

HelioNews



The sun protection news as proposed by



HelioScreen

Summary

News within HelioScreen Labs :

A new service is proposed: formulation support !

Patents review within sun business.

It happened under the sun....

News and gossips

File of the month:

Surface treatment of Ti and Zn oxides (part 2)

To be found out in next files....(non defined sequence)

• An unpublished and original quality control method of sun products.

• « In Vitro as a tool »: the opinion of a manufacturer.
• Sun products with repellent effect.

• « In vitro » Methods: a practical approach of main prerequisite.

Editorial of the month....

If we could accept the careful thought which is advised before going off into proposals of *in vitro* testing protocols, we could undoubtedly save a lot of energy and perhaps we would not too hastily publish affirmations— even marked with humility and doubt— which are always susceptible to be proven good or bad with the same ease!

Let us consider the issue: on one side, we have « *in vivo* » tests, based on biological responses, widely used for several years but known to be « generally » subject to some variability depending on different parameters. They are certainly not the Standard Meter! They are an ever averaged indicator, which undoubtedly is quite meaningful for a claim but is not accurate enough to make out of it the strict, unique, and unquestionable reference criteriae when looking for a correlation with an analytical method.

On the other side, we have the *in vitro* technique, based on an optical measurement of a product,—being the same for ANY product— spread on a UNIQUE type of substrate. It is well understood that the affinity between the product and the substrate, on which the surface tension depends, will have a direct impact on the measurement quality and will strongly vary from one product to the other. It will be easily understood either that the application methodology will never be the same for all products. A product with a good affinity for the substrate will request no effort for a good spreading and an ideal transmission of the beam, when a product with an antagonistic surface tension will request some mechanical pressure to penetrate the rough surface —although never yielding the ideal layer— physico-chemistry giving no choice— and give variable results according to the used methodology. This without speaking about the variability due to the product itself, and its potential photo instability!

For our several protocols/proposals, of which at least reproducibility can be checked, we need a « referee » to validate that one among the results is the « good one »! The *in vivo* result is not always enough because subject to the same ups and downs and for the same reasons!

Let us be honest, with the *in vivo* test, it's less visible, we accept it more easily, and in case of discrepancy, it will ever be more trusted!

Nothing is easy and can strictly be checked in this area and it's an illusion to think an universal method will be sooner or later described to strictly give the full guarantee to get the same result than the *in vivo* test. It's possible to come closer but a good mastery of the subject and a wide experience to somewhat take into account the product for each test are demanded.

This is our daily fight and each day brings new knowledge but also asks more questions. We went quite a long way, working on substrate quality but not everything is solved and trust us, sun protection evaluation is really an expert's business!

Ten years of exclusive experience allow us for sure to master the necessary parameters in this field to get a reproducible *in vitro* result with quite often a good correlation with *in vivo*, but also to question certain results....*in vivo* or *in vitro*! Probably, we'll need as much time to improve our knowledge and perhaps....for the *in vivo* result to no longer be systematically regarded as the « standard meter ».

Sometime, we must admit to be worried when looking at so close harmonization goals!

Let us speed down, we are in a hurry!

D.L

A new service proposal:

From now on HelioScreen Labs helps you for your development

Many customers have mentioned the need to get advice at development stage. Sun products being so specific, HelioScreen laboratory can from now on be requested for help within your formulation strategy and respond to some of your queries in the following way :

What we can do for you now :

- Help within your global strategy to reach the requested protection by thinking together with you about the best filters combinations taking into account your restraints.
- Validate —theoretically— your choice, or make documented remarks on your formula orientation or suggest modifications.
- Bring advice in terms of législation depending on your export market (filters, claims, and /or needed tests).
- Help you to set up your quality validation method or the follow up.
- **What we can't do :**
- Develop formulations and make products proposals .
- Establish a list of filters to use in order to assure a certain result.
- Assure the legal aspect of your formulations.

These provisions are proposed as customized to specific requests and will receive a response and a previous estimate.

One of our referent associate will then be chosen for a direct contact during the whole study.

More information? Contact us!

New business in next issues...

