Stabilization of Avobenzone in the Presence of Ultrafine TiO_2 and Titanated Mica

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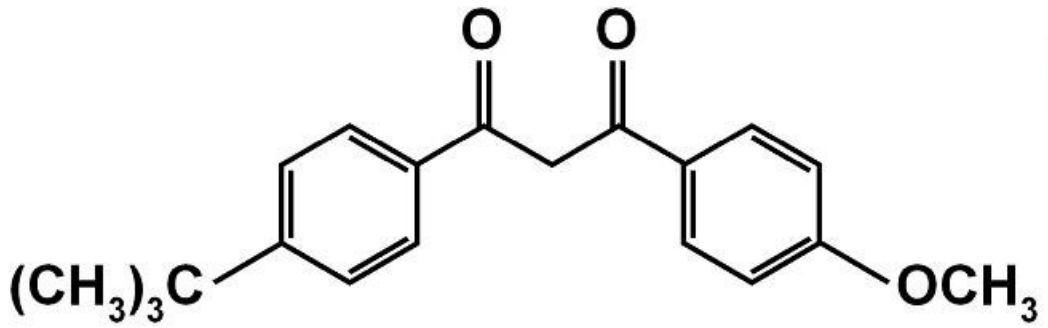
- Compatibility with Ultrafine Titanium Dioxide
- Compatibility with Titanated Mica
- Conclusions

Introduction

UV protection has become a major function of more type of cosmetic formulations

- Although UVB protection has been the main focus, UVA protection has gained more and more attention in recent years
- One of the major UVA sunscreen agents is Avobenzone (INCI name : Butyl Methoxydibenzoylmethane)



- Avobenzone is very effective and widely used. However, it is not allowed to be used with Titanium Dioxide in the USA.

Instability of Avobenzone

- There are concerns that metal ions must be avoided in a sunscreen composition that contains Avobenzone for achieving a broad-spectrum protection.

- It was discovered that the presence of titanium dioxide or zinc oxide had an unexpected result of stabilizing the Avobenzone (Stewart et al., US Patent, 6,090,369)

The Objectives of this study

- To investigate the chemical change of avobenzone in the presence of ultrafine TiO_2 and titanated mica

  a) Without UV exposure to understand shelf or storage stability
  b) With UV exposure to understand application stability

- To investigate the effect of surface treatment on the suppression of Avobenzone degradation in the presence of TiO_2

- To provide reference for safe and effective use of TiO_2 and Avobenzone in combination for broad spectrum protection

Experimental (1)

Instruments:

- UV lamp (Spectronics corporation, model XX-15NB) with an intensity of 550 $\mu W/cm^2$ for UV-A and 590 $\mu W/cm^2$ for UV-B at a distance of 25 cm.
- UV spectrophotometer (Hitachi, model U-3010/U-3310)
- Centrifuge (Labnet) 14,000 rpm

Materials:

- TiO_2: 15 - 180 nm, treated with various amount of alumina, silica and/or additional organic compounds
- Titanated Mica : various size and TiO_2 content, with or w/o surface treatment
- Avobenzone (Roche)
- Solvents : C12-15 Alkyl Benzoate; Ethanol

Experimental (2)

Sample preparation:

- 0.127% or 2% of Avobenzone and 8 to 33% of pigment in C12-15 Alkyl Benzoate

Storage stability study:

- Sample was placed in a test tube and incubated at 50°C for a period of 7 to 90 days.
- Sample is then centrifuged, the supernatant is diluted with Ethanol and absorbance at 357 nm is measured to calculate the percentage of residual Avobenzone.

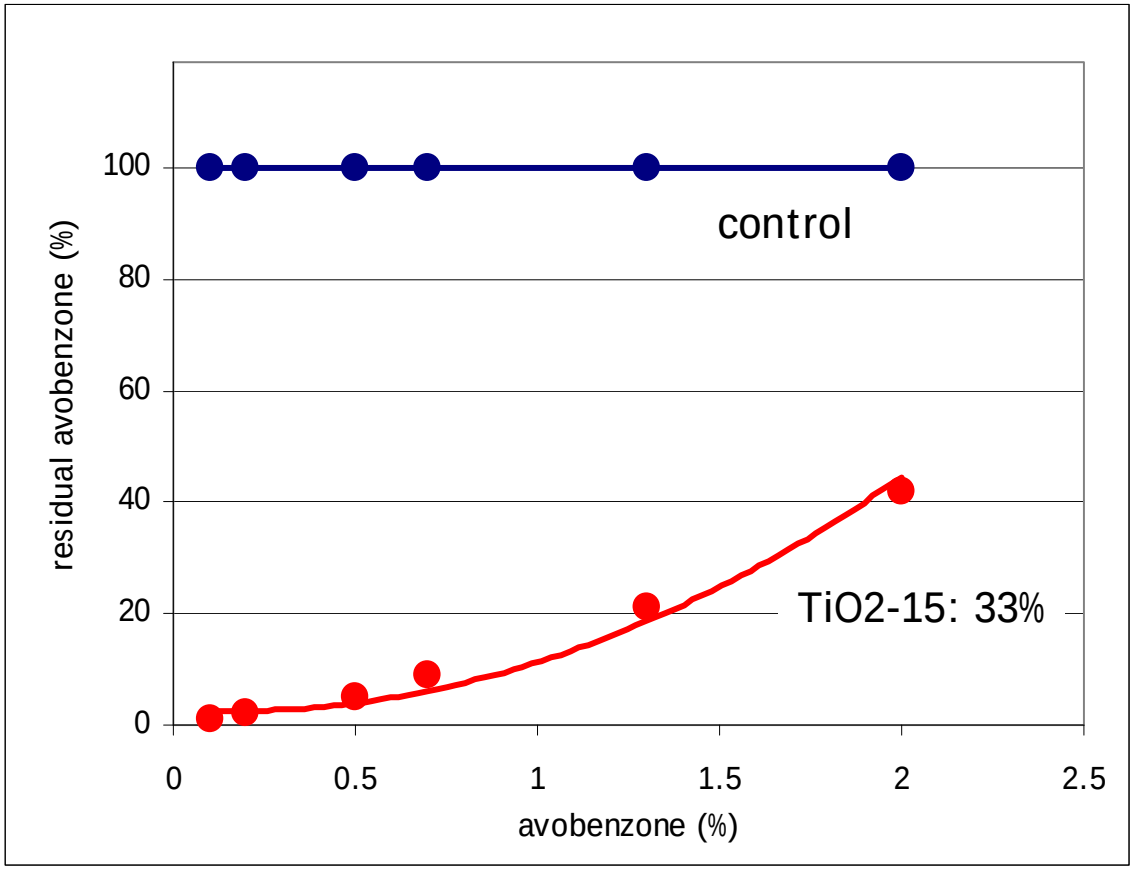
Photo-stability study:

- Sample was placed in a quartz test tube and irradiated at a distance of 5 cm for 5 days in a light box.
- Sample is then processed and analyzed the same way as above.

