Using TiO_2 and ZnO for Balanced UV Protection

Yun Shao, Ph.D. and David Schlossman - Kobo Products, Inc. - South Plainfield, NJ, USA

Introduction

Sunscreens have been widely used to protect people from harmful UV radiation, especially UVB radiation. In recent years, UVA protection has gained much attention from regulatory bodies as well as the consumers. In latest amendment of sunscreen monograph published by FDA, UVA testing and rating were incorporated. In September 2006, EU commission recommended that the PFA should be more than 1/3 of SPF value in order to provide complete UV protection. Therefore, it is essential for a sunscare product to be able to provide balanced UV protection.

Inorganic UV filters, TiO_2 and ZnO, are particulate and are widely used because they are inert and non-irritating to sensitive skin. Many grades are commercially available. Their performances are known to depend on their particle size, of which a thorough understanding is necessary.

Objective

- To investigate the attenuation behavior of TiO_2 and ZnO in UVA and UVB regions.
- To develop a combination of only inorganic UV filters that can provide a SPF of 30+ and SPF/PFA ratio of 3 or less.

Experimental

1. TiO_2 and ZnO of various sizes are dispersed in cyclomethicones and milled with bead mill to achieve optimal transparency or desired particle size.
2. SPF was tested according to FDA's method and PFA according to JCIA method (PPD). The panel consisted of three people.
3. Primary particle sizes were measured based on image analysis and reported by the supplier. The particle sizes in dispersion were measured using NiCOMp C370 Photo-correlation size analyzer. Intensity-weighted mean size was used.
4. UV transimttance curves were measured using Hitachi U-3010 spectrophotometer. Sample was prepared by diluting the dispersion in chloroform to 0.001% for TiO_2 and 0.005% for ZnO.

Acknowledgement

The authors are grateful to Shirley Wang, Scott Holzapfel for their help in preparing dispersions and sunscreen lotion, and to Dr. Pascal Delrieu for his work on graphics.

1. Evaluation of TiO_2 dispersions

Fig.1 - UV transmittance curves of TiO_2 dispersion in D5

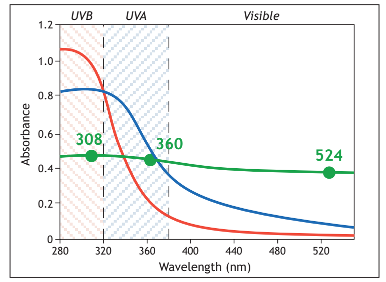


Fig.2 - Comparison of transparency of TiO_2 dispersions
(All dispersions diluted in Cylcopentasiloxane to 20% TiO_2)

The UV absorption curves in Fig. 1 indicate that TiO2 attenuation is very effective in UVB but not so much in UVA when size is very small. As size increases, UVB attenuation weakens but UVA attenuation increases. But when the size is too large, attenuation of visible light is strong, leading to unacceptable whitening (Fig. 2).

2. In-vivo study of TiO_2 performance

Table 1. In-vivo SPF and PFA test results of TiO_2 sunscreen lotions

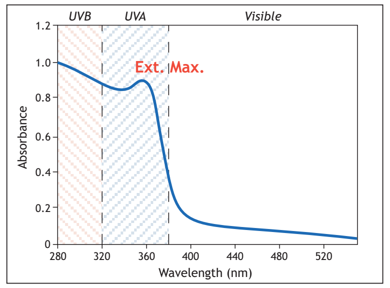
Formula	KSL-027A (O/W)	KSL-027 (O/W)	KSL-026 (O/W)	KSL-026B (O/W)
PPS (nm)	50	35	15	15
PS in disp. (nm)	162	154	125	173
Active (%)	10.29	10.29	10.29	10.29
SPF	25.6	28.4	50	30.8
SPF/Active%	2.49	2.76	4.85	2.99
PFA	7.58	6.75	4.50	5.6
PFA/Active%	0.74	0.65	0.44	0.54
SPF/PFA	3.4 /1	4.2 / 1	11 / 1	5.5 /1

TiO_2 has a very high refractive index and can give unacceptable whitening whitening when its primary particle size is too big (>50 nm). Therefore, the guidelines for the use of TiO_2 in actual sunscreen lotions are:

- Small primary particle size (10 - 15 nm) and aggregate size are good for both transparency and high SPF.
- TiO_2 should be used to achieve high SPF. It alone cannot provide balanced UV protection. To do so, UVA sunscreens need to be used in combination

3. Evaluation of ZnO dispersions

Fig.3 - UV transmittance curve of ZnO



The absorption curve of ZnO in UV region is fairly flat (or uniform) and the shape does not change much as the size changes. What is worth noting is that as the size gets smaller, , the absorbence becomes stronger, but the onset of absorption shifts to a shorter wavelength, meaning the stronger absorption in a narrower range.

