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Effective UVA and UVB protection from TiO_2 UV filter

T-80 from Sunjin is a patented[1] TiO_2 UV filter that enables formulators to use just one, physical TiO_2 UV filter to develop broad spectrum sun care products that meet the EC Recommendations. In this article Sunjin show that T-80:

- Does not contain nano-sized particles even after shearing, and so is not currently classed as a 'nanomaterial'.
- Can provide UVB protection comparable to that of 15 nm TiO_2.
- Can provide UVA protection better than that of 35 nm ZnO
- Can act as the sole UV filter in sunscreen formulations with UVB/UVA ratios below 3.
- Can act as the sole UV filter in sunscreen formulations with critical wavelengths over 370 nm.
- Is aesthetically pleasing on skin.
- Has good photostability.

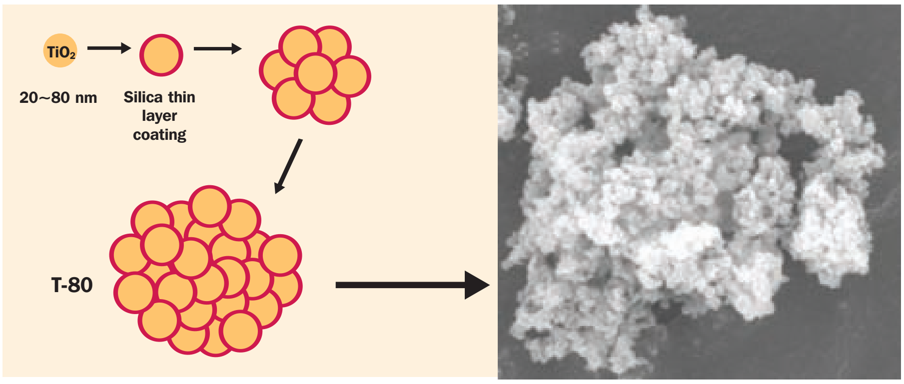

Figure 1: *The manufacturing process of T-80 and the appearance of the final TiO_2 'granule'.*

The European Commission Recommendation of 2006 states that the UVA protection factor (UVAPF) of a sunscreen product must be at least one third of the claimed UVB protection (SPF), and the critical wavelength should be at least 370 nm.[2] Most UV filters have a fairly narrow UV-absorption spectrum, and so a combination of sunscreen actives has usually been required to provide broad-spectrum UVA and UVB protection, for example:

- Combination of organic ('chemical') sunscreens. Organic sunscreens can be very effective but have some drawbacks, such as potential skin irritation, bioavailability after topical application, sub-optimal photostability, oily skin feel, solubility problems and crystallisation. Many of these issues can be resolved or reduced with careful formulation.
- Combination of organic and inorganic ('physical') sunscreens. These combinations can cause formulation problems due to interactions between the physical and chemical sunscreens, leading to crystal formation in emulsions, discolouration of the formulation and reduction in protection.
- Combination of inorganic sunscreens such as titanium dioxide (TiO_2) for UVB protection and zinc oxide (ZnO) for UVA protection. Inorganic sunscreens have very low irritation and sensitisation potential, and are photostable and non-reactive. However inorganic sunscreens can cause whitening on the skin, and can also cause a 'draggy' skin feel. ZnO is not a globally approved UV filter, and so TiO_2 is a more universally acceptable inorganic UV filter for use in personal care formulations.

It is possible to achieve good UVB protection using TiO_2 with a very small primary particle size, e.g. 15 nm. These particles are also virtually transparent on the skin and so have good aesthetic appeal. However it is not possible to use TiO_2 of this particle size to also achieve good UVA protection. It is possible to achieve good UVA protection using TiO_2 or ZnO with larger primary particle sizes, e.g.