Ultrafine TiO_2

Storage stability study

Influence of Avobenzone concentration

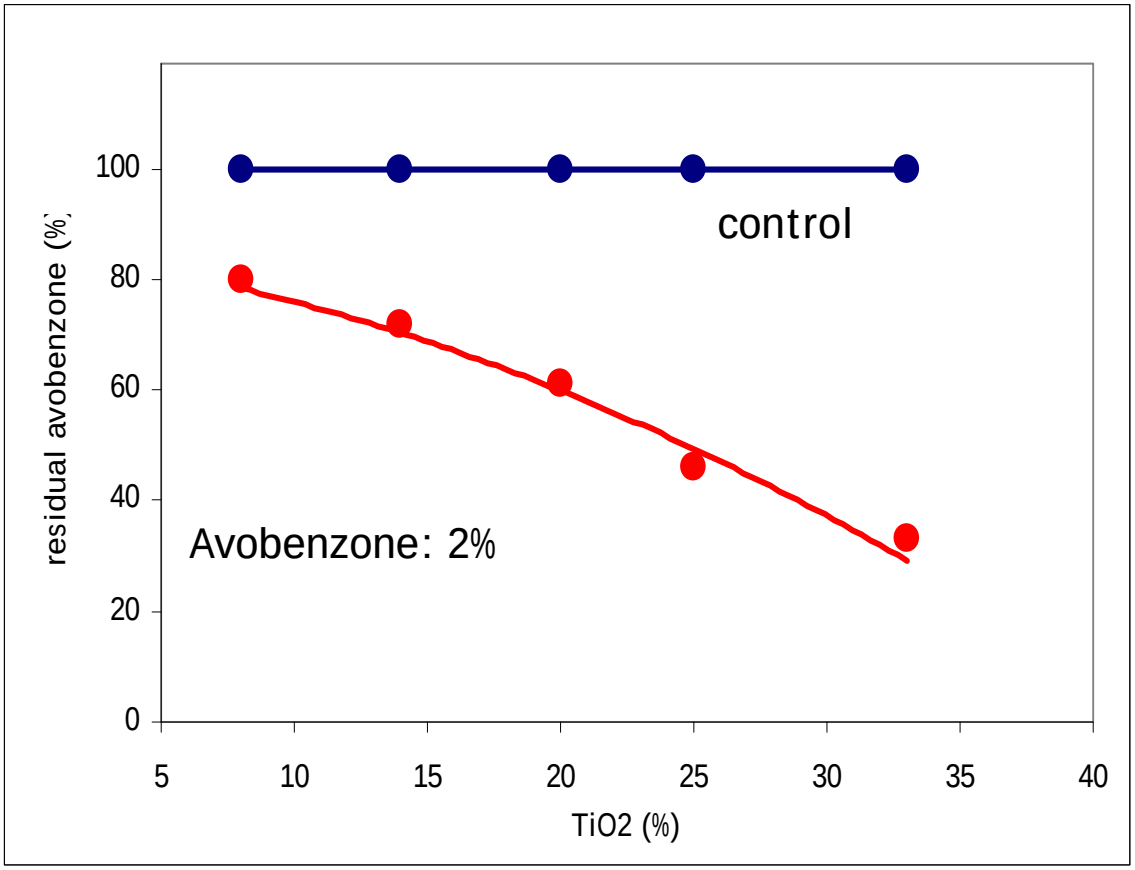


TiO2-15:

PPS: 15nm
Alumina: 10%

Higher concentration results in less degradation relatively:
pigment surface area is a limiting factor

Influence of pigment concentration



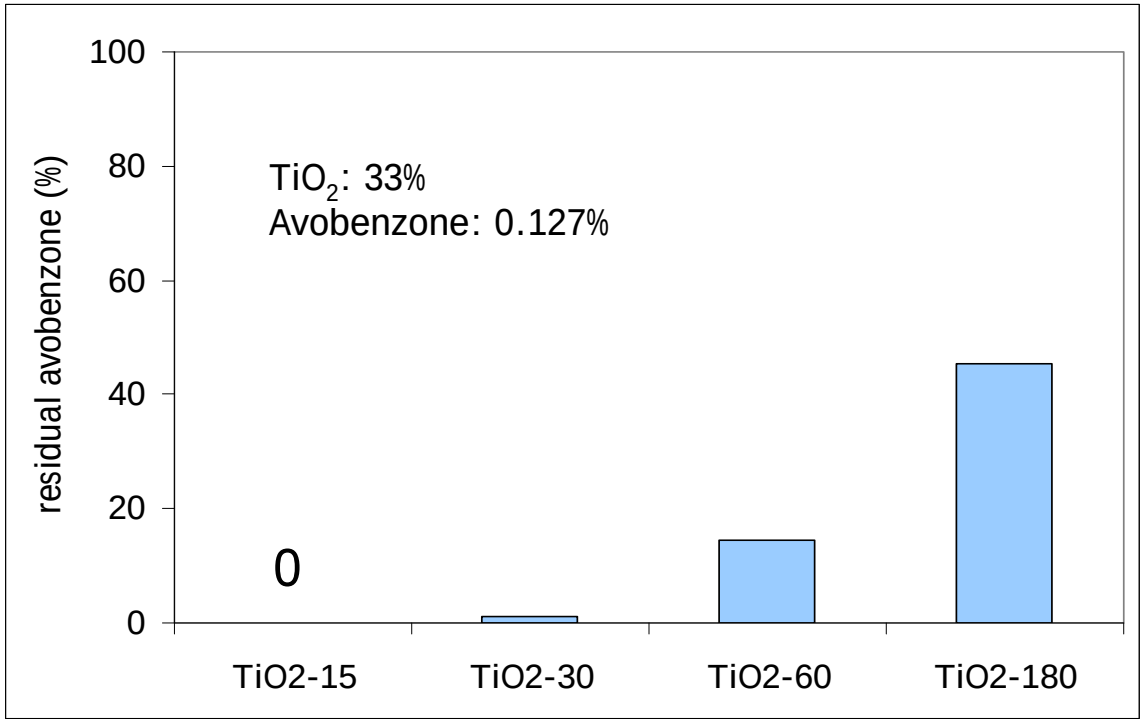
TiO2-15:

PPS: 15nm
Alumina: 10%

Higher concentration results in more degradation relatively : pigment surface area controls the reaction rate

Influence of TiO_2 primary particle size

Surface treatment : alumina

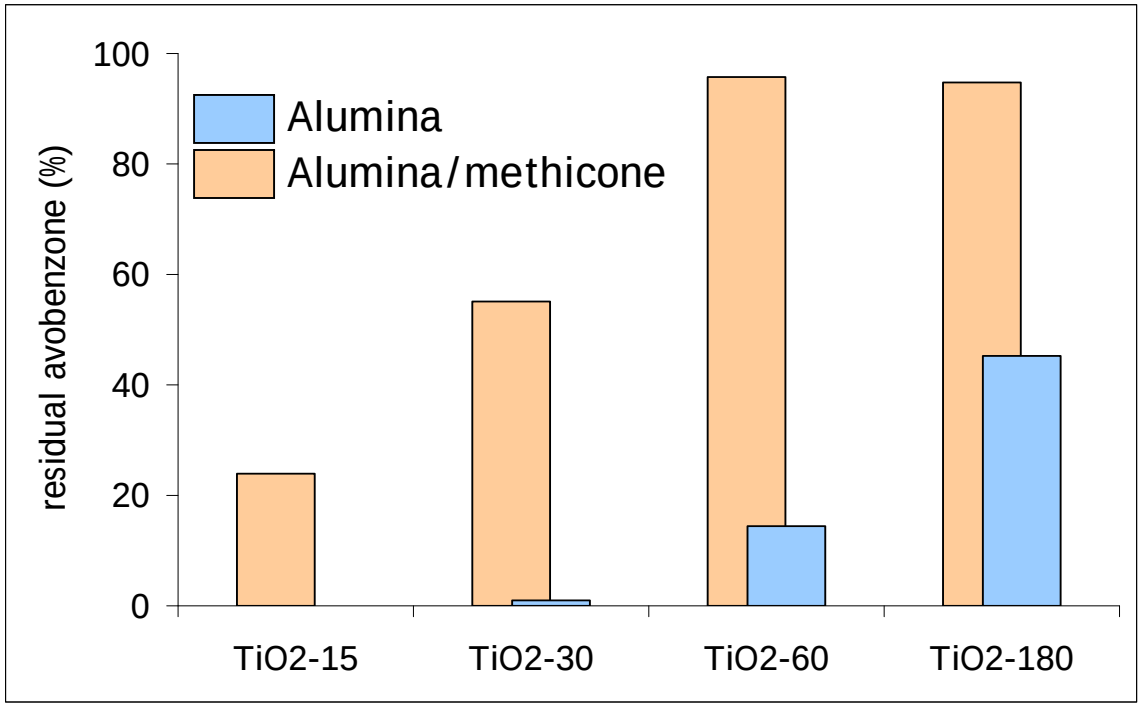


	TiO2-15	TiO2-30	TiO2-60	TiO2-180
Particle size	15 nm	30 nm	60 nm	180 nm
Alumina (%)	10	5	2.5	1.3

Smaller size results in more degradation

Influence of organic surface treatment

Surface treatment : alumina & 4 %methicone



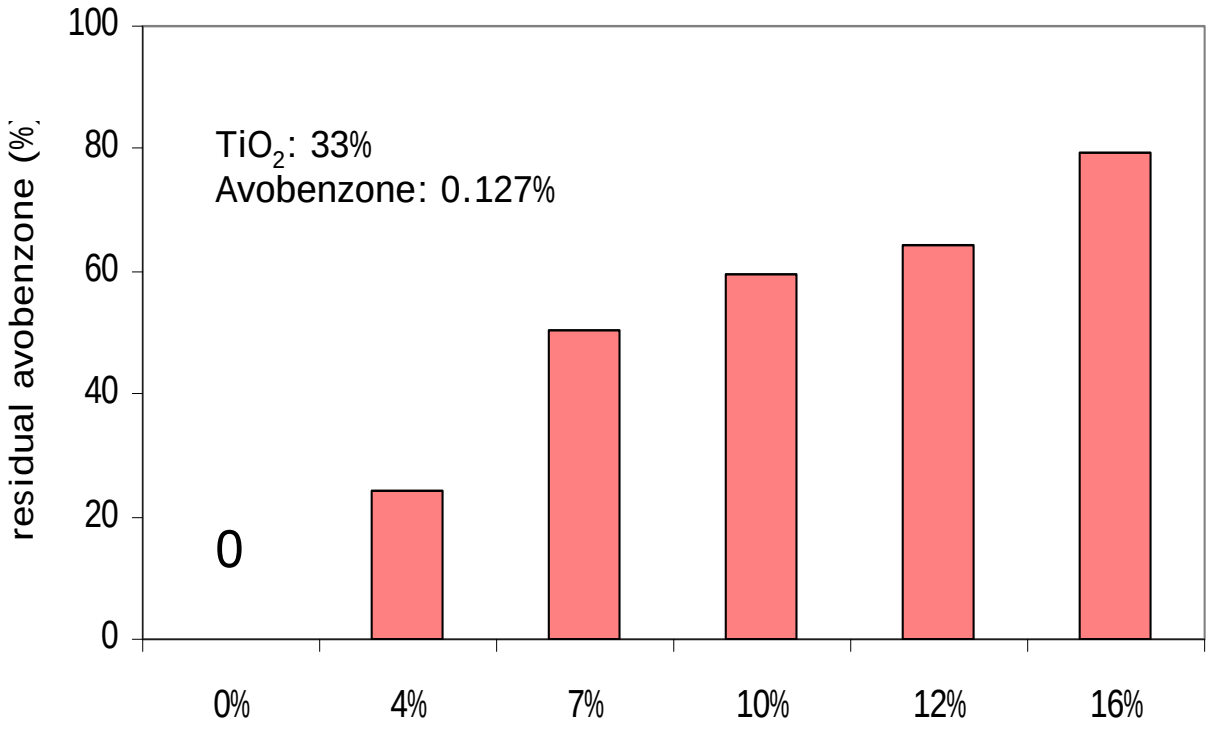
TiO_2: 33%
Avobenzone: 0.127%

	TiO2-15	TiO2-30	TiO2-60	TiO2-180
Particle size	15 nm	30 nm	60 nm	180 nm
Alumina (%)	10	5	2.5	1.3

