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Introduction:

What could seem a paradox for certain sun protective products is that when applying them on the skin for self protection it may induce at the same time a photo degradation and less efficiency, due to the UV irradiation.

The photo (un) stability of the solar products is often perceived like a negative contribution of such or such filters or formulas. Everyone would agree it would be necessary to do everything to have only filters and/or products fully photo stable. This may be for the future due the current state of the market offer about UV filters. Indeed, it is possible to make judicious choices of combination of filters to reduce this phenomena but most combinations are patented as it is a real know-how and advantage. However, it is not the usage to control and even less to assert the lost of performance due to the bad resistance to photo exposure of products which purpose... is to be irradiated!

What is photo stability? Which incidence on the product? Why were not methods earlier been organized? Can one be satisfied of a taking into account of the photo degradation of the products with pre irradiation step induced in the In Vivo and proceed as well for In Vitro testing? Which are the ideal conditions of realization of such a test? Does the formulator gain to know the photo behavior of his formula or would it be enough just to know the “residual” performance after a certain irradiation? Is it an advantage for the consumer to know about this characteristic of the product since the claim indices already take account of a certain degradation? Finally, if it is necessary to evaluate the photo stability of the products, what do we have to do?

How to define photo stability?

There is normally no photoreaction or photo-oxidation with the majority of the current ingredients of cosmetic products when they are in a bulk or packaged in good conditions. But when the products are spread out over the skin, the heat-transferring at skin surface and the contact of air charged with oxygen are adequate conditions for chemical reactions. The more the product undergoes an important photo irradiation, the more thermodynamic conditions are complied for a risk of inducing photo reactions (1). When besides, said product claims UV protection, it will be “normally” used under a consequent irradiation. Lastly, since it is formulated to this end, he contains particular molecules which are the filters. The principle of the UV filters (mainly organic ones) is to be photo reagents to absorb or convert the energy in order to avoid the noxious effects of UV by inducing photochemical reactions (2). The photo reactivity is thus complex.

Quite a surprising affair!

Last month a no commercial company has tried in a fruitless way to hijack(1) an order of Helioplates HD made by one of our US customer. They tried several times to substitute the HELIOPLATE™ HD with a “new” substrate so called SUNPLATE to enhance the confusion (1).

They didn’t hesitate to claim « We think that there is no difference between the two products! »

Our customers have to pay attention because it is not the first attempt to do it. Each time, all is done to create the confusion especially with the name of the companies. Even our protocols and reports are copied but of course, not our way of proceeding.

We have to remind we are no longer helioscience™ for several years and are HelioScreen™ the only lab created 10 years ago by myself.

It is quite obvious if any new competitor try to copy even create the confusion it is because we make reference and we are proud for that. But all the same, this is far from being honest!

Our laboratory is certified BVQI ISO 9001 and has a “real” infrastructure. Any customer can come and visit even audit our laboratory recently moved near Paris.

The fact is it still is possible for anyone to propose In Vitro testing even neither with any structure nor external controls but it’s up to the customer to check and you have to require references, not just words!

Fortunately time will come when In Vitro testing will be controlled as In Vivo and we do our best that it arrives the sooner as possible.

It is of our interest... but also of yours!

DL

A new representation of HelioScreen in Japan

Last year HelioScreen formed a partnership with Labsphere Inc in the United States for the distribution of the Helioplates HD in the Americas.

Since last month there is a new step in the worldwide representation of the company (which have now its 66% turnover coming out of France) with a new partnership formed in Tokyo with Sanyo Trading Co for the distribution in Japan.

With the US and the Japanese representations of HelioScreen, D Lutz had conferences in October with about 50 Nippon firms in Tokyo and Osaka.

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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.

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**Photo stability and pre irradiation:**  (Continuation.....)

Thus if all the filters have - a priori - a capacity to photo react, they will be classified as photo stable when the thermodynamic process is balanced more or less by a return at the initial state with to some extent of the remnant properties of protection during the exposure time.

The principle of reaction (3) consists of the absorption of a photon at a quite specific wavelength due to a chromophore (combination of several double connections) contain in UV filter molecules. These particular wavelengths and the type of reaction which will occurred will depend not only on the chromophoric groups but also on the chemical conformation which influences the resonance of the molecule. In other words, the reaction will not be only dependent on the molecule of filter considered but on the formulation itself!

