Discovering an Optimum Small Micropigment for High UV Shielding and Low Skin Whitening

Yun Shao, Ph.D., and David Schlossman - Kobo Products, Inc.
23d IFSCC Congress - Orlando 2004
For any inquiries about this presentation, please correspond to : yshao@koboproductsinc.com

1. Introduction

Theoretical calculation by Stamatakis et al. (1) and experimental data from Sakamoto et al. (2) have proven that the UVB attenuation by TiO_2 is predominately due to the absorption while the UVA attenuation is predominately due to the scattering. Stamatakis' work also shows that the absorption of ZnO increases as particle size decreases throughout the UV region.(1) Therefore, the size reduction of either TiO_2 or ZnO should theoretically enhance its absorption of UVB light, which in turn will always improve the SPF score. This conclusion was confirmed by in-vivo testing of sunscreen lotions that contain physical sunscreen of various particle sizes. (3) In that study, the primary particle size of TiO_2 was as small as 15 nm and that of ZnO was as small as 20 nm.

However, the advances in nano technology during the past several years have resulted in titanium dioxide with a smaller primary particle size of 10 nm and zinc oxide of much less aggregation. Furthermore, new surface treatments, dispersants, and grinding technologies have made the milling of these micropigments much more efficient. For example, the particle size of TiO_2 in dispersion has been reduced to approximately 100 nm that is about 20% smaller than what could be achieved previously. The particle size of ZnO dispersion has also been able to be dramatically reduced.

In this work, the UV attenuation of these new TiO_2 and ZnO dispersions and their SPF in-vivo efficacy were studied. In order to optimize the SPF and PFA of these dispersions in formulations, the potential synergy for combination with organic sunscreens and with medium sized micropigments was also investigated.

2. Experimental

1. Materials: 10 nm TiO_2 (TTO-V-3 from Ishihara Sangyo Kaisha. Ltd), 20 nm ZnO (MZ-500 from Tayca Corp. and Zinclear from ANT) were used as sunscreen agents. PEG-10 Dimethicone and Acrylates/Ethylhexyl Acrylate/Dimethicone Methylacrylate Copolymer from Shin-Etsu was used dispersants.
2. Pigment treatment and grinding: Treatment material was blended together with the pigment. The mixture was heated at 100 - 110°C for 3 hours. The treated pigments were mixed into cosmetic liquids and milled to obtain the finest size.
3. Viscosity and size: Samples were incubated at 25°C for 24 h and viscosity was measured using a Brookfield RVT viscometer. Particle size is analyzed with NICOMP C370 Photo-correlation particle analyzer.
4. UV/Visible transmittance curves: Dispersion sample was diluted in chloroform to a concentration of 0.001% for TiO_2 and 0.005% for ZnO. Measurement was done using a Hitachi UV-3301 spectroscopy.
5. SPF and PFA testing : FDA method was used for SPF testing. JCIA recommended persistent pigment darkening method was used for PFA testing. Both tests were on 3 panelists.
6. Color analysis was done using a Datacolor SF600.

3. Grinding of Pigment

PEG-10 dimethicone and polyhydroxystearic acid were found to be very effective dispersant for cyclomethicone based and ester based dispersions, respectively. The smallest size that could be achieved before was about 120 nm for TiO_2 and 220 nm for ZnO.(3) Although the viscosity of all dispersions in this study was very low, no settling was observed during 2-year storage.

Table 1. Formula and Properties of Ultrafine TiO_2 and ZnO Dispersions

	TiO_2 Dispersions		ZnO Dispersions		
	CM3K25VM	TNP40VTTS	CM3K50XZ4	TNP50ZSI	TNP50ZCLS
P.P.S.* (nm)	10	10	20	20	25
Treatment	Alumina/ Methicone	Alumina / ITT / TCS **	Methicone	Triethoxy Caprylylsilane	Triethoxy Caprylylsilane
Carrier	Cyclopenta-siloxane	C12-15 Alkyl Benzoate	Cyclopenta-siloxane	C12-15 Alkyl Benzoate	C12-15 Alkyl Benzoate
Dispersant	PEG-10 Dimethicone	Polyhydroxy-stearic Acid	PEG-10 Dimethicone	Polyhydroxy-stearic Acid	Polyhydroxy-stearic Acid
Active %	19.1	32	48	48	48
P.S.* (nm)	100	100	145	130	110
Viscosity (cPs)	100	150	200	100	60

