SIX KEY CRITERIA TO CHALLENGE TITANIUM DIOXIDE MATERIALS FOR HIGH PERFORMANCE AND COMPATIBILITY

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Summary

We developed a collection of six assessment methods to reliably predict stability and integrity of coated TiO_2 materials. Five of the six tests can easily be run in a normal equipped cosmetic application laboratory.
We ran nine commercial TiO_2 materials through the test battery. Surprisingly, most materials showed issues in one or several challenge tests. Only one material did fulfil all requirements. It is a double-coated rutile variant with silica and dimethicone.

Riassunto

Sono stati messi a punto sei diversi metodi per studiare la stabilità e l'integrità del biossido di titanio (TiO_2) utilizzato per le formulazioni cosmetiche.
Cinque di queste metodologie possono essere usate utilizzate facilmente con le attrezzature presenti in un normale laboratorio cosmetico.
Perciò sono state controllate nove diverse tipologie di TiO_2 presenti in commercio.
Con grande sorpresa si è visto che di questi campioni, soltanto quello ricoperto con un doppio strato di silicio e dimeticone rimaneva invariato a tutte le prove di stabilità a cui è stato sottoposto.

INTRODUCTION

Titanium Dioxide is widely used in cosmetic products and is well accepted by the consumer due to its outstanding safety profile. It has become a standard building block of high performance sun screen products. Numerous qualities of Titanium Dioxide are available. In particular, Aluminum Oxide coated materials are preferred due to the tightness of the coating, which gives them good photo stability. The current trend for modern sunscreens requires both a high SPF as well as significant UV A protection. Butyl Methoxydibenzoylmethane (BMDBM), due to its top performance and global regulatory approval, is the material of choice; and particularly since several suitable solutions have been developed for its photo stabilization. The compatibility of Titanium Dioxide with this powerful UV A filter is therefore a must. Although it has already been reported that there is an incompatibility between Aluminium Oxide coated Titanium Oxide and BMDBM, the impact of this interaction on the UV A performance was not studied in depth.

STABILITY AGAINST DISCOLORATION

BMDBM is well known to give color reactions with certain metal ions, e.g. with iron. The formed iron complex is deep red and is visible when present at a level of even a few ppm. The same discoloration will occur with TiO_2 qualities that bear a high level of impurities. Such discoloration can not be tolerated in consumer products. Here we describe a simple test that can be performed in an application lab and which will assess this quality. We compared different grades of Titanium Dioxide and their compatibility with BMDBM. The test setup is rigid, but gives a good indication as to what will happen under real usage conditions in a consumer formulation. The test is independent of the coating method of the TiO_2.

Description of the BMDBM compatibility test

Raw materials:

Caprylic/capric triglyceride	85%
Titanium Dioxide	10%
BMDBM	5%

Preparation

Disperse Titanium Dioxide in Caprylic/ capric triglyceride thoroughly. Add BMDBM and wait for 1hour at ambient temperature, then check for discoloration. Most likely you will need to look for two types of discoloration: yellow and red.
A yellow hue may be attributed to an incomplete coating which is caused by an excessively small primary crystal size below 17nm.
The red discoloration most likely originates from the presence of some residual iron coming from the crude TiO_2 source. If the iron impurity is present at too high a level in the TiO_2 crystal structure, there is no way to prevent the discoloration of the final product; not even by adding complexing agents like EDTA. If you observe a discoloration, most likely your final formulations will not be stable as well.

FORMULATION AND PERFORMANCE STABILITY

While iron forms colorful complexes with BMDBM, other complexes, such as those with Aluminium or Magnesium, are colorless. Nevertheless, there are other techniques to detect their presence. Certain aluminium complexes are marginally soluble in an emulsion system and can lead to crystal formation upon storage (figure 1). The crystals that form are large enough to be detected easily by the consumer through the resulting gritty feel of the emulsion. We also found that the formation of the crystals can be accelerated through higher temperature storage (43° C), and the beginning of crystal formation can be seen with a microscope already after 2-3 weeks storage. Additionally, we followed the crystal formation by HPLC measurements (figure 1).