VitroScreen

VitroScreen, an *in vitro* tests laboratory , specialized in biological tests on reconstituted human tissues , for safety and efficacy evaluation of ingredients and cosmetic products, complementary with our activity within the field of *in vitro* evaluation, will from now on propose a column in next Helionews issues.
We remind you that VitroScreen, as our partner in this field, is our agent on Italian market .

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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.

It happened under the sun...



Jing-Yi Lin, Joshua A. Tournas, James A. Burch, Nancy A. Monteiro-Riviere, Jan Zielinski (2008) Topical isoflavones provide effective photoprotection to skin - *Photodermatology, Photoimmunology & Photomedicine* 24 (2), 61–66.

A study done on pig skin has shown isoflavones are substances providing a good protection against cutaneous photodamages resulting from UV radiations.

Cosmetics and Toiletries - March 2008 p. 81 - **Natural Preservation from Concepts in Nature** - Fernando Ibarra, PhD, Dr. Straetmans GmbH and Christopher H. Johnson, Kinetik Technologies Inc.

Within plant kingdom, chemical defence mechanisms are the base of natural preservatives; two examples: organic acids and glycerol monoesters.

M. A. Farage, K. W. Miller, P. Elsner, H. I. Maibach (2008) Intrinsic and extrinsic factors in skin ageing: a review - *International Journal of Cosmetic Science* 30 (2), 87–95

Intrinsic rate of an individual skin ageing can be very much influenced by personal and environmental factors, especially the ultraviolet light exposure. The photodegradation which considerably speed up the visible skin ageing increases also a lot the risk of development of cutaneous neoplasm. It is crucial to try to get a better understanding of intrinsic and extrinsic factors which act on skin ageing and also to distinguish between reversible aspects of cutaneous ageing (mainly hormonal factors and way of life) and non reversible ones (mainly intrinsic ageing).

P. Perugini, et Col (2008) Efficacy of oleuropein against UVB irradiation: preliminary evaluation - *International Journal of Cosmetic Science* 30 (2), 113–120.

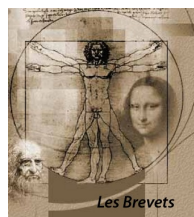
Oleuropein, the phenolic substance from olive leaves and the oil, is known to possess some biological properties, much of which can be attributed to its anti-oxylant activities. Oleuropein containing formulations have shown: erythral reduction, decrease of transepidermal waterloss and of blood stream, down to 35%. **Full article available.**



Merve Meinhardt, et Col (2008) Effect of ultraviolet adaptation on the ultraviolet absorption spectra of human skin *in vivo* - *Photodermatology, Photoimmunology & Photomedicine* 24 (2), 76–82.

The absorption spectrum of human skin was measured in-vivo by opto-acoustic laser. Spectrums have been compared (hidden and visible part of forearm) in order to check influence of native and acquired pigmentation. Influence of both main chromophors (melanin and keratin) have been ascertained.

Patents



B1 - WO2008025830 (A2) published on 6/03/08 by Declercq Wim [BE]; Denecker Geertrui [BE]; Vandenaabeele Peter [BE] which concerns a sun product formulation containing the ingredient caspase-14.

B2 - WO2008024738 – published on 02/28/08 by Avon. Repellent formulation and transparent water based sunscreen

B4 - WO2006003028 filed by L'Oréal and published on 01/12/06 is complementary to patent EP1618927 as it claims for a cosmetic or dermatological photo-protective composition characterized by its content:

a) at least one 1,3,5-triazine derivative; b) at least an oil containing in its structure at least one amide unit and c) at least an eutectical mix of n-butylphthalimid et d'isopropylphthalimid. Solvents used are important for sun products.

TiO₂ - ZnO

Formulation with mineral filters :

Formulation with mineral filters demands a strict distribution of their particles' size. The later is much essential when dispersed either in water or in oil. This is the large dissimilarity with organic filters which are solubilized.

To reach a good protection, not only a good distribution of particles'size is necessary but also reagglomeration is to be avoided... This is also true from an aesthetical point of view as there should be no whitening effect from the cream.

