SUNSCREEN TECHNOLOGIES
FOR FOUNDATIONS AND LIPSTICKS

DAVID SCHLOSSMAN : KOBO PRODUCTS INC.

Competition among manufacturers of color cosmetics is intense. In order to differentiate their brands, Companies formulate with added value ingredients to create products that can claim specific benefits, for example that are line minimizing, longwearing, moisturizing, transfer resistant, or provide oil control. Delivering sun protection in foundations and lipsticks is another way of increasing the value of these products to consumers. In the United States, there is a much greater awareness to the risks of exposure from UV light. The public is encouraged to wear a sunscreen with a SPF 15 daily by the American Academy of Dermatology.

This paper seeks to present sunscreen technologies suitable for foundations and lipsticks for providing broad-spectrum protection against the harmful effects of UV light. Surprisingly, unlike other value-added technologies, few patents have been issued for lipsticks or foundations containing sunscreens. Partly it is because of the myriad of government regulation. Around the world, sunscreen actives are highly regulated limiting the ingredients that may be contained in formulations. In the United States, the Food and Drug Administration regulates the sales of color cosmetics containing sunscreens under cosmetics and drug legislation. The FDA plans to publish an amended tentative final sunscreen monograph before the end of 2001 to finalize sunscreen regulations (Communication with CTFA 3/8/01). In Europe sunscreen products are regulated like cosmetics. COLIPA the trade association for the EEC works with regulatory agencies in individual countries to establish legislation. France and Italy, unlike other EEC countries, require labeling of active ingredients and concentration present in finished products.

All the while, scientific breakthroughs are being achieved providing further insight about the ways UV light effects our bodies. Sunlight is essential to our synthesis of Vitamin D, provides psychological comforts, and has useful therapeutic value. Too much exposure to higher energy UVB radiation (290-320 nm.) causes sunburn. However, skin damage from sunlight builds up with continued exposure to UV light, whether sunburn (erythema) occurs or not. This is because lower energy UVA (320-400 nm) light damages connective tissue at deeper levels, even if the skin's surface feels cool. Melanoma is responsible for 79% of all skin cancer deaths in the USA. Studies have found that the action spectrum for induction of melanoma is different than that for erythema. The harmful effects of UV light are summarized below:

- Sun-tanning (skin pigmentation)
- Sunburn
- Photo-aging / solar keratoses
- Immune suppression / Cataracts
- Photosensitivity and drug related photo-toxicity and photo-allergies
- Skin cancers

Sunscreen actives are generally classified as organic sunscreens or inorganic (physical sunscreens). Organic sunscreens absorb strongly at specific wavelengths and are transparent to visible light. Extensive use has led to increased frequency of allergy and photo-allergies. The photo-stability of these ingredients is also of great concern. Butylmethoxy Dibenzoyl Methane (BMDM) reacts with titanium dioxide and alumina and will yellow quickly.

Table 1 lists three organic sunscreen ingredients that are contained frequently in foundation and lipstick formulations to obtain broad-spectrum protection.

Popular Organic Sunscreens Found in Foundations and Lipsticks				
INCI Name	Spectral Efficacy	Concentration Limits		Skin Sensitivity
		USA	EEC	
Butylmethoxy Dibenzoyl Methane	UVA	3%	5%	May occur
Benzophenone-3	UVA	2-6%	10% If >0.5%*	(Photo) allergic reaction known
Octylmethoxy Cinnamate	UVB	7.5%	10%	Occasionally reported
*Warning required: Contains Oxybenzone				

Table 1

The growth in popularity of inorganic sunscreens in America and around the world followed Japan and is for several reasons. Most importantly, they are not known to cause eye or skin sensitization. Permitted concentration is 25% in the USA and Europe. Inorganic sunscreens are largely chemically and physically inert following surface treatment minimizing their photo-catalytic activity. Regulatory concerns about the purity of micronized titanium dioxide abided after USP 24 was published which classified titanium dioxide according to pigmentary and attenuation grades. The supplier base continues to increase. Pigment technology is available to manufacture primary particle size pigments with sizes as small as 10 nanometers and at 15, 25, 35, 60, 90, 120, and 150 nanometers. Formulators have the ability to design foundations that provide broad-spectrum protection with good coverage. The influence of particle size on absorption and scattering of ultraviolet and visible light has been closely examined by researchers at titanium dioxide producers such as Ishihara Sangyo. New silica coated titanium dioxide and zinc oxide pigments offered by Showa Denka can be used to create non-yellowing formulations with BMDM, subject to regulatory compliance.