Methicone treatment minimizes Avobenzone degradation

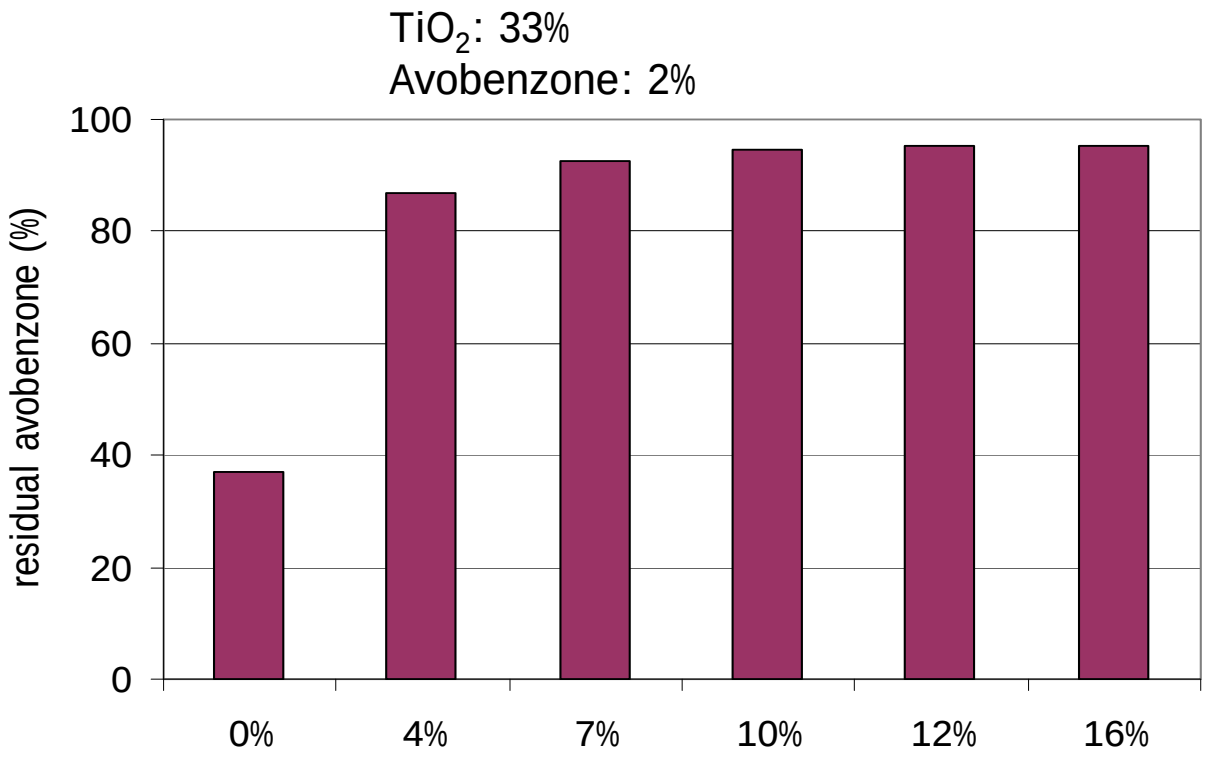
Influence of surface treatment percent

Surface treatment (TiO2-15) : alumina & methicone



Influence of surface treatment percent

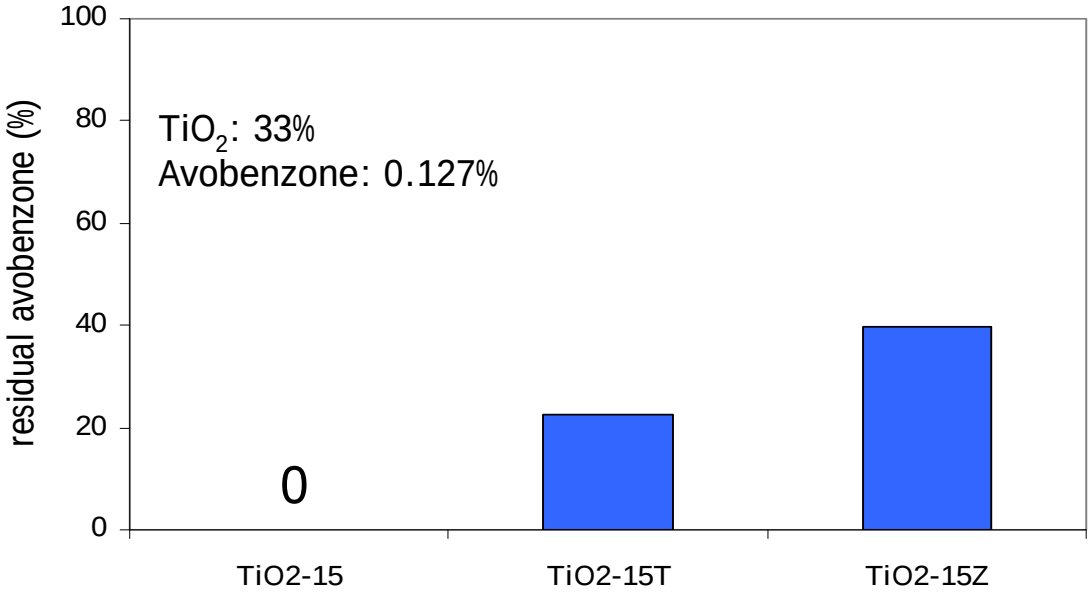
Surface treatment (TiO2-15): alumina & methicone



At higher Avobenzone concentration, degradation rate is limited by TiO_2 surface area and optimal coating level can be achieved

