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Understanding new Australian SPF and UVA tests

Table 1: Proposed product categories and requirements – static SPF and broad spectrum.

Tested SPF	Label SPF claim	Category description	Broad spectrum claim		
			Primary sunscreen	Secondary sunscreen	
				Skin care	Colour or lip
1 to 3		Not allowed			
4 to 14	4, 6, 8, 10	Low protection	Compulsory	Compulsory	Optional
15 to 29	15, 20, 25	Medium or moderate protection	Compulsory	Compulsory	Optional
30 to 59	30, 40, 50	High protection	Compulsory	Compulsory	Compulsory
60 or higher	50+	Very high protection	Compulsory	Compulsory	Compulsory

The new version of AS/NZS 2604 Sunscreen Standard is being implemented during 2012[1] and both TGA and NICNAS will issue new requirements in line with these long-awaited changes. This will require both primary and secondary sunscreens sold in Australia to comply with updated test requirements for both UVA 'broad spectrum' and SPF claims. With thorough understanding of these test requirements, development chemists will be able to target formulating to not only provide better sunscreen protection products but to be able to 'pass the test'.

New AS/NZS 2604 test requirements

Within the new version of AS/NZS 2604 Standard, there are three requirements for testing in order to support compliance.

- SPF *in vivo* testing on 10 human subjects.
- Broad spectrum – interpreted from ratios determined (*in vitro*) in a standardised absorption curve.
- Water resistance.

The first two apply according to the category of sunscreen (intended use) and the third, separately, for the additional, non-mandatory claim of water resistance when required.

Table 2: Comparison of current and new versions of (Static) SPF Test.

Specification	AS/NZS 2604	ISO 24444
Current Version	1998	2010
UV specifications		
Light source output	Xenon arc preferred	Xenon arc recommended
Filter	Schott WG 320	WG 320 and UG11
Dichroic filter	Yes	Yes
UVB	Yes	Yes
UVB definition	290 nm to 320 nm	290 nm to 320 nm
UVA definition	320 nm to 400 nm	320 nm to 400 nm
UVC definition	Outside of scope	Not referenced
UVA determination (broad spectrum)	3 *in vitro* methods	Covered in ISO 24443
Test panel		
Test subjects	NLT 10	10 to 20 from 25 max
Selection	Questionnaire, interview	Question, interview
Age limitation	Not defined	Not below age of consent or over 70 years
Skin types in test	I, II, III	I, II, III – not all the same type
Exclusions	Photosens, medication, skin disease, abnormal skin response	
Frequency of participation		NLT 2 months

SPF test

This will be the test method as described in ISO 24444, published in Dec 2010.[2] In all major attributes, the methodology has not changed significantly. Essentially, any product complying with the current SPF test should pass this part of the test requirement. Hence, TGA will not be requiring retrospective testing.

Supporting the validity of the ISO SPF test method are four ring studies, which evaluated the critical parameters, such as impact of the irradiation light source, reciprocity of exposure intensity and product application method. As well, qualification of calibration methodology was also covered. This included setting limits for reference sunscreens and development of analytical methods for these.

Table 3: Impact on SPF of dried down film thickness.

Form	Actives	Static SPF
Stick – water free (Dried 2 mg/cm^2)	EHMC 4% BMBM 2%	41
Lotion w/o 50% H_2O (Dried 1 mg/cm^2)	EHMC 4% BMBM 2%	29

Table 4: Comparison of test parameters.			
Test Parameter	**ISO & Aust Prop March 2012**	**COLIPA March 2011**	**FDA FINAL June 2011**
Plates	6 um PMMA plates	6 um PMMA plates	2 to 7 um PMMA plates
Plate surface characteristics	Moulded	Moulded	Etched or moulded
Application rate	1.3 mg/cm^2	1.3 mg/cm^2	0.75 mg/cm^2
Drying time	Minimum 15 min	Minimum 15 min	15 min
Pre-irradiation dose	Pre-irradiation 1.2 J x UVAPFo	Pre-irradiation 1.2 J x UVAPFo	Fixed pre-irradiation 4 MEDs
Pre-irradiation spectrum	UVA irradiance spectrum	UVA irradiance spectrum	SPF irradiance spectrum
SPF used in exposure calculation	*in vivo* SPF	*in vivo* SPF	*in vivo* SPF
Ratio calculation (UVAPFDx/label SPF	Ratio minimum 0.33	Ratio minimum 0.33	n/a
Critical wavelength	Minimum 370 nm	Minimum 370 nm	Minimum 370 nm
Final expression	Aust 'Broad Spectrum' ISO n/a	EU interprets pass/fail	'Broad spectrum'
Replicates	4 measurements on 4 plates	3 measurements on 4 plates	5 measurements on 3 plates

For SPF performance

The major change is the increase of SPF to the new 50 and 50+ categories. Formulations can be modified to achieve this using several approaches beyond the simple proportionate increase of actives.