We further assessed the solubility of the BMDBM-Al complex in Alkyl benzoate and found it to be below 2 %.

The complex formation and resulting crystal formation not only destroys the sensory properties of a formulation, but also affects its performance. The efficacy decreases due to uneven UV filter distribution. Nowadays, as UV A protection is more in the focus of both consumers and authorities, it is recommended and in some cases required to demonstrate that the UV A protective properties of a product are stable also after a period of storage.

To elaborate the effect on performance, we investigated the incompatibility between the two components in regards to UV A in vitro performance measurements. We employed the MUT System and discovered a very significant performance loss in UV A protection after storage. Figure 2 shows a dramatic decrease in the UV A region of an aluminium coated TiO_2 material vs. a silica/ dimethicone coated variant after storage. Each data point was assessed 5 times.

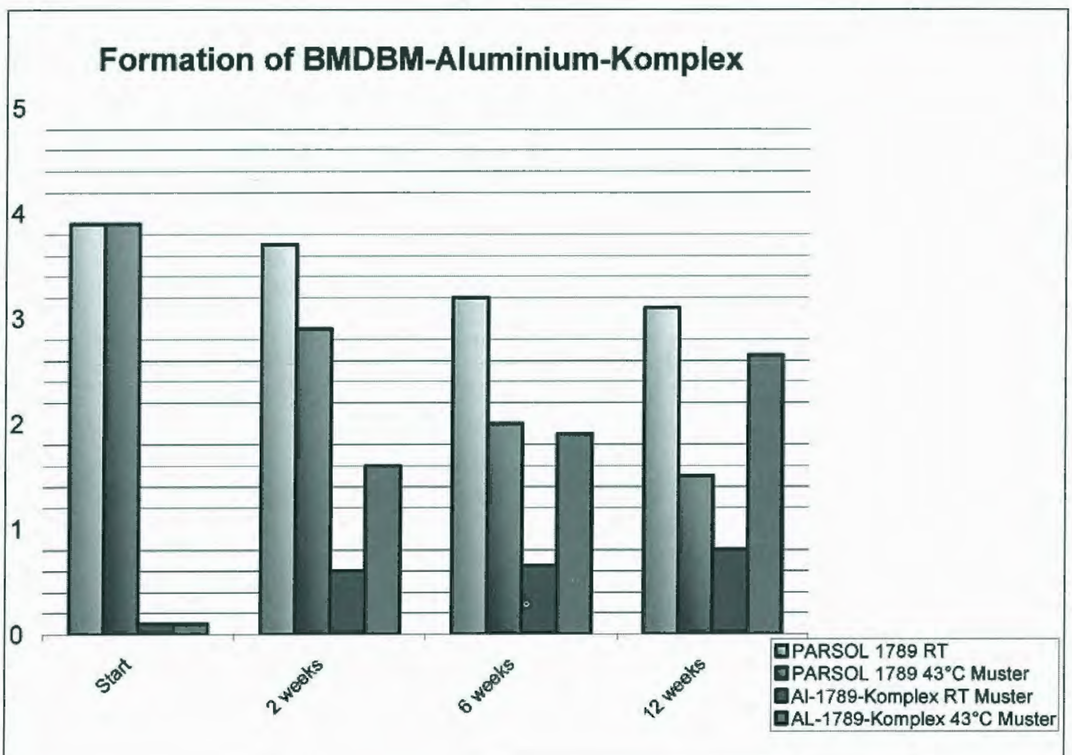


Fig. 1

PERFECTION OF COATING (APPLICATION LABORATORY METHOD)