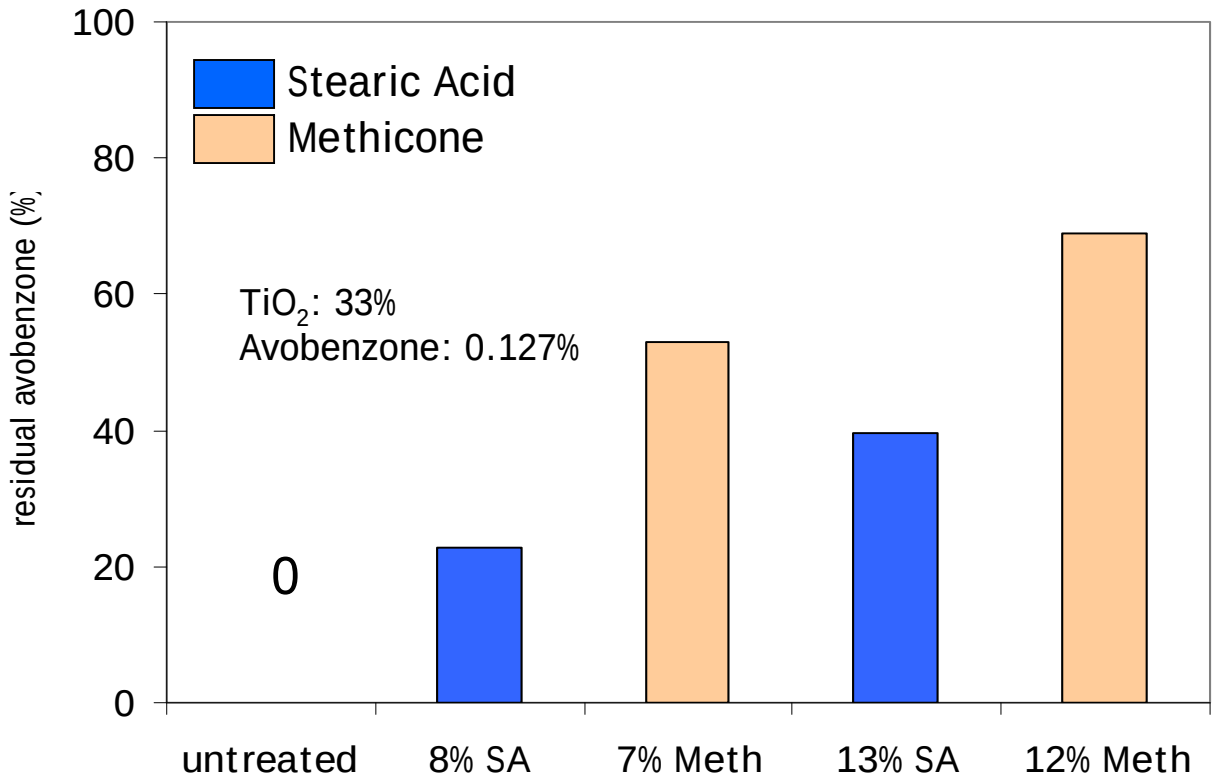
Alumina & Stearic Acid surface treatment

Surface treatment : alumina & stearic acid



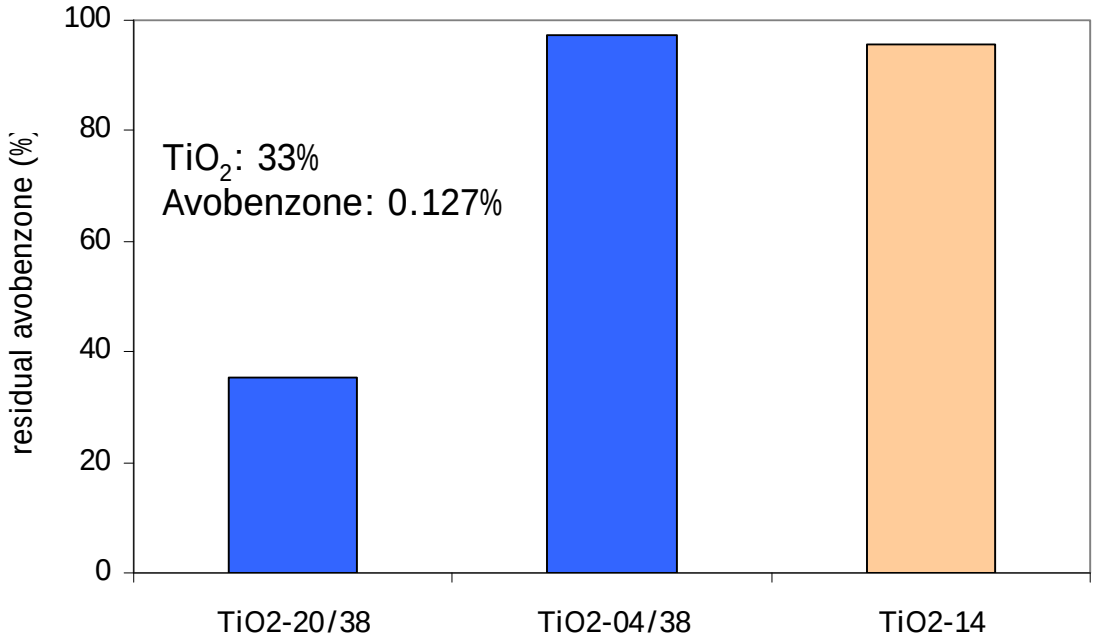
	TiO2-15	TiO2-15T	TiO2-15Z
Particle size	15 nm	15 nm	15 nm
Alumina (%)	10	5	12
Stearic Ac.(%)	0	8	13

Comparison of Stearic acid & Methicone treatments



Stearic acid surface treatment is not as effective as Methicone

Silica encapsulation



	TiO2-20/38	TiO2-04/38	TiO2-14
Particle size	34 nm	38 nm	14 nm
Silica (%)	20	33	10
Methicone(%)	0	0	9

A combination of Silica and Methicone can be as effective as high percentages of Silica