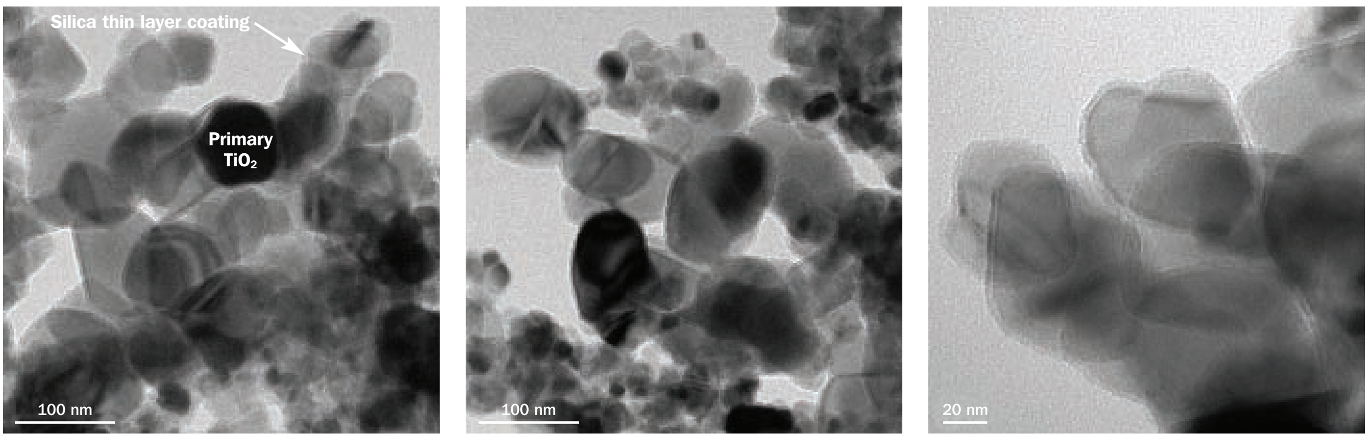

Figure 2: *Transmission electron microscope photographs showing T-80 aggregates.*

generally over 70 nm-80 nm for TiO_2 and over 40 nm for ZnO. These inorganic sunscreens all have primary particle sizes below 100 nm, which classes them as 'nanomaterials'.

The background to the issue of 'nanomaterials' in cosmetics is that Regulation EC1223/20092 comes into effect on 11 July 2013, and defines a nanomaterial as: *…an insoluble or biopersistent and intentionally manufactured material with one or more external dimensions, or an internal structure, on the scale from 1 to 100 nm*. After 11 July 2013 all products containing nanomaterials will have to show this by including '(nano)' after the ingredient name in the ingredient listing. According to the Regulation definition, both TiO_2 and ZnO UV filters with primary particle sizes below 100 nm are classed as nanomaterials, and so after 11 July 2013 products containing them will need to be labelled '(nano)'. However, according to the current industry interpretation, aggregates of TiO_2 and ZnO are only considered to be nanomaterials if their dimensions are below 100 nm, or if they release nanoparticles with dimensions below 100 nm.

On 18 October 2011 the EC published its 'Recommendation on the definition of a nanomaterial',[4] which gives a broad recommendation for how nanomaterials should be defined across sectors. The Recommendation defines a nanomaterial as: *'Nanomaterial' means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 nm*. The Recommendation includes further clarification on how it should be applied to aggregates and agglomerates: *Agglomerated or aggregated particles may exhibit the same properties as the unbound particles. Moreover, there can be cases during the life-cycle of a nanomaterial where the particles are released from the agglomerates or aggregates. The definition in this Recommendation should therefore also include particles in agglomerates or aggregates whenever the constituent particles are in the size range 1 nm-100 nm.*

In this Recommendation, the EC foresees that it may be necessary for specific legislation to exclude certain materials from their scope of application. Given that a nanomaterial definition was already provided in the Cosmetics Regulation before publication of the Recommendation, discussions are ongoing over how the Recommendation will impact the existing cosmetics Regulation definition.