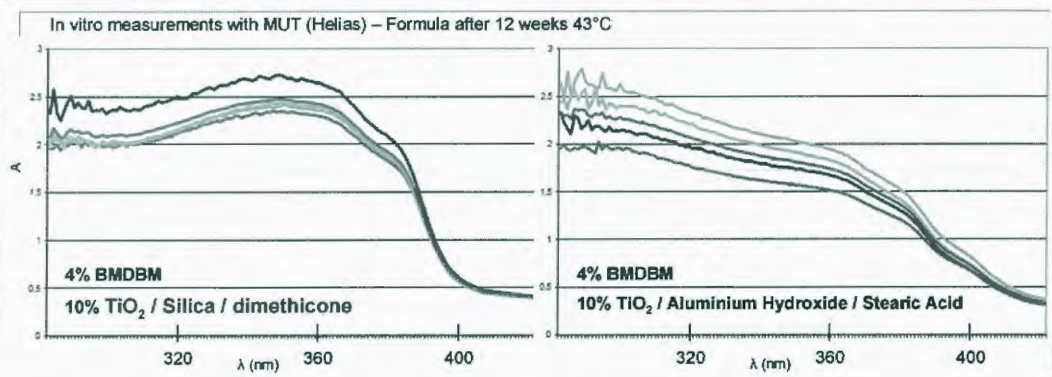
Today all cosmetic TiO_2 qualities are coated to avoid catalytic reactions leading for example to oxidative stress. However, the degree of coating varies. Sometimes there is a residual activity left, which may lead to discoloration of the formulation and bears an unwanted risk for oxidative stress on the skin. It is therefore crucial that the TiO_2 used has a highly complete coating. The aluminium hydroxide treated TiO_2 often has a fairly good coating, however, as demonstrated earlier is incompatible with BMDBM. Silica/ and or Stearic Acid coatings are compatible; however it is difficult to achieve a perfect coating with these components. Through careful consideration of the product parameters and advanced methods, we have improved the quality of the silica coating and also added a second layer to reach a complete and non-reactive coating on the TiO_2. With an easy test, a bench chemist can check the integrity of the coated TiO_2 material. It simply requires the use of Ascorbylpalmitate and the visualization of the reactivity with this ingredient.

Description of the Vitamin C reactivity test

<u>Composition of the test formulation:</u>

Caprylic/capric triglyceride	88%
Titanium Dioxide	10%
Ascorbylpalmitate	2%

UVA Protection
Incompatibilities between TiO_2 and Aluminium



In vitro SPF	UVA balance	PPD / SPF
126.3 ± 48.6	116.1 ± 10.8	1.16

In vitro SPF	UVA balance	PPD / SPF
118.3 ± 56.8	39.5 ± 5.1	**0.39**

→ UVA protection decreases when TiO_2 has Al-coating

Fig. 2

Preparation

Disperse Titanium Dioxide in Caprylic/ capric triglyceride or in any other solvent of your choice; add Ascorbylpalmitate, shake well and wait for 2 hours. After the two hours, check for discoloration.

If TiO_2 is not well coated, you will see a beige discoloration initially, which intensifies over time. We have seen color formation up to dark brown. The test result is independent of the type of coating.

We made a comparison of 9 different commercial TiO_2 qualities incorporated into the test formulation and stored for 2 hours. In particular, materials with a primary particle size smaller than 20 nm exhibit increased reactivity and discoloration.

LIGHT STABILITY TEST WITH GAS PHASE PHOTO REACTOR

To perform this test specific equipment is necessary.

The principle of this test is to determine the decomposition of Propanol-2 into acetone and carbon dioxide.

To check the sample, 20 gr of TiO_2 is placed onto a Petri dish in this photo reactor. After preparation 1ml of 2-propanol is injected into the reactor. After a while UV light is switched on. The degradation processes of 2-propanol and the formation of acetone and CO_2 are monitored by using FTIR, as a function of time. After the photoreaction, the reactor is flushed with synthetic air to obtain information about the amount of substance of the remaining reactants and the products formed in the photo catalytic reaction (figures 3 and 4).