Figure 1 compares BMDM with CM3K50XZ4 the 25-nanometer primary particle size zinc oxide dispersion. BMDM is the more potent absorber, but both are effective attenuators of short wave UVA. Zinc oxide also absorbs UVB light.

ZnO dispersion vs. BMDM

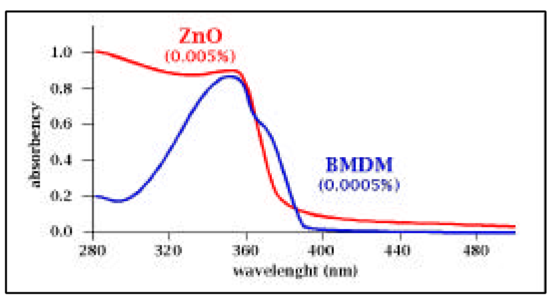


Figure 1

The spectral efficacy of zinc oxide is related to primary particle size (PPS) and dispersion particle size (PS) as shown in Table 2 and Figure 2.

Influence of Particle Size on ZnO Dispersions

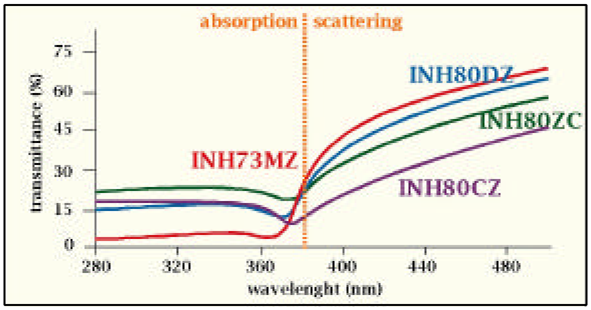


Figure 2

Zinc Oxide Dispersions

PPS (nm)	Product	PS (nm)	%
15/35	INH73MZ	228	73
60	INH80DZ	246	80
120	INH80ZC	264	80
<200	INH80ZC	292	80

Table 2

The absorption edge of zinc oxide is 380 nanometers. Zinc oxide pigments with greater scattering power have higher UVA/B ratios facilitating critical wavelength measurements over 370 nm. These same pigments do not protect the skin from UVA as well as smaller and highly transparent particles of zinc oxide based on PFA in-vivo measurements of erythema. New low viscosity dispersions of methicone treated zinc oxide and titanium dioxide have smaller particle sizes are highly transparent with better UVB absorption. Please refer to Table 3 and Figures 3 and 4. The influence of particle size on light scattering for titanium dioxide dispersions in Isononyl Isononanoate is shown in Figure 5 and Table 4 and light transmittance in Figure 6. The absorption edge of titanium dioxide is 350 nanometers.