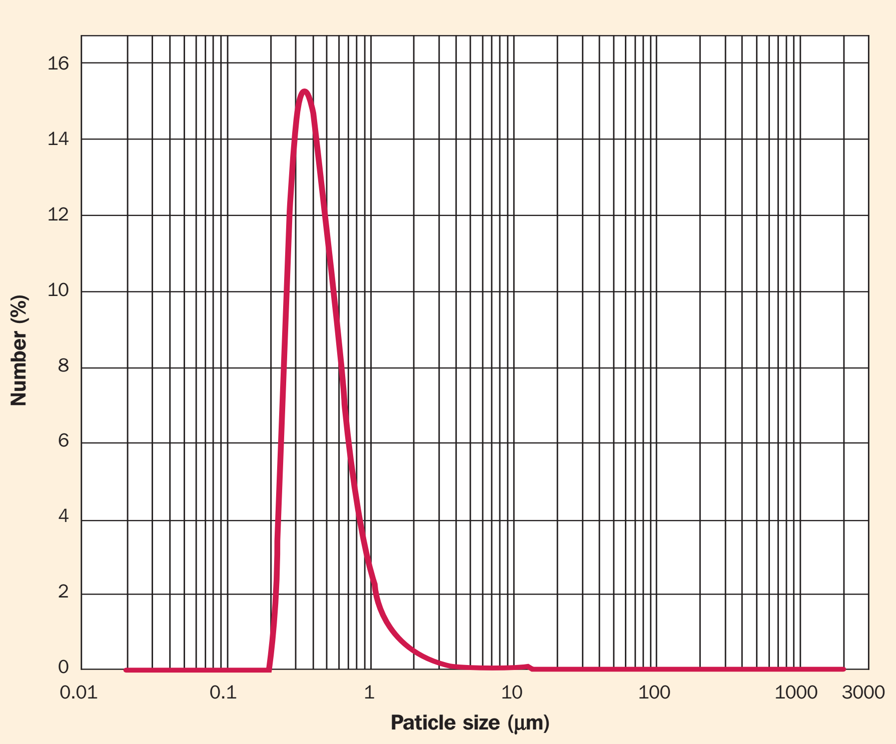

Figure 3: *Results of particle size analysis of T-80 by dynamic light scattering.*

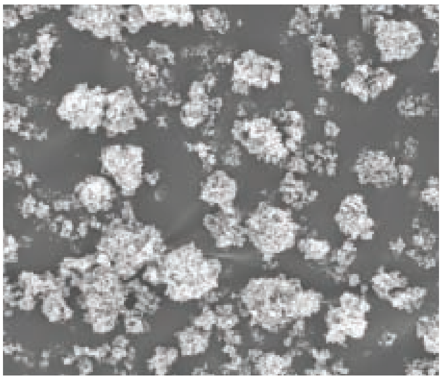

Figure 4: *Scanning electron microscope image of T-80.*

In the current absence of any official guidance, the Cosmetics Europe interpretation is provided as industry guidance. With regard to the 'internal structure' element of the Cosmetics Regulation definition, in the view of Cosmetics Europe, the regulator's intention is to focus on materials that may be present in the form of free elements between 1 nm-100 nm. Thus, materials with constitutive elements having a dimension in the nano-range (e.g. aggregates, agglomerates, composites) but that are themselves greater than 100 nm in size would not be considered as nanomaterials unless they release nano-objects or aggregates of less than 100 nm in size in cosmetic products under normal use conditions.[5]

As described in the above summary, the regulatory situation surrounding nanomaterials is in a state of change. It is unclear exactly how a nanomaterial will be defined in the cosmetics legislation in the future, and how the definition will be interpreted. In light of this uncertainty, formulators may prefer to use UV filters that can be shown to have particle sizes above 100 nm. However UV filters with particle sizes over 100 nm might not be expected to give a sun care formulation the necessary broad spectrum UV protection.

A sun care product that gives high SPF, meets the EC's requirements for UVA/UVB ratio and critical wavelength, is globally approved, has good aesthetics on skin

Table 1: Summary of the T-80 series.

Product name	TiO_2	Silica	Other ingredients	Comments
T-80	84%	16%	–	–
T-80AS	80%	15%	5% alkyl silane	Most hydrophobic coating
T-80JJ	80%	12%	8% jojoba ester	Best hydrophobic Ecocert coating
T-80LL	80%	12%	8% lauroyl lysine	Best soft feel for Ecocert make-up
T-80SA	80%	12%	8% stearic acid	Least expensive Ecocert for mass market