Compatibility with ultrafine TiO_2

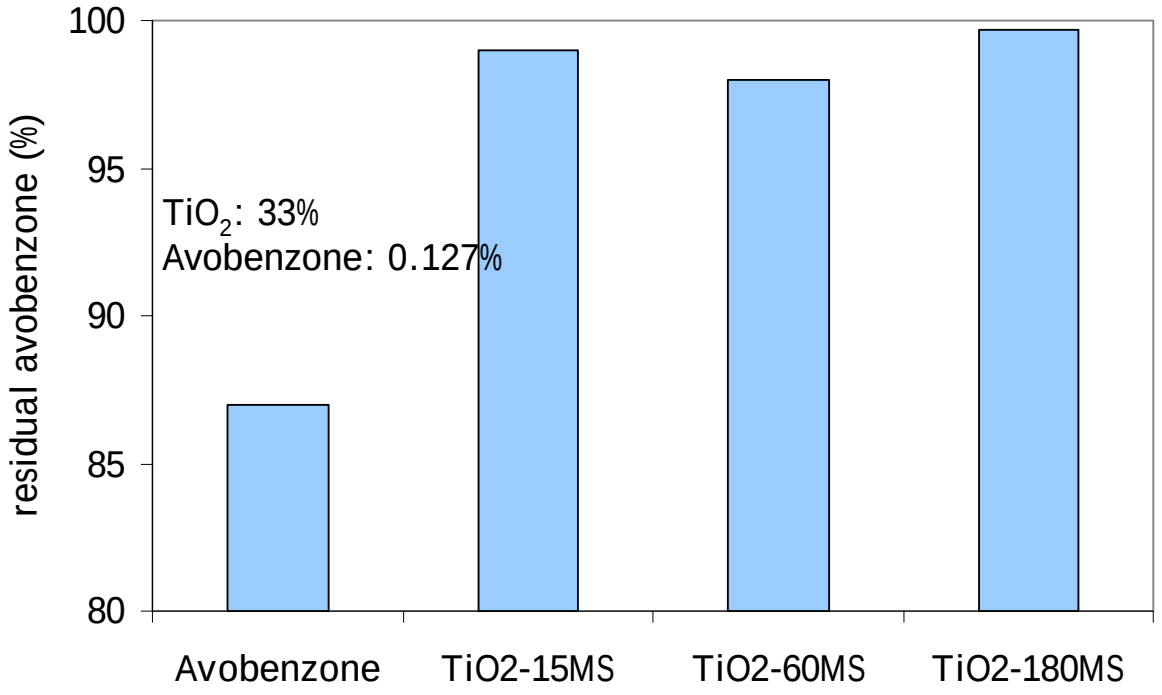
- Primary particle size of the pigment is a limiting factor for the degradation of Avobenzone.

- Surface treatments reduce the reactivity of TiO_2 to Avobenzone :
  - inorganic treatment : silica encapsulation can be very effective at high concentration
  - organic coating : Methicone treatment provide with great protection from the degradation
  - Proper organic & inorganic coating have additive effects

Ultrafine TiO_2

Photo-stability study

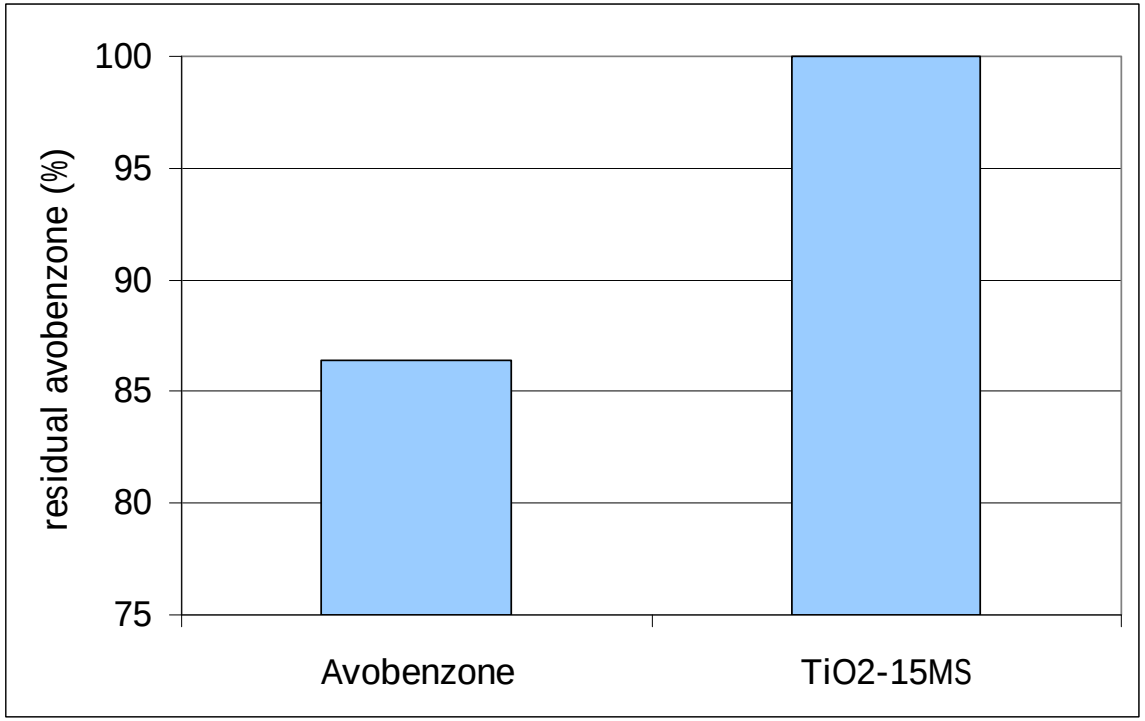
Protection of TiO_2 against photodegradation



	TiO2-15MS	TiO2-60MS	TiO2-180MS
Particle size	15 nm	60 nm	180 nm
Methicone (%)	16	4	4

Protection of TiO_2 against photodegradation

Avobenzone concentration : 2%



Protection of Avobenzone by TiO_2

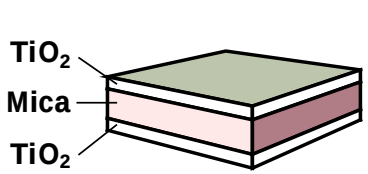
- Ultrafine TiO_2 reduces the photodegradation of Avobenzone under UV irradiation by primarily absorption of UV light , especially those near 320 nm that are most responsible for the photodegradation.