4. In-vivo study of ZnO performance

Table 2. In-vivo SPF and PFA test results of ZnO sunscreen lotions

Formula	KSL-037B	KSL-016	KSL-016A	KSL-016B	KSL-043
PPS (nm)	~100	15 - 35	60	20	20
PS in disp. (nm)	263	228	163	166	130
Active (%)	16	14.97	14.97	14.97	13.80
SPF	12.6	14	20.4	17.4	25.4
SPF/Active%	0.79	0.93	1.36	1.16	1.84
PFA	5.83	7.50	7.58	8.17	4.75
PFA/Active%	0.46	0.50	0.51	0.54	0.34
SPF/PFA	2.2 / 1	1.9 / 1	2.7 /1	2.1 /1	5.4 / 1

Fig. 4. Drawdowns of sunscreen lotions containing different ZnO
(15% ZnO - 12μm film thickness)

PPS	60 nm	13/15 nm	20 nm	20 nm
Size in Dispersion	165 nm	228 nm	167 nm	130 nm

ZnO has a much lower refractive index than TiO_2 does. A wide range of particle size can be used without causing noticeable whitening. The in-vivo test results show :

- ZnO can provide balanced UV protection provided that SPF is moderate (<20). When its size becomes very small, ZnO becomes very effective in providing SPF but not PFA.
- For high SPF (30+) sunscreen lotions, ZnO alone cannot provide balanced UV protection unless being used at a very high level (close to 25%).

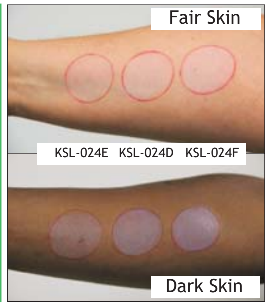
5. Formulation for high and balanced UV protection

From the above in-vivo study, it is clear that neither TiO_2 nor ZnO along can provide a sunscreen lotion with high transparency, high SPF and a SPF/PFA ratio of 3 or less. To achieve this goal, the following combinations can be used:

a. combination of TiO_2 and ZnO
b. combination of two grades of ZnO that have different dispersion particle sizes

Table 3. In-vivo SPF and PFA test results of sunscreen lotions using TiO_2 and ZnO

	Formula	KSL-024E (W/O)	KSL-024D (W/O)	KSL-024F (W/O)
TiO_2	PPS (nm)	15	35	35
	PS (nm)	125	160	160
	Active (%)	6	6.3	6
ZnO	PPS (nm)	15-35	15-35	15-35
	PS (nm)	220	220	220
	Active (%)	12	5.9	12
	SPF	32.9	26.6	27.4
	PFA	10.84	8.8	11.68
	FDA rating	High	High	High
	Ratio	3 / 1	3 / 1	2.3 / 1



TiO_2 dispersion with a mean size in the range of 110 - 130 nm is very effective in UVB and ideal for combinational use. ZnO dispersion with large mean size needs to be used to provide adequate UVA protection. The right combination can result in a high and yet balanced UV protection. It is easier to get a SPF/PFA ratio of < 3 with larger size TiO_2 (35 nm), but the whitening became noticeable.

Table 4. In-vivo SPF and PFA test results of sunscreen lotions using two ZnO

	Formula	KSL-016C (W/O)	KSL-016D (W/O)	KSL-016E (W/O)
ZnO 1	PPS (nm)	20		
	PS (nm)	130		
	Active (%)	12	10	10
ZnO 2	PPS (nm)	60		15-35
	PS (nm)	250	193	220
	Active (%)	10	10	12
	SPF	31.4	30	30.7
	PFA	11.6	8.7	9.3
	FDA rating	High	High	High
	Ratio	2.7 / 1	3.4 / 1	3.3 / 1

To provide adequate SPF, one of two grades of ZnO should have smaller size possible and be used at a high level. The UVA protection of this fine size ZnO is poor. Therefore, the second ZnO needs to have a very large size in order to make up the deficiency in PFA. Although the total active content in this series is much higher than that in case with TiO_2/ZnO combination, the sunscreen lotions made showed very good transparency and little ashy color even on the dark skin.

Conclusions

- TiO_2 is effective for UVB protection. It cannot provide enough UVA protection without sacrificing the transparency. ZnO in general is not an efficient UVB agent and is not suitable for high SPF products.
- By combining TiO_2 and ZnO of right sizes, balanced UV protection with SPF of 30 or higher can be achieved.
- Combination of very fine ZnO and large ZnO can also give high and balanced UV protection.

KOBO

www.koboproducts.com