Both ZnO and TiO₂ are available as pigments or micronized. Let us remind that the state is of little impact on product performance as there is no chemical activity. The physical difference between different grades is of no influence on the intrinsic quality of the product: easiness during it's worked out and **dispersion final result will make the difference.**

It's not sufficient to be able to correctly disperse particles, it's also necessary to keep a correct dispersion.

The micronized version will make light able to go through, thus allowing transparent products.

Of course, difficulties increase when there are several filters to mix. Very often, the tendency is to process the different particles in the same way, although their reactivity is very different. Dispersion of mixed particles rarely leads to good results.

It's important to have a good control of the surface chemistry of these compounds and of the components of the formula to assure a correct dispersion.

ZETA potential influence

All particles, when placed in a solvent, develop an electrical charge. When there are sites or charged groups on the particle's surface, performances are modified. In an aqueous medium, parameters such as pH or electrolytes concentration have an influence.

ZETA potential is a good indicator of surface properties change and gives a good control of the particles dispersion state.

To know particles' surface charge at a given pH makes it possible to predict particles interactions.

The key for suspensions of different oxydes is the isoelectrical point. At this pH, ZETA potential is zero. It means there is no surface charge and therefore no attraction or repulsion between particles is possible. Stabilization will be optimal when particles are charged because this gives a repulsion, which makes a good quality dispersion.

ZETA potential measurement is therefore an important criteriae for the control of distribution's quality.

The choice of ionic ingredients as a function of the residual polarity is therefore an important formulation parameter.

Filters or mineral screens? (Part 2)

However, this is a little bit complicated in terms of formulation as there is a risk of transfer from one or the other oxydes, from one phase to the other during emulsification and then re-agglomeration.

As surface properties are frequently modified by the oxydes manufacturing process, **Zéta potential should be measured for every batch.**

Impurities on the oxyde surface can thoroughly modify its properties. With a coated oxyde, it's necessary to check the oxyde surface before coating. Clearly, it's difficult to use oxydes under their basic state for obvious reasons of reactivity.

The coating quality may also have a strong influence on oxyde reactivity. The bond kind and energy (Electrostaticity, lipophilic interaction, hydrogen bond) depend on the kind of substrate and on the coating material.

Coating may be modified by a formulation ingredient which has more affinity than the oxyde itself. The manufacturing process itself (with the physical and mechanical restraints it induces) may be the origin of coating deterioration.

However, most of coatings are produced (covalent bond) with different oxydes such as silica or aluminum. Again, the ZETA potential before coating is preponderant. The quantitative analysis of aluminum or of silica will give but few information because it doesn't take into account the distribution on the surface.

Encapsulation also is a process which allows to get rid of surface incompatibilities, but it is rarely used for mineral filters because of its high cost.

Clearly, even if mineral filters are known to be non-reactive,

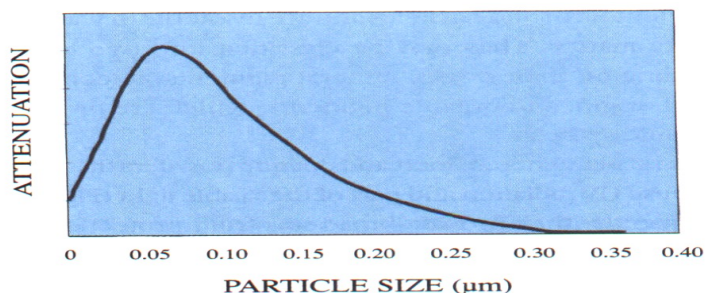


Figure 5. Attenuation of UVA radiation at 360 nm according to the particle size of zinc oxide⁵

A practical example of making a mineral filters mix.....

As a water suspension, at a pH of about 6, ZnO particles are positively charged, and at the same pH, TiO₂ particles are rather negatively charged. To mix these particles under these conditions would yield an agglomeration.

What would happen ?

The particle size of the TiO₂ and ZnO mixture will fastly increase with time a few minutes after the mix.

If this is to happen with a formulation, the result will be an important drop of the SPF and a development of a whitish compound.

What to do ?

According to the theory, it's possible to design a formula with pH lower than 5 or higher than 10. At these pH, both oxydes will have the same type of charge and there will be a repulsion instead of an attraction.

But practically, these pH are not acceptable!