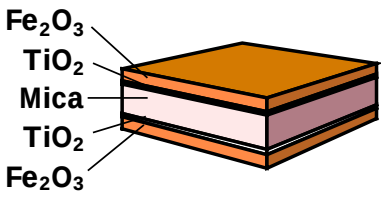
Titanated Micas

Storage stability study

Pearlescent pigments

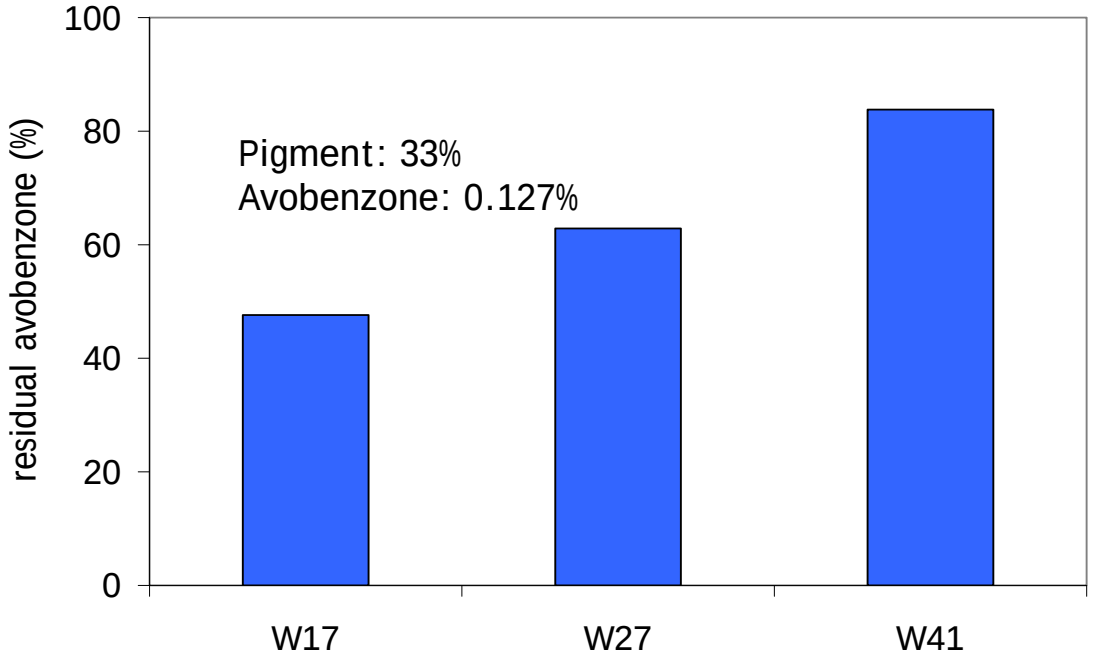
- Formulators nowadays want to use more and more UVA protection in other types of formulas
- Titanated micas (pearlescent pigments) have a very thin TiO_2 layer on Mica : this TiO_2 resemble ultrafine TiO_2 at least in one dimension. Therefore, it became another focus for our study with Avobenzone.
- Surface treatments can also be applied to such titanated micas





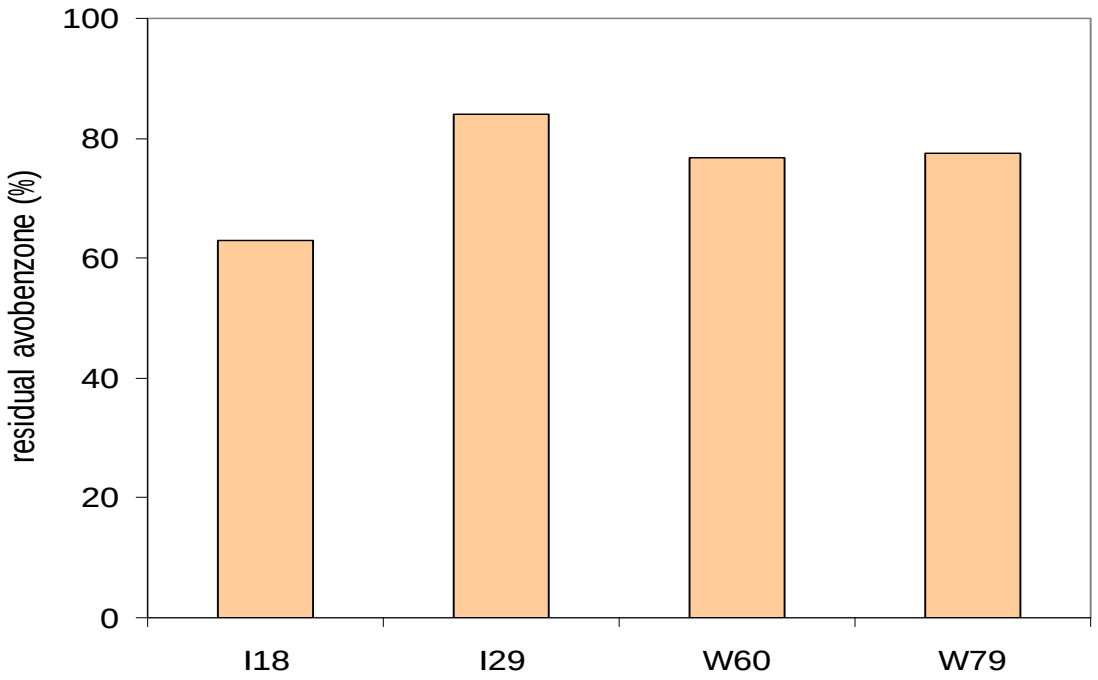
TiO_2 layer thickness : 60 to 163 nm

Untreated titanated Micas : Anatase



	W17	W27	W41
Particle size	17 µm	27 µm	41 µm
TiO_2 (%)	38	29	19
Type TiO_2	Anatase	Anatase	Anatase