Under the influence of UV light, TiO_2 can become photoreactive and discolor. The anatase form of the TiO_2 crystal is particularly sensitive to UV exposure. A proper coating will also work to prevent this reactivity.

To perform this assessment a sun tester is required. We used the Suntest XL+ from Atlas. The minimum radiation dose is 40 MED. This test has been performed in cosmetic oil with and without additional UV filters; however, our recommendation is to use a simple dispersion of TiO_2 in Alkyl benzoate or Caprylic/Capric Triglyceride. Incorporating additional sun filters can lead to a false positive discoloration reaction.

PHOTOSTABILITY OF TiO2

Description of the UV challenge Test

Test formulation:

Finsolv TN	90%
Titanium Dioxide microfine	10%

Preparation

Disperse Titanium Dioxide completely in Alkyl benzoate. Apply this dispersion with a 20 micron film applicator on to normal microscope slides. Cover it with another slide and put it into the Sun Tester. Radiate with 40 MED and check the color after radiation. After the radiation you may see a greyish/bluish discoloration which is indicative of photo reactive behavior.

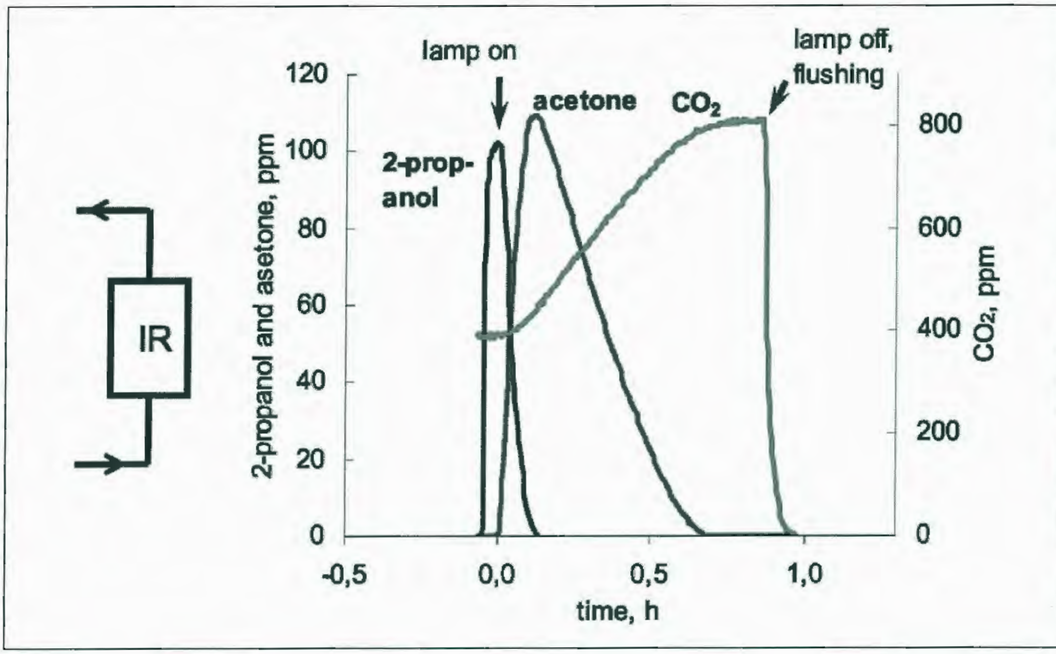

lamp on
lamp off, flushing
acetone
CO_2
2-prop-anol
2-propanol and asetone, ppm
CO_2, ppm
IR
time, h
120
100
80
60
40
20
0
800
600
400
200
0
-0,5
0,0
0,5
1,0