* PPS: Primary particle size. PS. Particle size.
** ITT/TCS : Isopropyl Titanium Triisostearate / Triethoxy Caprylysilane Crosspolymer

4. Drawdowns & Whitening

When the particle size was further reduced, the transparency was greatly improved for both TiO_2 and ZnO. Moreover, the bluing associated with physical sunscreen was also significantly reduced, especially for TiO_2. This enables the use of TiO_2 for ethic skin type.

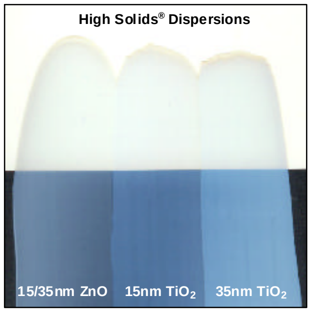
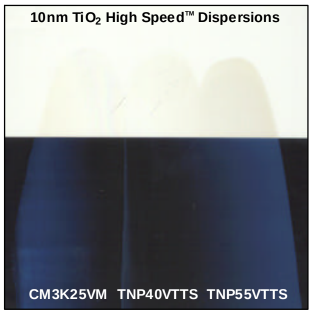


Table 2. TiO_2 and ZnO Dispersions

	TiO_2 Dispersions	ZnO Dispersions
Size (nm)	120 - 180	200 - 300
Solids (%)	45 - 65	50 - 75
Viscosity (cPs)	200K - 2,000K	10K - 220K

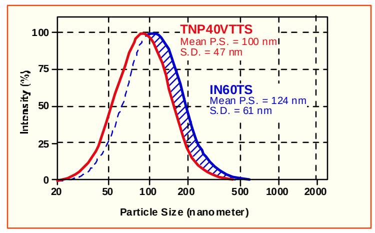


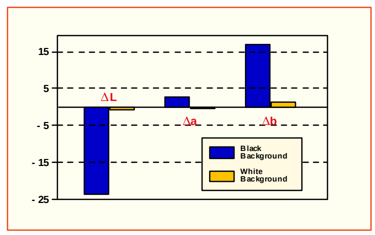
High Speed™ TiO_2 Dispersions :

On a Black Background
→ Low L = Less Whitening
→ High b = Less Bluing

On a White Background
→ Little Improvement
→ Whitening and Bluing

Minimal



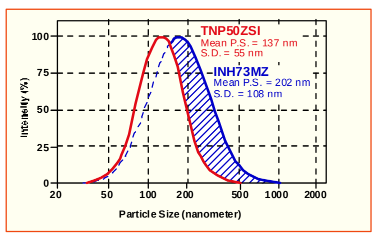


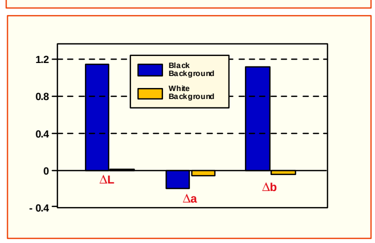
Drawdown on Laneta opacity chart
TiO_2 : 31.5% for both samples

High Speed™ ZnO Dispersions :

On a Black Background
→ Low L = Less Whitening
→ High b = Less Bluing

On a White Background
→ Little Improvement





Drawdown on Laneta opacity chart
ZnO : 47% for both samples

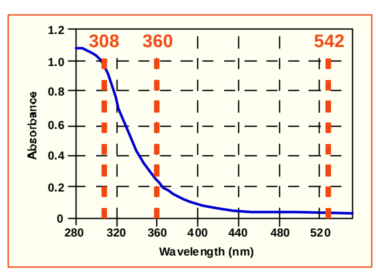
5. Extinction Ratios

$$\text{Extinction Coefficient} = \frac{\text{Absorption}}{\text{Active Conc. x Cell Length}}$$