This energy is considerable since a photon around 300nm has the same energy as that necessary to break a covalent bond in an organic molecule (3). It will cause the passage of the molecule of an at-rest state towards an excited state.

It is in fact the “return” towards the normal state after having dissipated the energy which will precipitate of what one identifies like a state of photo instability for a filter given in his environment.

**What are the consequences of the photo stability?**

The most current consequence is of course the modification of the protection properties, often a loss of effectiveness progressively with the exposure of the product, thus of its use. The behavior can however sometimes surprise because one can also note an increased SPF for example whereas one would have expect a fall of the index, because of transformation of certain UVA filters towards compounds which will absorb in the UVB.

It should not also be forgotten that in its decomposition or its photo transformation, the molecules give birth directly or indirectly to new compounds which are not always wished and even known in the formulation. As shown previously, not only the level of degradation but also the nature of these compounds can be different according to conformation from the same molecule when being irradiate. To quote only one known example Butyl methoxy di benzoyl methane, very much used in filtration UVA with fact the object of many studies on becoming to it molecule with the irradiation according to its environment (3) (4). That has been also studied on other filters depending on the vehicle or solvent (5). One can thus never envisage the photochemical behavior of the product by considering only the filters, except choosing filters fully photo stable whatever their condition of use but these ones alone do not make it possible to fill all requirements of the market!

An unexpected consequence of the level of photo (un) stability which does not influence the quality of the product is that… the validation of In Vivo method is made very difficult due to the behavior of these products! Indeed the In Vivo method including in its principle a phase of irradiation, the In Vivo SPF takes into account the photo degradation if it occurs but without for that, neither determining it qualitatively or quantitatively, not even identifying it.

In Vivo method will be considered as validated only when a perfect correlation is established. However if that is relatively established when the products do not evolve, it is much more difficult to regulate the problem of the relevance of a "preliminary degradation" by a pre irradiation of which the effects would be identical to what occurs during the In Vivo test. Too many studies of correlation without pre irradiation do not even make a difference in analysis according to the potential photo degradation of the product because they do not evaluate although having values of In Vivo index. The result of the correlation (6) may be quite affected for photo unstable products.

It is not that the “tools” do not exist, although as for other types of evaluation, a consensus has not been yet reach on a specific method, it is rather than it seems that the lack of such a consensus method is not so critical!! One can consider that there are for that there simple and pragmatic reasons:

1) If one considers the way of controlling the products by the methods recognized as “references” (In Vivo methods), they consist in their basic principle, in exposing under a controlled irradiation a subject, with and without protection, so as to estimate the difference of the duration until the appearance of the "biological end point". Due to the principle of the method, there are not an other choice than irradiate a volunteer with a consequent energy since it requires lower duration of irradiation than that which it is under “natural” conditions of exposure, the phenomenon of photo degradation, occurs (if the formula is photo unstable…) and thus it is considered that this “negative” aspect of the formulation is to some extent taken into account in the final result.

The so called “reference methods” are historically based on biological processes (reaction of the skin to a certain irradiation). In the past the SPF was regarded besides as the only indicator. The photo degradation is of course due to a chemical reaction and it cannot be evaluated by a biological "endpoint". At the very least, if one wanted to In Vivo carry out a method in conformity with the spirit of the methods, one could only measure the effects of a photo degradation by comparing a product not irradiated vs irradiated considering its level of protection. And still in this case, there would be a new degradation during the evaluation. Thus the “traditional” methods did not make it possible to consider this characteristic of the formula (except considering filter by filter, which is not satisfactory as explained further on) and photo in stability possibility although known and recognized could not be evaluated on an overall basis without the...
The conditions of realization of a test of photo stability by an *In Vitro* method

irradiation of an *In Vitro* test.