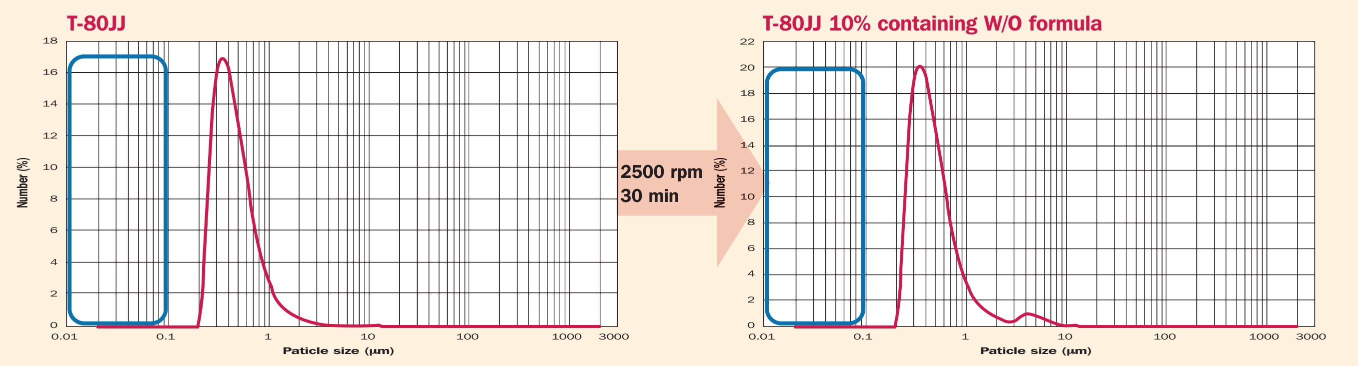

Figure 5: *Particle size analyses of T-80JJ before (left) and after shearing at 2500 rpm for 30 minutes.*

and skin feel, and contains only inorganic sunscreens would be expected to appeal to consumers. If such a product could be formulated using just one TiO_2 particle as the UV filter, and if that TiO_2 could be shown not to contain nano-sized particles, that would also be expected to appeal to sun care formulators. In this article Sunjin demonstrate that their T-80 series of TiO_2 UV-filters enable formulators to meet all of these requirements.

Materials and methods

Manufacturing process and versions available

During manufacture of T-80 (now referred to as 'the new broad spectrum TiO_2'), the primary particles of TiO_2 are strongly bound together by silica into a 'granule' with a final composition of 84% TiO_2 and 16% silica. This is shown in Figure 1.

There are five versions of T-80 available, with different surface treatments for ease of dispersion in different media. Three of these versions are Ecocert certified, and none of them contain alumina. A summary of these five versions is shown in Table 1. The new broad spectrum TiO_2 is also available in a series of three dispersions in different media, for ease of formulation. A summary of the three dispersions currently available is shown in Table 2. Two of these dispersions are Ecocert certified, and again none contain alumina.

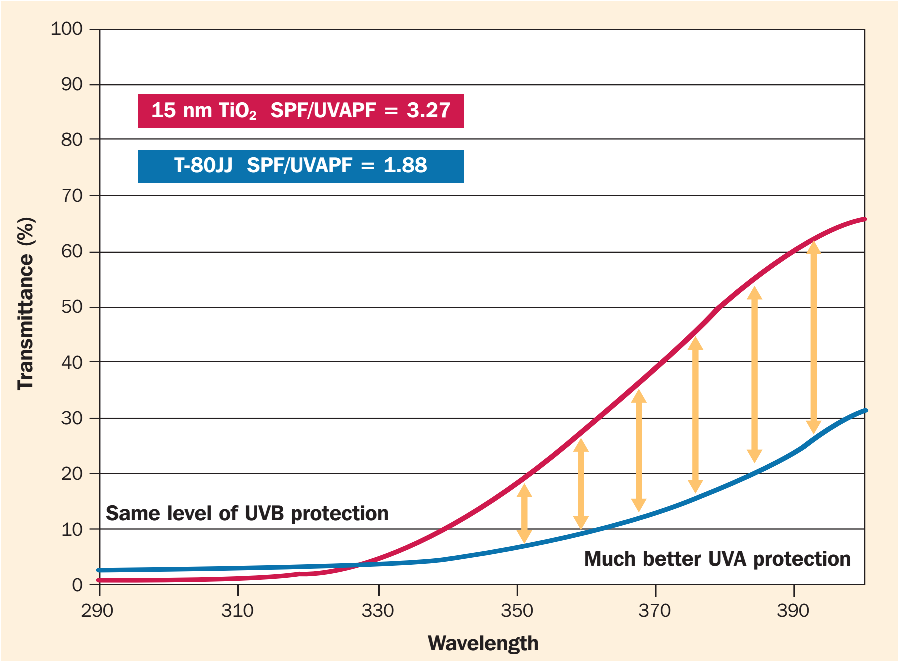

Figure 6: *Transmittance curves of W/O sun creams formulated with 15 nm TiO_2 and T-80JJ, showing that T-80 gives the same level of UVB protection as 15 nm TiO_2, and better UVA protection.*

Evidence that the new broad spectrum TiO_2 does not contain nano-particles

Sunjin have performed several tests on samples from industrial batches of the new broad spectrum TiO_2 to show that the TiO_2 primary particles are strongly aggregated in the final material so that their dimensions are above 100 nm. Tests have also shown that the aggregates do not dissociate to release nano-sized particles during formulation and usage.