Building dried down film thickness when the formulation is applied to the skin can also be key to optimising the yield (SPF units per percentage of active). An example is shown in Table 3.

UVA broad spectrum test

It would appear that an increasing number of 'secondary' sunscreens will incorporate a claim of broad spectrum protection. This is understandable, as the trend in other markets has been for mandatory UVA protection. The broad spectrum test in the new version of the standard will be more challenging.

Conducting the *in vitro* UVA test for broad spectrum compliance requirement may appear to be simple, but recent experimentation has shown that reproducibility requires attention to detail. Although ISO has spelt out the test parameters in some detail, a great deal of attention to calibration and procedures is required when conducting this test.

Subsequent to further validation work that has been conducted as a result of the Sunscreen Working Group of ISO Technical Committee, in which the Colipa In vitro UV Protection Method Task Force has had heavy commitment, some of the advances in the test methodology proposed for ISO 24443[3] have already been incorporated into the recent update to the Colipa document version published in March 2011.[4] When it was released in early 2012, the ISO document, and thus the Australian method, reflected the latest state of the art of this test methodology.

Several UVAPF ring studies conducted during the ISO development process have highlighted the extreme importance of the control of test parameters when performing

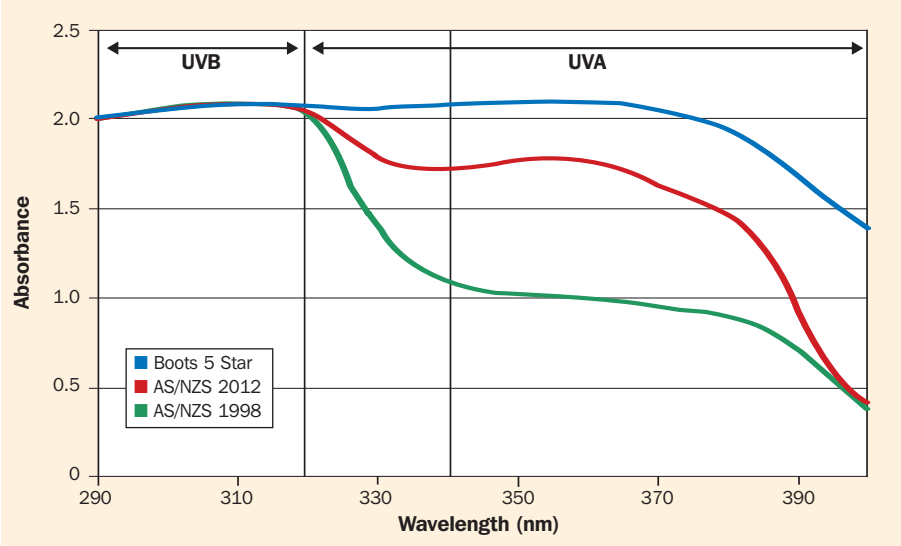

Figure 1: *Indicative UVA performance for test methods.*

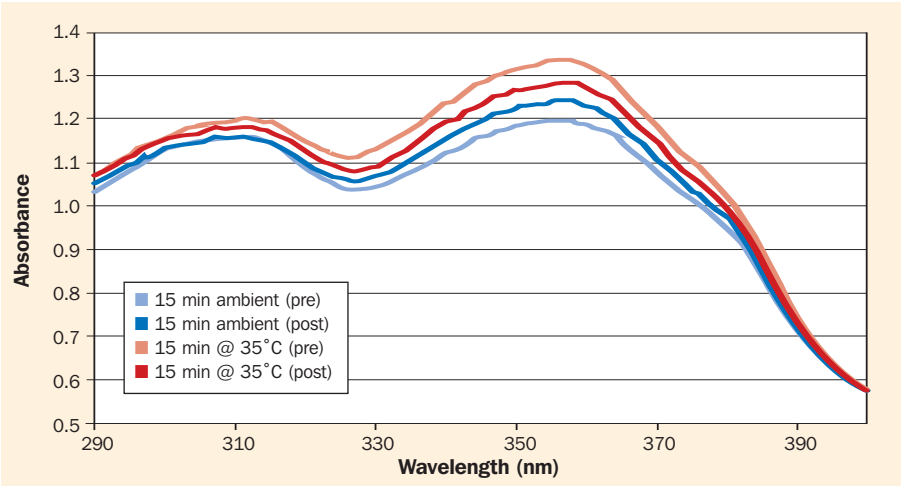

Figure 2: *Example of dry down effect during irradiation.*

Table 5: Measured parameters *vis* film thickness.						
SPF	**PMMA plate Roughness**	**App rate mg/cm**	**UV Exposure J/cm^2**	**λc pre**	**λc post**	**Ratio UVAPFDx/SPF**
30	6 µm	0.75	17	369.0	367.6	0.330
30	6 µm	1.3	17	369.9	368.3	0.337
30	6 µm	2.0	17	370.7	368.8	0.346