Methicone Treated TiO_2 and ZnO

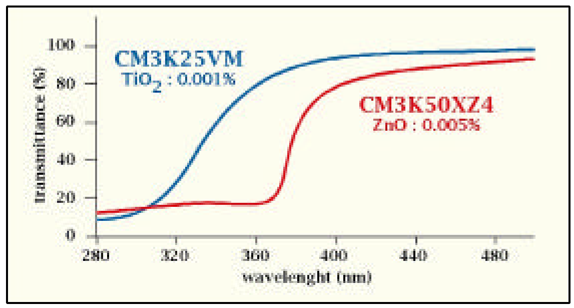


Figure 3

Low Viscosity Dispersions
Cyclopentasiloxane and Dimethicone Copolyol

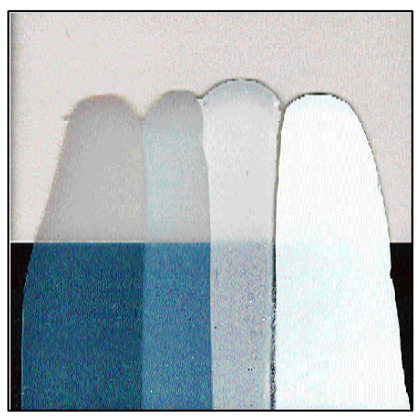
ZnO CM3K50XZ4 **TiO_2** CM3K25VM

Figure 4

PPS (nm)	Product	PS (nm)	%
10	CM3K25VM	113	25
25	CM3K50XZ4	146	50

Table 3

Titanium Dioxide Dispersions
Isononyl Isononanoate



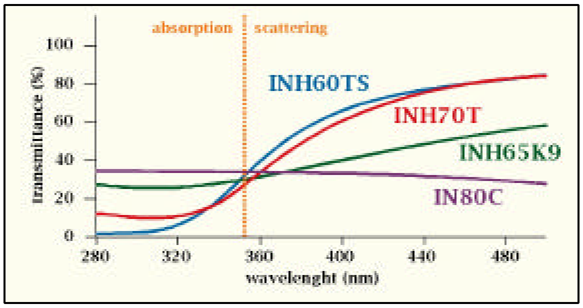
15 nm 35 nm 90 nm 200 nm

Figure 5

PPS (nm)	Product	PS (nm)	%
15	INH60TS	125	60
35	INH70T	154	70
90	INH65K9	251	65
<200	IN80C	263	80

Table 4

Titanium Dioxide Dispersions
Isononyl Isononanoate



All 0.001% in $CHCl_3$ (except IN80C: 0.002%)

Figure 6

Formulating with titanium dioxide that is 35 nanometers results in higher critical wavelength measurements. In addition, it will scatter visible light providing coverage.

Pigmentary titanium dioxide will contribute approximately one SPF unit / per weight and also increases UVA protection.

Lipstick formulations containing attenuation grades of titanium dioxide have been difficult to find. Some reasons might be they impair texture and limit the color palette.

The influence of particle size on SPF and UVA measurements is presented in Tables 5 and 6.

In-vivo SPF decreased by almost forty percent when 35 nm. TiO_2 was used in 3103/4. In these formulations the concentration of actives contained were approximately 10.5, 10.5, 10.3, 16.0, 15.0, and 15.0, respectively.

TiO_2 may provide almost 5 SPF units / weight, while ZnO about 1 SPF units / weight. The differences between in-vivo and in-vitro results are significant, 3103/4 scores a higher SPF than 3103/2 measured in-vitro. 3103/4 has better UVA protection than 3103/2 measured in-vivo and in-vitro, INH70T and INH60TS were the dispersions used. Recall that INH70T is a larger particle size and the light transmittance is lower in UVA. The significance of the measurements should not be overlooked because it is conceivable that both in-vivo PFA measurements and critical wavelength measurements will be required for foundations in the future to make a UVA claim. 3120/1 is the only product with a UVA/B ratio greater than 0.8.

SPF Testing of Sunscreen Formulations

Formula	Active Ingred.	PPS (nm)	In-Vitro SPF		In-Vivo SPF
			IMS **	CPT***	
3103/2 (O/W)	TiO_2	15	40.4	24.7	50.0
2504/2 (W/O)	TiO_2	15	73.4	59.3	37.5
3103/4 (O/W)	TiO_2	35	65.4	50.2	28.4
3120/1 (O/W)	ZnO	120	-	-	13.8
2577/1 (W/O)	ZnO	35	22.3	22.3	14.0
3103/3 (O/W)	ZnO	35	11.5	26.8	16.2

** Innovative Measuring Solutions (avg. of two measurements).
***Consumer Product Testing Company.

Table 5

PFA Testing of Sunscreen Formulations

Formula	Active Ingred.	PPS nm	In-Vitro UVA/B		In-Vivo PFA
			IMS **	CPT***	
3103/2 (O/W)	TiO_2	15	0.45	0.55	4.50
2504/2 (W/O)	TiO_2	15	0.47	0.61	3.05
3103/4 (O/W)	TiO_2	35	0.64	0.69	6.75
3120/1 (O/W)	ZnO	120	------	0.84	4.73
2577/1 (W/O)	ZnO	35	0.71	0.72	7.50
3103/3 (O/W)	ZnO	35	0.74	0.70	7.50

** Innovative Measuring Solutions (avg. of two measurements).
***Consumer Product Testing Company.

Table 6

Iron oxide pigments are not approved active ingredients. Nonetheless, they are effective to attenuate UV light and increase critical wavelength. Dispersions of iron oxide pigments are contained in Figure 7. The iron oxides were treated with isopropyl titanium triisostearate to obtain High Solids® better gloss and color development. The percent solids and particle sizes are contained in Table 7. Transmittance curves for the iron oxide dispersions are contained in Figure 8. Yellow is most effective followed by red. Titanium dioxide pigments are contained in IN80C (rutile) and WE70U (anatase) dispersions. IN80C provides better attenuation because the dispersion particle size is smaller. WE70U is bluer.