Fig. 3

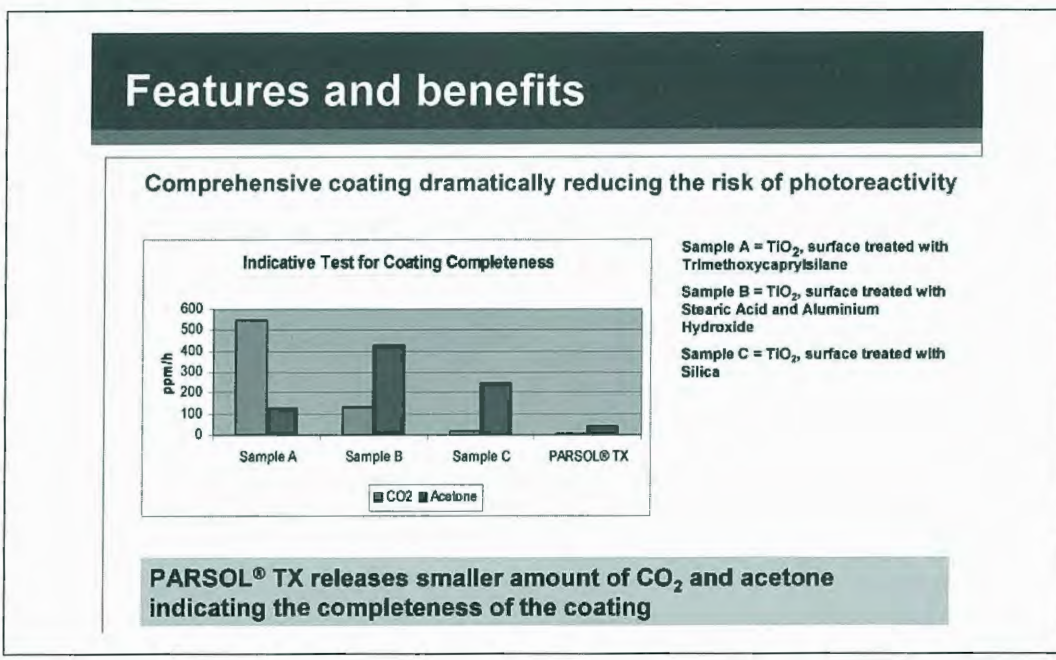

Features and benefits
Comprehensive coating dramatically reducing the risk of photoreactivity
Indicative Test for Coating Completeness
ppm/h
600
500
400
300
200
100
0
Sample A
Sample B
Sample C
PARSOL® TX
CO2 Acetone
Sample A = TiO_2, surface treated with Trimethoxycaprylsilane
Sample B = TiO_2, surface treated with Stearic Acid and Aluminium Hydroxide
Sample C = TiO_2, surface treated with Silica
PARSOL® TX releases smaller amount of CO_2 and acetone indicating the completeness of the coating

Fig. 4

DAY LIGHT PHOTO STABILITY OF TiO2 IN FORMULATIONS

All described tests above are challenge tests that can help to find the most appropriate TiO_2 grade in a relative early stage of the development work. But as we have learned in the past, not every challenge test gives you all the information you need to bring a product onto the market. In addition to indicative short term challenge tests, also long term testing should be performed to ensure that your product is stable and ready for launch. One particularly important feature is stability under ambient light conditions. It is recommended to perform this test even if all prior tests were passed without issues. Instability will be demonstrated by a discoloration of the formulation.

Description of the day light photo stability test

Test formulation:
Launch product formulation
Store the samples near the window, preferentially the north side of the building with minimal direct radiation.

Preparation

The products, filled in glass jars or in the finished packaging, are simply stored for 2 to 3 months near the window. In addition to color change caused by TiO_2 reactivity, oxidation of unstable ingredients and fragrances can be assessed.

References

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2) **EU Recommendation 2006/647/EC.**
3) **Colipa Project Team IV, (2007)** Method for the in vitro determination of UVA protection provided by sun care products.

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