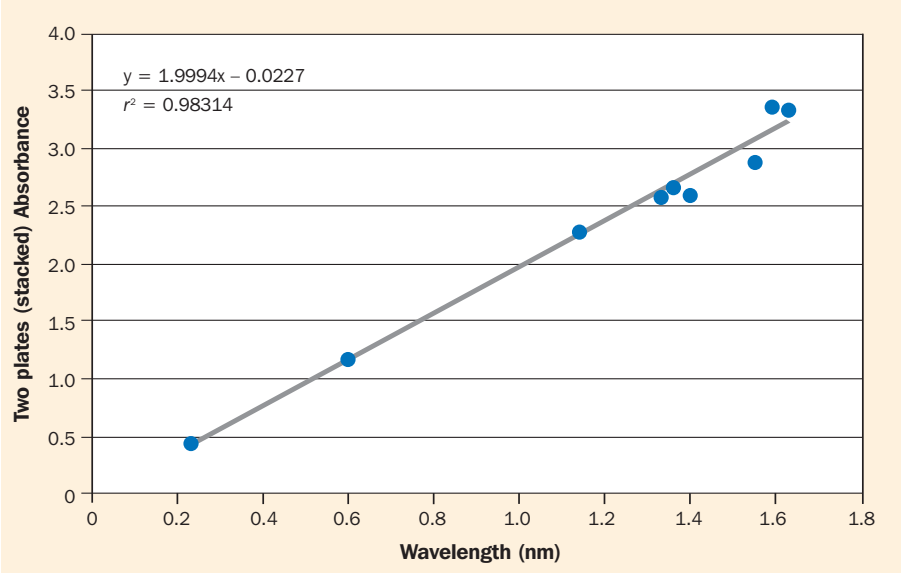

Figure 4: *One vis two calibration plate correlation.*

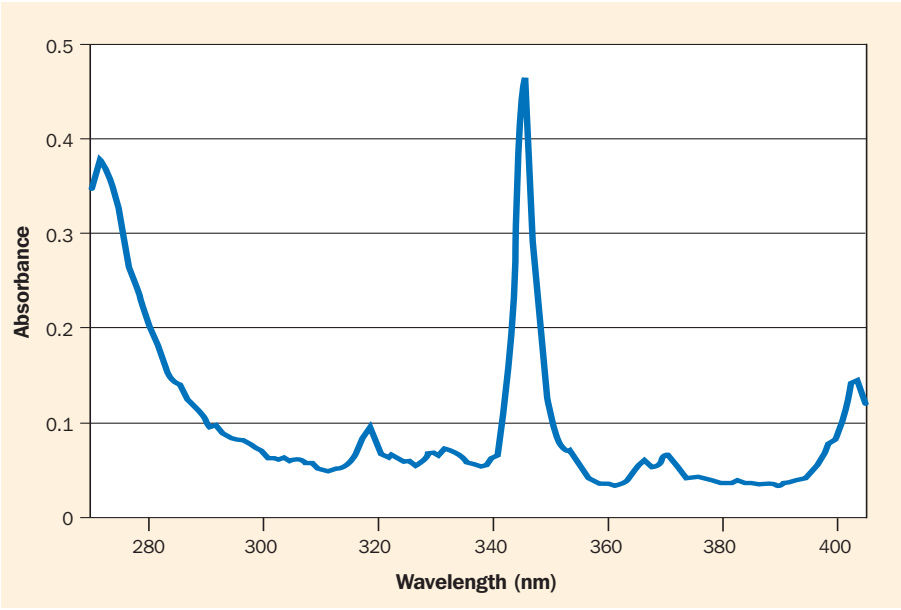

Figure 5: *Holmium spectrum.*

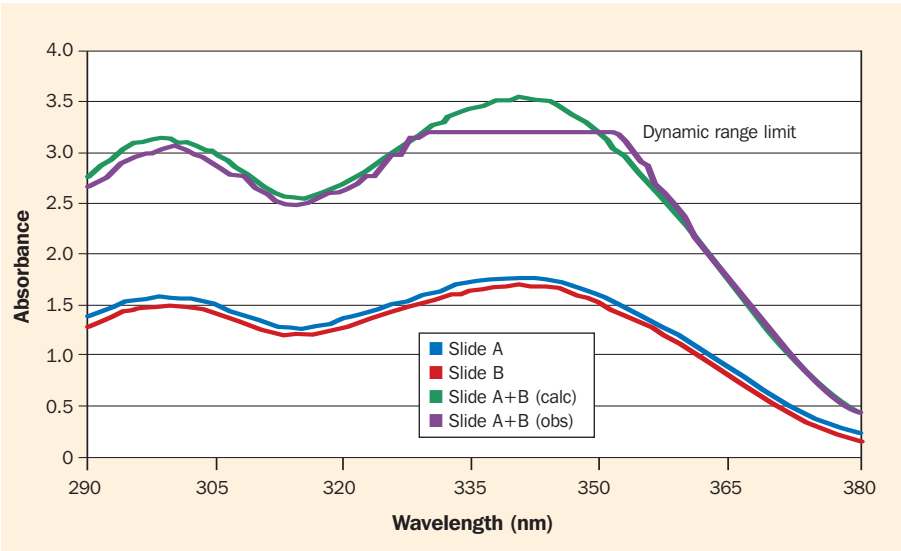

Figure 3: *Showing the flat line effect when the instrumental limit is exceeded (i.e. at dynamic range 3.2).*

this *in vitro* test. In particular, to obtain consistency inter-lab, attention needs to be given to product application technique, substrate selection and exposure and test instrument calibration.

UVA test method outline

ISO (for Australia), Colipa and FDA methods are all very similar (Table 4).

The essential and common steps for all are:

- Apply the sunscreen to a rigid transparent substrate.
- Dry the film down onto the substrate.
- Measure the absorbance over the wavelength range of 290 nm to 400 nm.
- Expose the sample to UV irradiation to imitate in use effect of sunlight.
- Repeat the measurement post irradiation.
- Compute the results to arrive at the required value. For ISO and Colipa, this is UVA Protection Factor Post Irradiation/SPF – a ratio. For AS/NZS, this is the Broad Spectrum. An additional requirement is the critical wavelength at 370 nm (where 90% of the cumulative area under the total absorbance curve from 290 nm to 400 nm occurs).

Application technique

According to ISO and Colipa, this test parameter is the most critical for providing reproducibility. Colipa has produced a short training video with the purpose of demonstrating a standardised technique found to provide consistency. This can be downloaded from their website.[5] Thorough practice is needed in order to achieve the same answer on the replicate films and to achieve consistent results between technicians within the same laboratory.

When formulating a sunscreen with a view to optimising performance in this test, the rheology needs to be considered – effect of emollients, silicones – film formers. Testing on PMMA plates of the same grade as used in the test, will give an indication of how well the product adheres to the surface and how evenly it rubs out. Alcohol based formulas are very often difficult to apply without streaking.

Drying down time

The monograph requires that the sample is held for a period of time in order to allow the film to dry down. This is in line with what is applied for *in vivo* SPF testing and reflects what happens in use. Colipa 2007 and 2011 require a minimum period of 15 minutes and the current ISO wording is: 'During the exposure the samples should be maintained at between 25˚C and 35˚C at the same temperature used for the drying period'. Our experience is that some

Table 6: Example of relationship of SPF to UVAPF ratio and pass for broad spectrum.