308 nm = maximal erythemal effectivenes
360 nm = mid of UVA
524 nm = blue end of visible light

$\frac{\text{Ext. 308}}{\text{Ext. 524}}$ → UVB Attenuation / Transparency

$\frac{\text{Ext. 308}}{\text{Ext. 360}}$ → UVA / UBV ratio



6. Optical Properties of TiO_2 & ZnO Dispersions

Table 3. Optical Properties of Ultrafine TiO_2 and ZnO Dispersions

	TiO_2 Dispersions		ZnO Dispersions		
	CM3K25VM	TNP40VTTS	CM3K50XZ4	TNP50ZSI	TNP50ZCLS
Ext. ratio (308/360)	7.9	6.9	1.0	1.1	1.0
Ext. ratio (308/524)	93	74	-	-	-
Ext. ratio (max/524)	-	-	32.3	27.7	34.4
λ max (nm)	278	274	359	358	360

Table 4. Optical Properties of Common TiO_2 Dispersions

PPS of TiO2 (nm)	Ext. Ratio 308/360	Ext. Ratio 308/524	λ max. (nm)
10	7.0 - 8.0	70 - 90	275
15 (High Speed Disp.)	4.5 - 5.5	50 - 55	280 - 290
15 (High Solids Disp.)	3.4 - 3.9	11 - 26	290 - 305
20	2.0	9.0	300
35	2.0	17	313
150	1.1	2.6	318

Table 5. Optical Properties of Common ZnO Dispersions

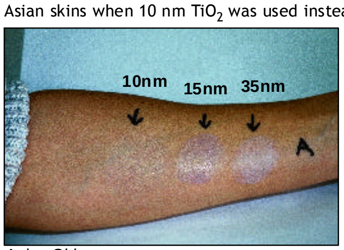
PPS of ZnO (nm)	Ext. Ratio 308/360	Ext. Ratio max/524	λ max. (nm)
20 - 25	1.0	25 - 35	360
60 - 100	0.9	7.8	371
120	0.9	4.1	375

1. For 10 nm TiO_2 dispersions, the maximum absorption occurs in UVC region. Therefore, the attenuation in UVB may not be optimized
2. 20 nm ZnO dispersions in Table 3 have the highest extinction ratios for λ max /524 nm, indicating the high transparency and strong absorption of UV of short wavelength leading to a high SPF. The λ max, however, was moved to mid of UVA indicating the loss of attenuation of UVA-II, which subsequently will affect its PFA score adversely.

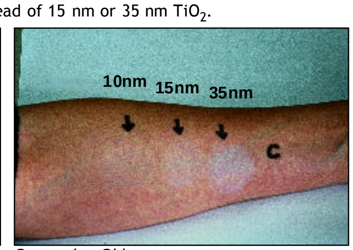
7. In Vivo Testing

A. Transparency

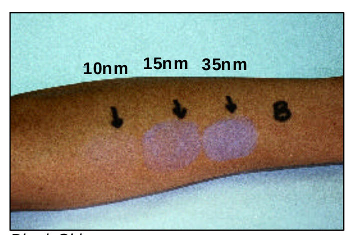
Sunscreen formulas were made with TiO_2 dispersions of various particle sizes and were applied on the skin at a dose of 2 mg/cm^2. It was found that the spreading was noticeably improved and the whitening effect was decreased on Black, Caucasian, Hispanic and Asian skins when 10 nm TiO_2 was used instead of 15 nm or 35 nm TiO_2.