A method had been studied one decade ago within the framework of a COLIPA task force. It broke up into two parts: on the one hand a measurement of transmission and on the other hand a method of dosage of the filters by HPLC (7) being not stripped of interest! Even by imagining very complicated solutions, there will be no “ideal” conditions of simulations of the degradation of the products during the testing *In Vitro* to reproduce it in a phase of pre and after irradiation. The difficulty at that time of controlling the acquisition of the curves of absorption undoubtedly related on the used substrate and the spread out quantity (quartz Plates home made roughened between 2 and 10 microns). Results made retain for the final publication incomplete and undoubtedly very little used analytical method based on HPLC. However, the total method of the comparison of the absorption spectra is that which is the most relevant to get a total evaluation of the *in vivo* photo stability of a product anti UV. It remains to control in a way as reproducible and reliable as possible the absorption spectra and the COLIPA soon will start again the study of this method under conditions of study which could be only more adequate. As example, in the case of a strong absorption (DO > 2.5), the difference of the spectra before and after the various irradiations could be difficult to interpret or will have a very weak mathematical significance. It seems obvious not to attempt to follow the conditions of the protocol related to the SPF (spreading out a quantity of 1.3mg/cm² on a plate with a 6 µ roughness) if that does not allow a good sensitivity of the measured curves but to find, case-by-case adequate quantities allowing to have the most reliable measuring of the spectrum.

3/ The substrate of measurement will have to be perfectly adapted in quality and roughness. It is a comparative method determining the curve of absorption of the same spreading out on a gradually irradiated plate. That limits variability considerably but all the same, it is necessary to stick to best conditions for a lower variability intra laboratory and more especially by using rigorous plates because precise measurements are not inevitably taken again on the same portion of the substrate. Two types of PMMA plates currently proposed were compared (10). It clearly was thus shown a variability definitely improved for the plates manufactured starting from a process of molding (Helioplate™, H6D).

After having shown the relevance of the taking into account of a phase of pre irradiation in the method evaluation of *In Vitro* SPF (8), the JCOLIPA made recently a proposal on a method of *in vitro* SPF evaluation within the framework of work of the group ISO TC 217 on the standardization of the methods. In order to mimic at close as possible what occurs during the *In vivo* test. It is thus proposed to spread out on a substrate which seems to take again a standard topography of the skin and especially a roughness of 16 µ instead of 6 µ of the plate. In addition the products would be irradiated in a dynamic way with a duration proportional to protection. As a matter of fact it had already been offered with an existing specific apparatus on the market (9).

This brings two comments.

There is a sempiternal debate about the dose of irradiation to apply before testing. There have been a proposal to consider the dynamic evolu-
The evaluation of the photo stability should be an essential element even compulsory of the sun protection claim!

method and the need to add this important parameter with other claims. It however seems logical, even essential, to have the knowledge of this phenomenon as it is the case for the thermo degradation for new products put on the market. Can we imagine a producer of hair dyes not to study the behaviour of his formula applied to hair when this one is exposed to the visible light or of the sun and to only consider the colour after such an arbitrarily defined exposure??

They are however the same phenomena except that our eyes do not see the degradation of the filters in UV as they see that of the dyes in the visible!

References:

(1) MM Riegger, Reaction of oxygen affecting skin products) Cosm & tol 104 (10) 83-90 1989
(3) M Sayre Photostability testing of avobenzone Cosm & tol 114 (10) 85-91 1999
(7) COLIPA Guidelines on Photostability Testing of UV Filters in Sunscreen Formulations 2004
(8) Experimental report JCA Unpublished

Next meeting of the ISO TC217 group has been held in Kyoto (Japan) with a little progress for the different projects.

JClA, the host have been prepared the meeting with a huge commercial presentation of its new proposal for the SPF determination the Sisheido SPF master and new worldwide patented substrate. Some thing quite unusual for a normalization meeting! (See patent N°1 F2)
The In Vivo SPF ISO FDIS 24444, leads by France (D Moyal) has been reviewed in its approval stage not far from being published.
The In Vivo UVA DIS 24442 is not expected for any evolution as long it is expected to be shortly in FDIS stage...

Unless every one agreed from different countries in the last meeting in Monaco, to advance the vote for In Vivo UVA DIS 24443 from December to October, in order to be able to discuss the item at this meeting and go to the FDIS stage, only France and Japan did it. So nothing to do than expect, including for US vote, unless they are project leader. The dead line is December and we just had some remarks from Australia (J Staton ) about the range of the C values proposed in the method which is too low for certain products in the proposed method. Every one agreed this rules coming from the original COLIPA method is just an indication and could be adapt.

In Vitro SPF couldn't be discuss as long an expert independent group (from which we are member) is working to find improvements to the existing protocol.

Photo stability has been postpone especially from France delegation but we start a discussion on working draft for future Water resistance method.