	Primary	Secondary		UVAPF Ratio
Label SPF		Skin Care	Colour/Lip	
4	Compulsory	Compulsory	Optional	3.67 PASS
6	Compulsory	Compulsory	Optional	2.45 PASS
8	Compulsory	Compulsory	Optional	1.83 PASS
10	Compulsory	Compulsory	Optional	1.47 PASS
15	Compulsory	Compulsory	Optional	.98 PASS
20	Compulsory	Compulsory	Optional	.735 PASS
25	Compulsory	Compulsory	Optional	.588 PASS
30	Compulsory	Compulsory	Compulsory	.49 PASS
40	Compulsory	Compulsory	Compulsory	.367 PASS
50	Compulsory	Compulsory	Compulsory	.294 FAIL
50+	Compulsory	Compulsory	Compulsory	.245 FAIL

sunscreen products will continue to dry out for up to several hours after the film has been applied (Fig. 2). In some instances, this is apparent as a change in the spectral appearance pre- and post-irradiation, as an effect of light and heat during the UV exposure, and this can be misinterpreted as sample degradation. If the temperature of the plates during exposure exceeds the dry down temperature, further dry out will occur for those samples containing volatiles. Slower dry down also appears to occur in w/o formulations where the emulsion is fine and the escape of volatiles may be suppressed.

UV light exposure device

This is the source of the irradiation required for the test and, in effect, is a challenge for photo-stability. Critical parameters are the light intensity, the quality of the spectrum and the control limit on heat buildup in the device.

Proposed ISO 24443 has addressed this in detail.

Spectrophotometer calibration

Dynamic range

The film thickness used in the AS/NZS Broad Spectrum test is 1.3 mg/cm^2. This differs from the 2 mg/cm^2 used in the *in vivo* SPF test. The importance of this becomes evident when high SPF sunscreens are measured. At an application film thickness of 1.3 mg/cm^2, an SPF 30 sunscreen typically has an absorbance max around Abs 1.5 and an SPF 60 around Abs 2.0. As both the UVAPF and critical wavelength end points essentially involve the measurement of areas under a curve, it is obvious that the areas need to be fully plottable on the spectrophotometer used for this measurement (see Fig. 3). Colipa/ISO approach this by requiring a dynamic range of not less than 2.2.

The impact for formulating is the question of the confidence of measurement of a ratio for very high SPF products, where the sensitivity of the instrument can easily be exceeded. At 2 mg/cm^2 film thickness, an absorbance of 3 corresponds to an SPF of around 50, so testing of *in vitro* SPF performance at this thickness can give misleading results.

Linearity

This is a measurement of the ability of the spectrophotometer to produce the same sensitivity response over its dynamic range. Colipa and ISO protocols address this by utilising two matching PMMA plates, which have been impregnated with UV absorber. The shape of the spectral absorbance curve should be the same when two plates are stacked in the light path, vis one plate. The absorbance value of two at all wavelengths should be double the value obtained by one. A similar effect can be achieved by use of neutral density filters, utilising the same principle of 2 *vis* 1 in order to determine linearity.

Table 7: Water resistance requirement – current and proposed (same).

SPF range	Allowable maximum
At least 4 but less than 8	No claim
At least 8 but less than 15	40 min
At least 15 but less than 30	2 h
At least 30 or above	4 h

Wavelength calibration

A reference spectrum is utilised for this purpose. Holmium is most commonly used and Colipa 2011 recommends holmium perchlorate solution, while ISO and instrument supplier utilise a holmium oxide filter.

It is important that the measurement instrument is accurate to within one nanometer as any greater variation could mean that one lab reports a pass and another a failure.

Compilation of results

The new standards provide a standard format spreadsheet in which the data can be computed and documented. This is most important for consistency and for reducing the chance of transcription errors.

Test method oriented approach to formulating

Target the ratio. It is simpler to adjust actives in the same ratio of content once the desired 'curve' has been achieved. It is much more difficult to adjust the curve once the desired SPF has been reached.

Consider photostable UVA absorbers or stabilisers. The additional cost may well offset the use of excess active to compensate for photo-degradation challenge in the UVA test.

Based on a sampling of 200

Table 8: ISO water resistance ring study 2 test parameters.