- *Transmission electron microscope (TEM) photographs showing aggregate dimensions larger than 100 nm*

The TEM photographs in Figure 2 show the aggregates of TiO_2 primary particles, bound together by their silica coating. The scale at the bottom of each photograph allows the dimensions of the aggregates to be measured and show that the aggregates are considerably larger than 100 nm.

- *Particle size analysis by dynamic light scattering*

Particle size analysis of the new broad spectrum TiO_2 was performed using a Malvern Master Sizer 2000. 0.1% of the new broad spectrum TiO_2 was stirred into 200 mL IPA solution and sonicated for 2 minutes. The particle size of the sample was then analysed in the Malvern Master Sizer, giving the data in Figure 3. The results of the particle size analysis show that the new broad spectrum TiO_2 has the following particle size distribution:

Table 2: Summary of the T-80 range of dispersions.

	SFT85-AB	SFT85-CC	SFT85-CCTG
Carrier	C12-15 alkyl benzoate	Dicaprylyl carbonate	Caprylic capric triglyceride
Solid	60%	60%	60%
Net TiO_2	48%	48%	48%
TiO_2 coating	Silica/triethoxy caprylylsilane	Silica/jojoba ester	Silica/jojoba ester
Dispersing agent	Polyhydroxystearic acid	Polyhydroxy stearic acid	Polyhydroxy stearic acid
T-80 grade used	T-80AS	T-80JJ	T-80JJ
Ecocert?	No	Yes	Yes
Alumina-free?	Yes	Yes	Yes

- D10: 364 nm
- D50: 562 nm
- D90: 988 nm

No particles were detected below 209 nm.

● *Scanning electron microscope picture showing aggregation*

The aggregates of the new broad spectrum TiO_2 were measured using a Hitachi S-4700 scanning electron microscope, as shown in Figure 4.

Do aggregates break apart during shearing processes involved in formulation?

Sunjin made sunscreen formulations containing 10% of the new broad spectrum TiO_2 (T-80JJ) and sheared the formulation at 2500 rpm for 30 minutes, replicating the forces that could be expected to be applied to the new broad spectrum TiO_2 during the manufacture of sun care products. The particle size distribution of the new broad spectrum TiO_2 was measured by dynamic light scattering both before and after the shear was applied. The results in Figure 5 indicate that even with shearing, the new broad spectrum TiO_2 aggregates are bonded together so strongly that they do not break down to release nano-sized particles. The new broad spectrum TiO_2 therefore does not release nano-objects or aggregates of less than 100 nm in size under normal use conditions.

UVB/UVA protection and critical wavelengths

With the new broad spectrum TiO_2 it is possible to achieve UVB protection comparable to that of 15 nm TiO_2, UVA protection better than that of 40 nm ZnO, UVB/UVA ratios below 3, and critical wavelengths over 370 nm. Sunjin developed sunscreen formulations using the new broad spectrum TiO_2 as the only UV filter. The *in vivo* SPF of the formulations was measured using a 601-300 W Multiport UV Solar Simulator, and the *in vitro* UVA PF and critical wavelength of the formulation were measured using an Optometrics 290.

The UVA/UVB ratios were calculated according to the Colipa Guidelines Method for the *in vitro* determination of UVA Protection,[6] using the *in vivo* Sun Protection Factor ('Labelled SPF') and the *in vitro* UVA PF to calculate: Ratio = SPF_{Label}/UVAPF.

