek to enhance product safety while reducing costs for companies.