It will be necessary to revert to an O/W or W/O emulsion to mix ZnO and TiO₂. Most often, ZnO is prepared in the oil phase and TiO₂ in the water phase, in order to, as much as possible, get rid of re-agglomeration problems.

they may cause difficult problems and the protection level is far to depend only on the quantity of these filters. However, in case of a wrong « galenic choice », unexpected effects would not be necessarily as much highlighted as in the case of organic filters. Let us also remind that unlike with TiO₂, which offers quite a good specific absorbance, ZnO is not a very efficient filter.

Work is going on about quality of coating and future lies overall on new oxydes (cerium, zirconium, etc...) which would give a lower toxicity risk, a better stability and naturally, a « broad spectrum » protection.

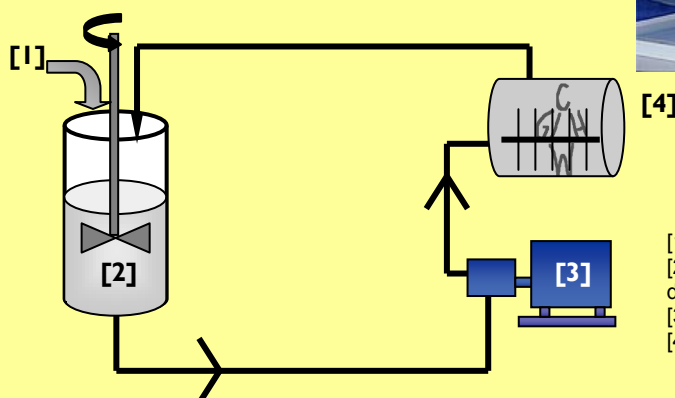
How to make oxydes dispersions

When the wish is to use titanium or zinc oxide for a sun product, two possibilities are given : a direct dispersion of the powder into the formula or use an oxyde dispersion in a dispersion medium adapted to the said formula. This last solution should be rather selected for two main reasons:

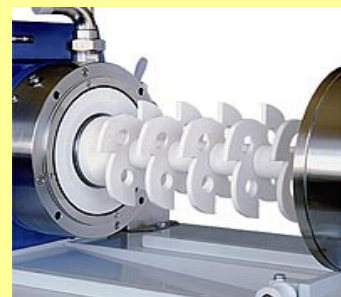
Dispersion is made with a much better equipment in terms of particles grinding, with optimal particles (aggregates) size.

- the dispersion contains additives which coat or stabilize ground particles, so as to avoid re-agglomeration.
- Quite often, these dispersions are produced with ball mills (as shown in the picture opposite: manufacturing process and ball mill) or high pressure homogenizers. Balls used in the grinding

are made up of a dense material (ceramic) and their size may go down to 50µ.



[4] Ball mill



[7]

- [1] : powder addition
[2] : vessel + dispersion medium
[3] : pump
[4] : ball mill

Regulations :

Although Titanium oxyde is not a problem for a worldwide use (except in the USA), there is no rule about zinc oxyde in Europe, but it should always been coupled with another sun filter .

Filter	USA		CEE		Japan		Australia
	reference	%	N° order	%	CLS	%	
titanium oxyde	p	25	27	25	520925	n.l.	25%
zinc oxyde	r	25		n.r.	1281	n.l.	n.l.

A few formulation advices :

- When zinc oxyde is used, a coated version should always been choosen, if it's planned to work with an aqueous phase; if to work with an anhydrous phase is the choice, a lipophilic coating should be used. Be cautious about possible incompatibilities of ZnO with acids (Carbomers, stearic acid...).
- Precautions are to be taken when both titanium and zinc oxydes are used together so as to take into account the difference of zeta potential between these two oxydes and avoid agglomeration. It's better to put each oxyde in a different phase (titanium oxyde in aqueous phase, zinc oxyde in anhydrous phase) .
- Titanium oxyde compatibility with some organic filters (ex:Butyl methoxy di benzoyl methane) should not be an issue if the oxyde is coated with silica or alumina (caution, this mix is forbidden in the USA).
- Check the SPF value with time: measure it just after production and then after 2 or 3 months at 45°C. A noticeable difference means a re-agglomeration of particles on aging.