The higher the critical wavelength, the better the UVA protection provided by the sunscreen. During the critical wavelength evaluation, UV light of 290 nm to 400 nm (the UVB-UVA range) is reproduced in a laboratory device designed to measure the amount of radiation absorbed by a sunscreen. Starting at the beginning of the UVB range (290 nm), progressively higher wavelengths of light are aimed at the sunscreen. The UV absorbance of the sunscreen is measured and plotted on a graph, with absorbance (i.e. *in vivo* SPF)

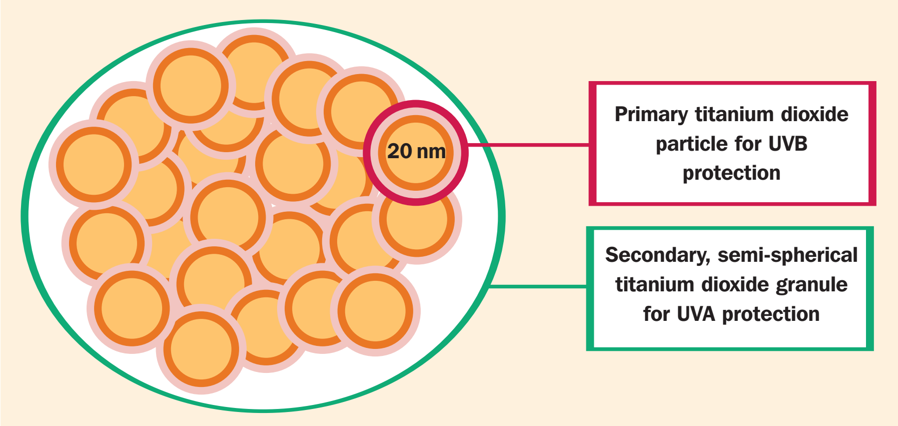

Figure 7: *Diagram of T-80 'granule' and its mode of action for protecting against both UVA and UVB.*

Table 3: Comparison of 15 nm TiO_2 and T-80JJ.

	15 nm TiO_2	T-80JJ
Crystal size	15 nm	500 nm
TiO_2	82%	80%
Surface coating	Alumina and stearic acid	Silica and jojoba ester

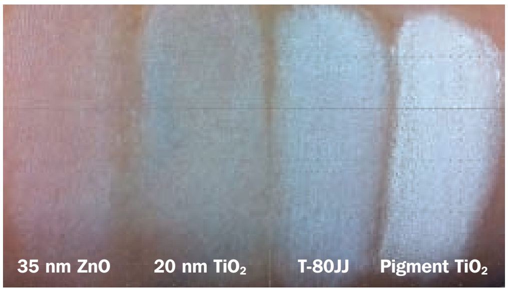

Figure 8: *T-80 on skin, compared to other TiO_2 and ZnO.*

Table 4: Comparison of W/O sunscreen formulations made with 10% 15 nm TiO_2 and 10% T-80JJ.

Part	Trade name	%
A	D.I. Water	65.0
	Natural Extract	5.0
	NACL	1.0
B	Cetiol CC	13.0
	Lameform TGI	2.0
	Dehymuls PGPH	2.0
C	15 nm TiO_2 *vs.* T-80JJ	10.0
	Sunsil – 150H	2.0

Test result	15 nm TiO_2	T-80JJ
In vivo SPF	28	26
In vivo UVA PF	3.6	6.0
In vitro SPF	25.77	27.83
In vitro UVA PF	8.56	13.79
SPF/UVA PF	=28/8.56 = 3.27	=26/13.79 = 1.88
Critical wavelength	363.3	379.5

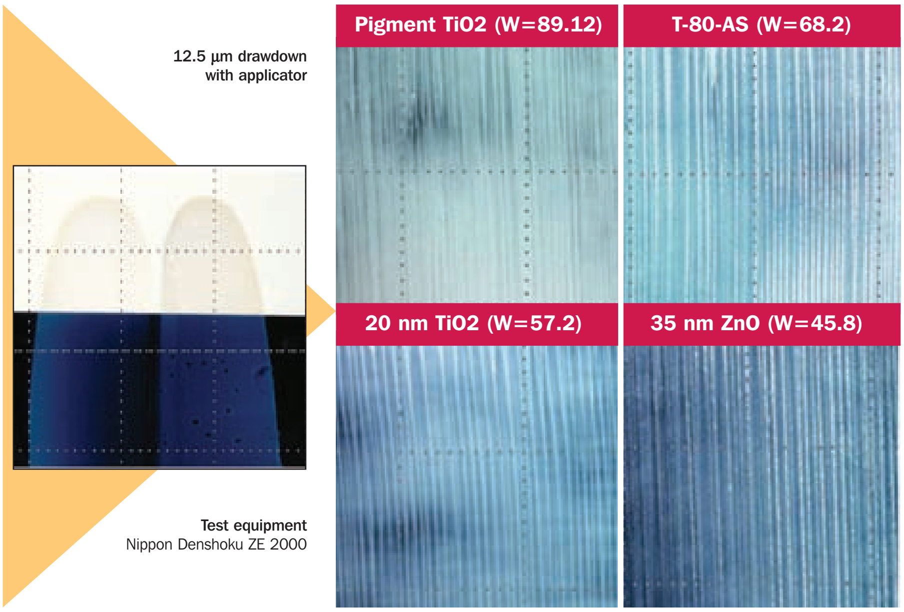

Figure 9: *Drawdowns of T-80 compared to 20 nm TiO_2, 35 nm ZnO and Pigmentary TiO_2.*