Asian Skin



Caucasian Skin



Black Skin

B: SPF testing of TiO_2 sunscreens

Table 6. SPF scores of Sun Lotions using TiO_2 Dispersions

Formula	Dispersion	PPS (nm)	PS (nm)	Active (%)	SPF	SPF / % Active
W / O	TNP40VTTS	10	100.0	9.3	24.0	2.58
W / Si	CM3K25VM	10	100.0	11.7	40.0	3.42
2504/2 (W/O)	IN60TS	15	132.1	10.49	37.5	3.57
3103/2 (O/W)	INH60TS	15	125.3	10.49	50.0	4.77
3103/4 (W/O)	INH70T	35	154.1	10.49	28.4	2.76

The data in Table 6 reveals that :

1. 10 nm TiO_2 dispersion was not as effective as 15 nm TiO_2 dispersions for SPF score
2. The sunscreen formulation can affect the SPF efficacy of TiO_2 of the same particle size

8. UV Protection of ZnO Dispersions

Table 7. SPF & PFA scores of Sun Lotions unsing ZnO Dispersions

Formula	Dispersion	PPS (nm)	PS (nm)	Active (%)	SPF	SPF / % Active	PFA
O/W Spray	TNP50ZCLS	25	110	8.9	15	1.7	-
W / O	TNP50ZCLS	25	110	14.1	26.9	1.9	-
W / O	TNP50ZSI	20	130	14.1	25	1.8	-
W / O	TNP50ZCLS TNP50HP1	25 ~100	110 230	14.1 4.75	23.5	1.25	3.25
3103/3 (O/W)	INH73MZ	15-35	228.2	14.97	16.2	1.08	7.5
2577/1 (W/O)	INH73MZ	15-35	228.2	14.97	14.0	0.93	7.5
3120/2 (W/O)	INH80ZC	~100	263	16.0	12.6	0.79	5.83

The in-vivo PFA data indicates that:

1. It was obvious now that the reduction of the particle size of ZnO is significant for achieving high SPF and ZnO can be quite effective if the size was small enough.
2. Due to the fact that the absorption peak of these ZnO dispersions has shifted to 360 nm and some UVA protection will be lost, a larger size ZnO was added in order to improve PFA score.

9. Synergy between TiO_2 & Organic Sunscreens

Table 8. In-Vivo SPF testing of TiO_2 and organic combination

Active	Formula A	Formula B	Formula C
Octinate	8.5	8.5	8.5
Octocrylene	10	10	10
Benzophenone-3	1.5	1.5	1.5
TiO_2 (PPS : 15nm - PS : 150nm) TNP55M170	-	3.2	-
TiO_2 (PPS : 10nm - PS : 100nm) TNP40VTTS	-	-	3.2
SPF	41	45	50

In US patent 5,028,417, Bhat, et al. demonstrated the synergy between TiO_2 of a primary particle size of 10 - 70 nm and para-amino benzoic acid and derivatives such as oxybenzones, methoxy cinnamates, salicylates and vinylogous amides. It was reported that synergy was most pronounced when the TiO_2 is less than 10 nm.

The synergy was not observed in our study. Nonetheless, TiO_2 with a smaller size did give higher a SPF when used in combination of organics. Obviously, more data points need to be collected for a better understanding.

10. Conclusion

The size reduction of titanium dioxide and zinc oxide can remarkably improve the appearance of a sunscreen lotion and improve SPF score in most cases.
However, when the size of titanium becomes too small, the absorption can shift to UVC and attenuation at UVA and UVB weakens. But the smaller TiO_2 may show better synergetic effect with organic sunscreens. ZnO can be effective for SPF at the cost of UVA protection when its particle size is brought to under 130 nm.

11. References

1. P. Stamatakis and B. R. Palmer, J. Coating Tech. , Vol. 62, No. 789, p95, October, 1990
2. M. Sakamoto, H. Okuda, H. Futamata, A. Sakai and M. Iida, J. Jpn. Soc. Mater. (Shikizai), 68 (4), P 203- 210, 195.
3. Y. Shao and D. Schlossman. Effect of Particle Size on Performance Of Physical Sunscreen Formulas, PCIA Proceeding Book, 1999.
4. G. R. Bhat et al. US Pat. 5,028,417 , 1991
5. Formulation: M17/36/A, Advanced Powder Technology, Pty, Ltd. ZC Ver. 1, 02/25/03