Inorganic Color Dispersions

Cetyl Dimethicone Copolyol and Hexyl Laureate and Polyglycerol 4-Isostearate

WE70U WE55Y WE70R WE70B

Figure 7

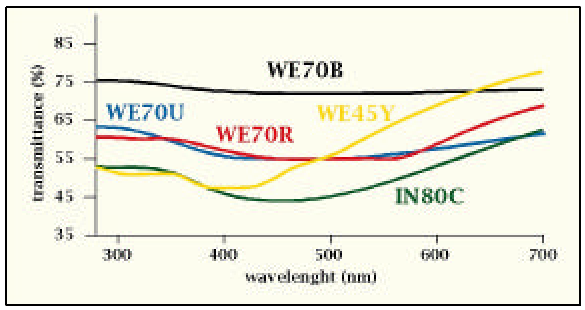
Inorganic Color Dispersions

Product	WE70U	WE55Y	WE70R	WE70B
% Solids	70	55	70	70
PS	328	317	227	1065

Table 7

Inorganic Color Dispersions

Cetyl Dimethicone Copolyol and Hexyl Laureate and Polyglycerol 4-Isostearate



All 0.001% in $CHCl_3$

Figure 8

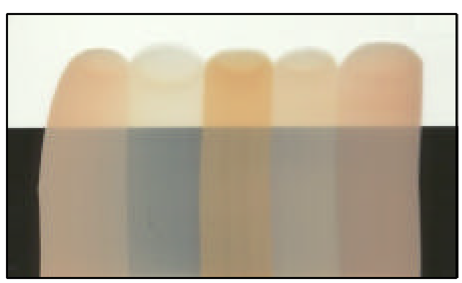
Marketed foundations usually contain both titanium dioxide and iron oxides. Five products containing titanium dioxide as the principal sunscreen are compared in Figure 9. R15 is noticeably sheerer as shown. Table 8 below provides SPF results and the labeled concentration of active ingredients. R20 also contains zinc oxide. Neutrogena's foundation makes a label claim greater than 8 SPF units per active titanium dioxide, much higher than the other products.

Comparison of Marketed Foundations

Code	Product	SPF	% TiO2
R20	Revlon Age Defying All Day Lifting	20	8.6% +3.25 ZnO
R15	Revlon Colorstay Lite Make-up	15	5.2%
Oil	Oil of Olay	15	4.0%
HR	Helena Rubinstein Spectacular Make-up	10	3.1%
N	Neutrogena Oil Free	20	2.4%

Table 8

Comparison of Marketed Foundations

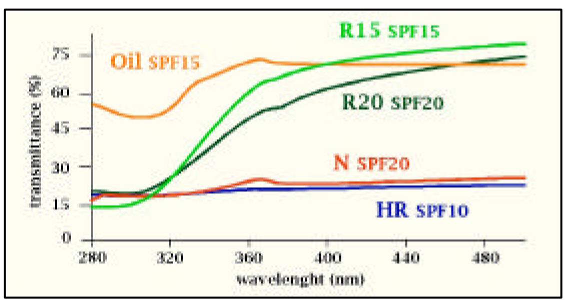


R20 R15 Oil HR N

Figure 9

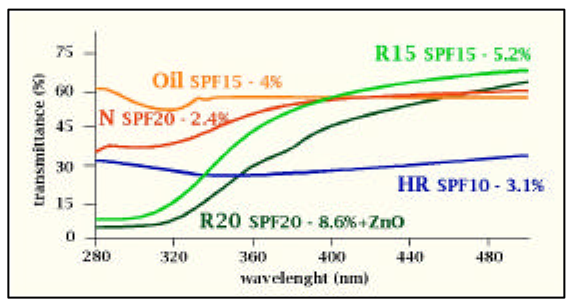
Further comparisons of these marketed foundations were made by titanium dioxide concentration and on a formula weight basis.
Please refer to the transmittance curves contained in Figures 10 and 11 below. Considering the transmittance curves by same titanium dioxide concentration, the Neutrogena and Rubenstein foundations permit the least amount of light to pass through. Each product is also likely to contain pigmentary titanium dioxide considering the flatness of each curve between 360 and 400 nm. This made Neutrogena's formula SPF claim more difficult to understand. Neutrogena, Rubenstien and Revlon all are likely to contain 15 nm. TiO_2. The light transmittance is less than 25% in UVB. The Olay product transmits greater than 50% in UVB. The expectation of a very high critical wavelength would follow since their SPF is coming from larger particle size titanium dioxide and iron oxides. The Revlon 15 curve has the greatest slope. Revlon 20 contains zinc oxide and is more effective in UVA than the Revlon 15. The transmittance curves reveal more about the products when prepared at the same formula concentration. The Rubenstein's formula appears to be the most opaque. Neutrogena's transmittance in UVB curve has shifted closer to 40%, because the product was tested by ICP and found out to contain 7.9% titanium dioxide (Apparently, Neutrogena has only claimed the amount of attenuation grade on their label).