on the x axis and the wavelength of the incident light (280 nm – 400 nm) on the y axis. The width of the curve plotted on the graph shows how broadly effective a sunscreen is across the UV spectrum. When the area beneath the curve is measured, a line can be drawn separating the lower 90% of the absorption from the upper 10% of the absorption. The wavelength at which this line falls is the 'critical wavelength'.[7]

Table 4 shows a comparison of two W/O sunscreen formulations, one made using 15 nm TiO_2 and the other using the new broad spectrum TiO_2 (T-80JJ). The specifications of the new broad spectrum TiO_2 and the 15 nm TiO_2 used in the comparative formulations are summarised in Table 3.

The formulation containing the new broad spectrum TiO_2 (T-80JJ) has an *in vivo* SPF of 26, a critical wavelength of 379.5 (above the EC recommended lower limit of 370 nm) and a labelled UVB/UVA ratio of 1.88 (significantly within the EC Recommended ratio of below 3.0). In contrast, the formulation containing 15 nm TiO_2 has a slightly higher *in vivo* SPF of 28, but a critical wavelength of 363.3 nm (below the EC recommended lower limit of 370 nm) and a labelled SPF/UVA ratio of 3.27 (outside the EC recommended ratio of below 3.0). These results and the transmittance curve in Figure 6 demonstrate that the new broad spectrum TiO_2 can provide comparable UVB protection to that of 15 nm TiO_2, UVA protection factor (UVAPF) of at least one third of the claimed SPF, and a critical wavelength above 370 nm. 10% of the new broad spectrum TiO_2 (T-80JJ) gives an *in vivo* SPF of 26. 1% can therefore be expected to give an SPF of 2.6.

The new broad spectrum TiO2 therefore allows formulators to meet the EC Recommended criteria for sunscreens, using just one inorganic UV filter.

Table 4 also shows that 10% of the new broad spectrum TiO_2 gives an *in vivo* UVA PF of 6.0, indicating that 1% of the new broad spectrum TiO_2 gives a UVA PF of 0.6.

This is significantly higher than the UVA PF of 15nm TiO_2, at 0.36 per 1% of 15nm TiO_2. Sunjin also performed *in vivo* tests on a formulation containing 20% 35nm ZnO and found that it had a UVA PF of 6.0, and hence that 1% 35 nm ZnO gave a UVA PF of 0.3. Sunjin therefore consider that the new broad spectrum TiO_2 also provides better UVA protection than 35 nm ZnO.

Method for providing both UVA and UVB protection

The ability of TiO_2 particles to protect skin against UVA and UVB light depends on their ability to reflect, scatter and absorb the light that hits each particle. For sub-micrometre particles, reflection from the surface of the particle is often very small, and scattering and absorption of light are the major mechanisms of attenuation. The degrees of scattering and absorption are related to the wavelength of the light, and the size and chemical composition of the particle.

UVB attenuation by TiO_2 is predominately due to its absorption[8] which increases as the particle size decreases. The absorption is a function of the number of atoms that interact with the light in its pathway. For a single photon, the size of the TiO_2 particle has no effect on the absorption. In reality however, when the particle size is reduced, there will generally be more particles that become available to interact with and hence absorb UV light. Smaller particle sizes will therefore result in stronger UVB absorption.

UVA attenuation by TiO_2 is due to scattering of light as well as absorption. Scattering will increase as the particle size increases and there is a larger surface area available to reflect and scatter light. The light scattering power of a particle is generally considered to be at its maximum when the particle size is half the wavelength of the incident light.[9]

By utilising both of these mechanisms, the new broad spectrum TiO_2 attenuates both UVA and UVB light and provides highly efficient broad-spectrum UV protection for the skin.