Untreated titanated Micas : Rutile

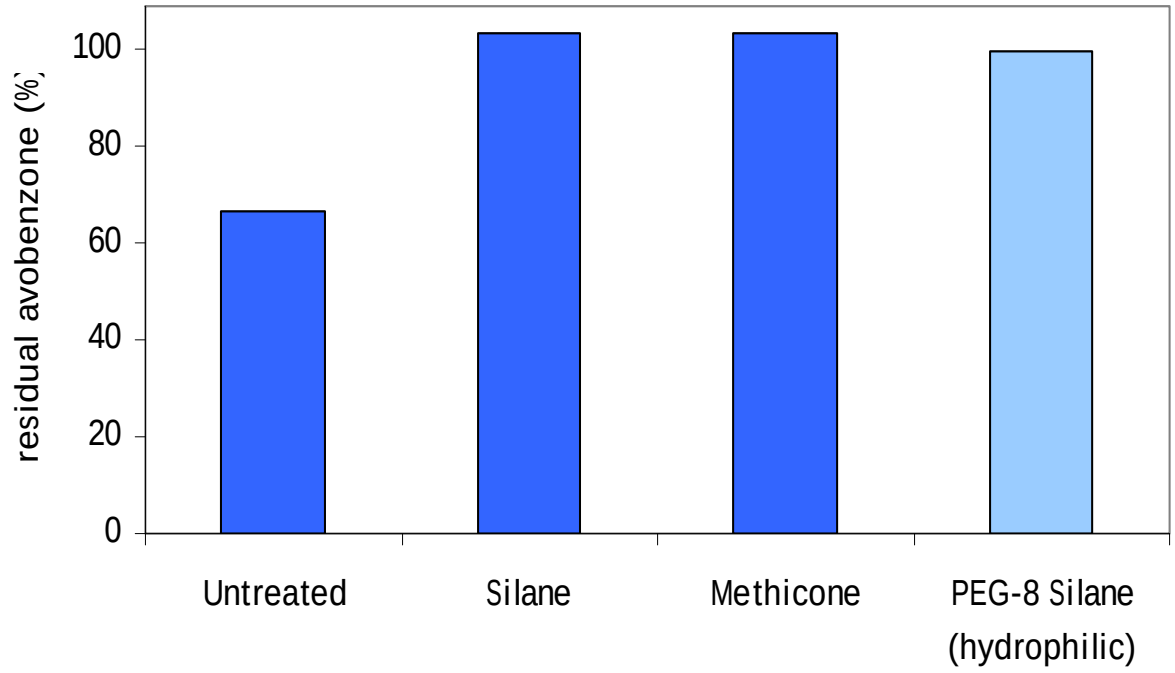


pigment: 33%
Avobenzone: 0.127%

	I18	I29	W60	W79
Particle size	18 µm	29 µm	60 µm	79 µm
TiO_2 (%)	58	48	16	13
Type TiO_2	Rutile	Rutile	Rutile	Rutile

Surface-treated titanated Micas

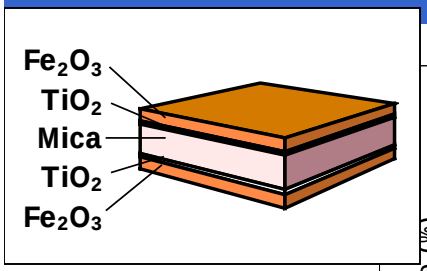
W27 : Anatase TiO_2 - Particle size : 27µm
Treatment: 2%

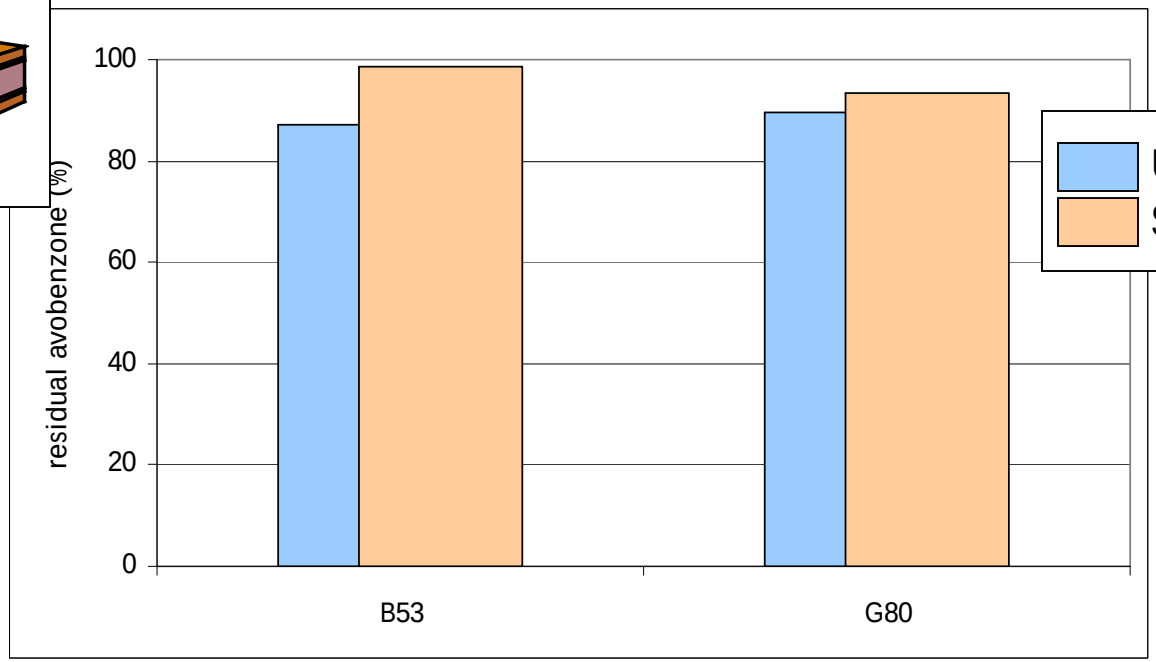


TiO_2: 33%
Avobenzone: 0.127%

Titanated Micas can be well coated and rendered almost non-reactive due to their relatively small surface area and low aggregation

Earth Tone Pearls : effect of Iron Oxide





Pigment$_2$: 33%
Avobenzone: 0.127%

	B53	G80
Particle size	53 µm	80 µm
TiO_2 (%)	0	19
Iron Oxide (%)	26.5	9

Iron Oxide can also cause slight degradation of Avobenzone

Compatibility with pearlescent pigments

- Like with ultrafine TiO_2, particle size of pearlescent pigment is an important factor for the compatibility with Avobenzone.
- Rutile TiO_2 seems less reactive than Anatase TiO_2
- Surface treatment inhibits the reactivity of pearl surface

Summary

- We have evaluated two mechanisms of degradation of Avobenzone : reaction with Metal Oxide surface (TiO_2) and UV irradiation
- Reaction with TiO_2 is limited by the pigment surface area
- Suitable treatments (both organic and inorganic) reduce the reactivity
- UV irradiation also causes degradation of Avobenzone : this degradation can be minimized by UV absorption by attenuation grade TiO_2
- Titanated-mica pearlescent pigments also show a reactivity with Avobenzone that can almost completely be reduced by surface treatment