Strange allusion

Stars themselves use sun products ...

The german astronomer David Fabricius noticed, in 1596, that the giant star Mira regularly changed its brightness for an unknown reason.

Astrophysicians from the Harvard-Smithsonian center (Reid and Goldston) found the explanation: Mira, like some other stars, has pulsations, which means its diameter increases and then decreases just like a heart. When Mira's diameter increases, the star cools down which causes..... titanium oxyde vapour formation! This vapour completely absorbs the light emitted by the star which then appears dark. When its diameter decreases, titanium oxyde vapour diappears and the star brights again.

Companies information

03.25.2008 - COSSMA – The Whole Foods Market company, a food massmarket company, started a cosmetic products range which include sun products containing zinc and titanium oxydes.

27.03.2008 - COSSMA – The Kemira company increases the titanium oxyde price. From 04/01/08, the increase should be 0.25 \$ per kg.

Scientific articles

B. Pérez-Gómez, et Col Do sex and site matter? Different age distribution in melanoma of the trunk among Swedish men and women - British Journal of Dermatology 158 (4), 766–772. A swedish analysis on nearly 3 millions people, shows that melanoma frequency is 17,4 cases out of 100.000 for men and 16,5 for women. Big differences for the trunk located melanoma as a function of age: the frequency is 5 times less for young people than for aged ones.

Safety aspects of the sunscreen products use - S. Krus, et Col Cosmet. Sci., Vol.10, 4, 2007, pp. 165-179. Comparison between organic and mineral filters, advantages and disadvantages of both types.

Oral suncare and photoprotection with carotenoids – R. Goralczyk – J. Polish Society Cosmet. Sci., Vol.10, 4,

.....MUNIQUE.....COMMUNIQUE.....COMMUNIQUE.....COMMUNIQUE.....

HelioScreen informs you....

Since its start, our laboratory (SARL Helios Science Cosmétique) carried out its activities under the name **Helioscience**

As the **HelioScreen labs** brand has been filed in 2007 to mark the internationalization of the laboratory, we now exclusively communicate **under this brand**.

We feel it necessary to inform our customers that any proposal and / or delivery of service by any structure under the HELIOS-SCIENCE brand has absolutely nothing to do with our laboratory and that it is by no way the result of a transfer or license from our part as we didn't registered it .

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2007, pp. 197-208.

Carotenoids are known for their anti-oxydant effect, they have also a protective effect against UV by oxygen singulet capture, retinoic acid formation). In this study, new action mechanisms have been brought out.

NR Janjua, et Col (2008) Sunscreens in human plasma and urine after repeated whole-body topical application - Journal of the European Academy of Dermatology and Venereology 22 (4) , 456–461.

The percutaneous absorption and excretion of 3 different sun filters: benzophenone-3 (BP-3), octyl-methoxycinnamate (OMC) and 3-(4-methylbenzylidene) camphor (4-MBC) have been studied on 32 subjects. They have been submitted to 4 sun product applications on the whole body (2mg/cm²), the product containing 10% of each filter. Nothing was detected in plasma and urine after one application but the 3 filters are detected in urine and plasma after 96 hours. BP-3 being detected at a much higher concentration than the other filters (~10 times more).

Ecology

Compass: Seeing Green - Rachel Chapman, *Cosmetics & Toiletries* magazin The author asks the question: what is « to be green » for the cosmetic industry? This question was discussed during conferences before In-Cosmetics which started on 14 april in Amsterdam.

Cosmetics and Toiletries - (March 2008) page 91 - **Green Formulations: Not All Components Are Equal** - A. Cristoni, G. Maramaldi and C. Artaria, Indena SpA.

In consumers'mind, a green or a natural cosmetic product is automatically safe; in fact, quality, safety and efficacy of a natural ingredient should be carefully scrutinized.

Evaluation of black tea and its protection against UV – M. Turkoglu, N. Cigirgil – International J. Cosmet. Sci. UK, Vol.29, 6, 2007, pp. 437-442.

Aqueous and alcoolic extracts of black tea have been tested for their UV absorption: a peak appears between 250 and 300nm. Applications on subjects of a gel containing these extracts have shown a wide protection between 200 and 400nm.

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