Evidence that the new broad spectrum TiO_2 is aesthetically pleasing

Sunjin have compared the new broad spectrum TiO_2 to TiO_2 and ZnO of various particle sizes, as shown in Figures 8 and 9. Sunjin found that the new broad spectrum TiO_2 is more whitening than 35 nm ZnO and 20 nm TiO_2, as would be expected as the new broad spectrum TiO_2 aggregates are much larger than the TiO_2 and ZnO nano-particles. The new broad spectrum TiO_2 was less whitening and more transparent than pigmentary TiO_2, 150 nm ZnO and other non-nano TiO_2 and ZnO particles. Transparency is affected by particle shape, with flat particles reflecting light in a uniform direction to produce a glossy appearance, whereas spherical particles scatter light into many directions to produce a more matte appearance. Some of the improved transparency of the new broad spectrum TiO_2 can be attributed to the rounded shape of the aggregates. Sunjin also found that the new broad spectrum TiO_2 had a smoother skin feel than other TiO_2 and ZnO particles of similar size, which Sunjin also attribute to the morphology of the the new broad spectrum TiO_2 granules.

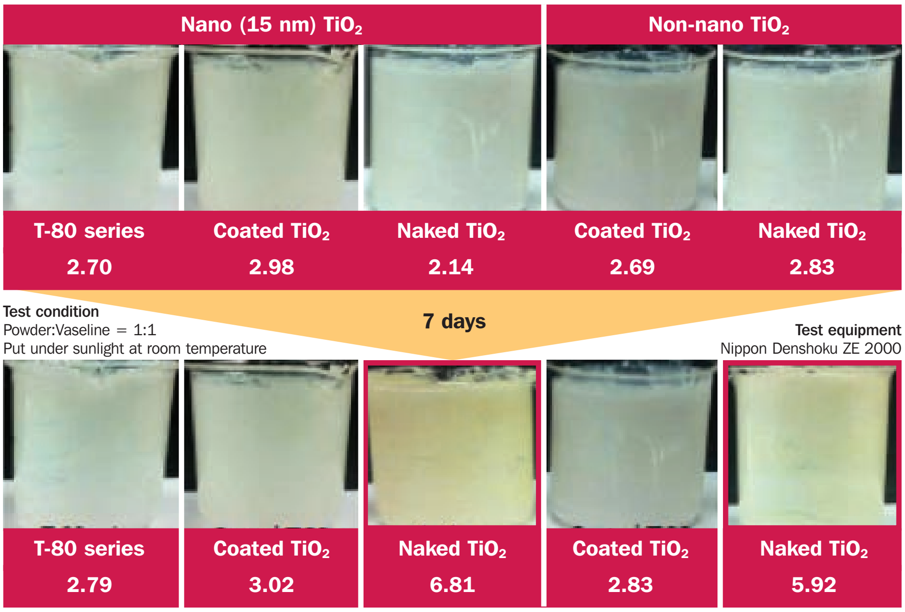

Figure 10: *Measurement of the photostability of T-80 compared to 15 nm and non-nano TiO_2.*

Evidence that the new broad spectrum TiO_2 has good photostability

Sunjin compared the photostability of the new broad spectrum TiO_2 against other TiO_2 and ZnO UV filters. Approximately 2 g of each powder was sieved and mixed with 2 g of petroleum jelly for 5 minutes. Each sample was then evenly spread onto a glass beaker and left in sunlight for 7 days at 23˚C-26˚C. The photostability of each powder was then judged by the degree of colour change of the mixture, measured by the 'Yellow Index' using a Nippon Denshoku (ZE 2000). The results are shown in Figure 10. The colour of the new broad spectrum TiO_2 mixture did not change significantly over the test period. These tests indicated that the new broad spectrum TiO_2 was significantly more photostable than TiO_2 that had not been surface-treated.

Conclusion

The T-80 series provides sun care formulators with a range of TiO_2 powders and dispersions, allowing them to formulate products with effective UVA and UVB protection from a single, globally approved physical UV filter. T-80 consists of aggregates with sizes over 100 nm, even after shearing.

The T-80 series can be used as the sole UV filter to formulate sunscreen products that provide high levels of UVA and UVB protection in the EC-Recommended ratio of at least 1:3, UVA PF: *in vivo* SPF, provide critical wavelengths above 370 nm, do not contain nano-particles even after shearing, have good aesthetics on the skin and good photostability, can be Ecocert certified and do not contain alumina. PC

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