Comparison of Marketed Foundations
Same TiO_2 Concentration



0.001% TiO_2 in $CHCl_3$
Figure 10

Comparison of Marketed Foundations
Same Formula Concentration



0.019%of formulas in $CHCl_3$
Figure 11

Table 9 provides in-vitro results. These marketed foundations protect against UVA, usually defined by a critical wavelength over 370 nm. The Oil of Olay product has the best UVA/B ratio. Revlon's Colorstay Light Make-up provides less.

Comparison of Marketed Foundations
In-vitro results

Product	Product	Average SPF	Critical Wavelength	Average UVA/B Ratio
R20	Revlon Age Defying All Day Lifting	86.64	385 nm	0.80
R15	Revlon Colorstay Lite Make-up	90.10	384 nm	0.72
Oil	Oil of Olay	194.51	388 nm	0.93
HR	Helena Rubinstein Spectacular Make-up	77.71	387 nm	0.88
N	Neutrogena Oil Free	87.38	386 nm	0.82

Table 9

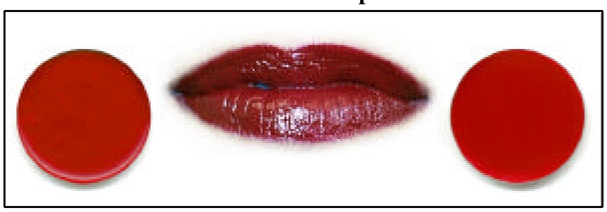
UVA protection it needs to be sheer. Transparent iron oxides in combination with titanium dioxide and zinc oxide might be useful to create a sheer foundation with broad-spectrum protection.
Lipsticks containing 2.4% titanium dioxide did not change color when the primary particle size was 10 nanometers, as shown in Figure 12 and 13 and Table 10.

Brown Shade of Lipstick

With TiO_2 Without TiO_2

Figure 12

Pink Shade of Lipstick



With TiO_2 Without TiO_2

Figure 13

Color Changes

Brown Shade
Delta L: -0.4 (Darker)
Delta a: 1.3 (Redder)
Delta b: -0.5 (Bluer)

Pink Shade
Delta L: 0.4 (Whiter)
Delta a: -0.5 (Greener)
Delta b: 0.9 (Yellower)

Table 10

Except for Asian countries, whitening is unacceptable in beach and skin care products with SPF. It is difficult to create elegant formulations useful to protect against harmful UVA/B rays. Broad-spectrum protection in foundations is achievable using titanium dioxide with greater scattering power and iron oxides. Formulations with SPF 15 and UVA/B ratios over 0.9 have been made with inorganic sunscreens. These pigments have low toxicity important for a product to be applied daily. Manufacturers of pigments, surface treatments and dispersions continue to improve on their technologies. New applications such as Lipsticks, which can now be formulated with inorganic sunscreens to increase UV protection while maintaining overall product desirability, will continue to be found.

Regulatory barriers to using newly marketed organic sunscreens such as Bis-Ethylhexyloxyphenol Methoxyphenyl Triazone, touted to be the first broadband UV absorber on the market and Methylene Bis-Benzotriazolyl Tetramethylbutylphenol a micro-fine powder may fall in the future. New product opportunities will be created. These added value products create a win-win situation for finished product manufacturers, suppliers and most importantly the public.

The author would like to acknowledge the contributions of Yun Shao, PhD., Uyen Nguyen, Jennifer Hudson, Scott Holzapfel, working at the laboratory and Pascal Delrieu, PhD., of Kobo Products, Inc. for their technical contributions to this paper.

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