Parameter	For ring study
Device	Spa, Jacuzzi or bath tub – record shape
Water Temperature	30˚C +/--2˚C
pH	6.5 to 7.5
Water supply	Potable (hardened)
Water hardness	50 to 300 ppm
Sanitisation	To be recorded
Conductivity	To be recorded
Relative humidity	Not recorded
Water resistance	Vis static
Extra water resistance	Not determined
Water flow rate	0.02 – 0.05 m/sec
Control without circulation	Additional arm to the study
Jets	Not directed to subject
Aeration	Not to be used

formulations from our own testing completed in 2011, one in ten sunscreens was found to exhibit a critical wavelength which fell between 368 nm and 372 nm. Subtle changes in test technique will mean the difference between pass and fail for these candidates. Zinc oxide sunscreens are the most likely examples of the effect of the pass/fail margin for both UVAPF and critical wavelength. This is because the absorption curve for ZnO sits very much on the limits. Additionally, variation in grade can change the shape of the curve and product thin film tends to be more thickness dependent than organic sunscreens.

Other observed effects include SPF which increases after exposure. This effect was reported consistently from multiple labs for one (organic actives based) formulation included in an ISO ring study. SPF can also increase post water immersion, possibly explained as film swelling.

As the critical wavelength pass is based on a relationship between SPF and UVA performance, a formulator may prefer to fall back to a lower label SPF rater than to reformulate. This relationship and its effect is shown for the three categories of sunscreens proposed for AS/NZS 2604, in Table 6.

Water resistance test

In the 2012 version of AS/NZS 2604, the requirements are as follows (Table 6).

A task group under ISO is still developing a harmonised test method for sunscreen water resistance. For now, the AS/NZS method remains unchanged.

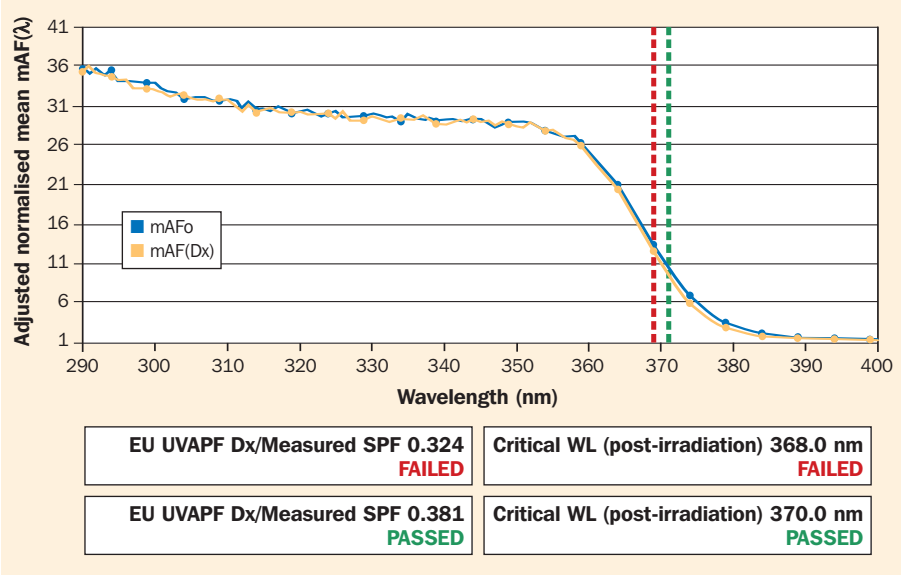

Figure 6: *Effect of 2 nm wavelength shift on pass/fail.*

The following parameters (Table 8) were set for a recent ISO ring study conducted in 12 labs. A second ring study has been completed and the report was under consideration by the ISO WG 7 committee in June 2012.

For water resistance performance

For providing water resistance characteristics, focus on this property being inherent in the base formulation. Where formulations rely on the residual SPF after partial wash-off, such as is permitted in the EU (>50% SPF retained post immersion), then these types of formulations usually will not perform for higher water resistance times of two hours and four hours. Also, as SPF increases, small variations in wash-off can lead to large drop in SPF.

Cost effective approach to testing

The total cost of testing a sunscreen can be minimised if a logical sequential approach is taken. Although test sequence strategies might vary, due to prior experience with similar formulations, or marketing priorities and deadlines, the following sequence can help to minimise both time and cost.

Although making adjustments to formulations and retesting can sometimes be frustrating, the additional cost is often recovered many times over if a formulation is optimised and thus cost per kilo is reduced. This applies particularly for expensive sunscreen actives. PC

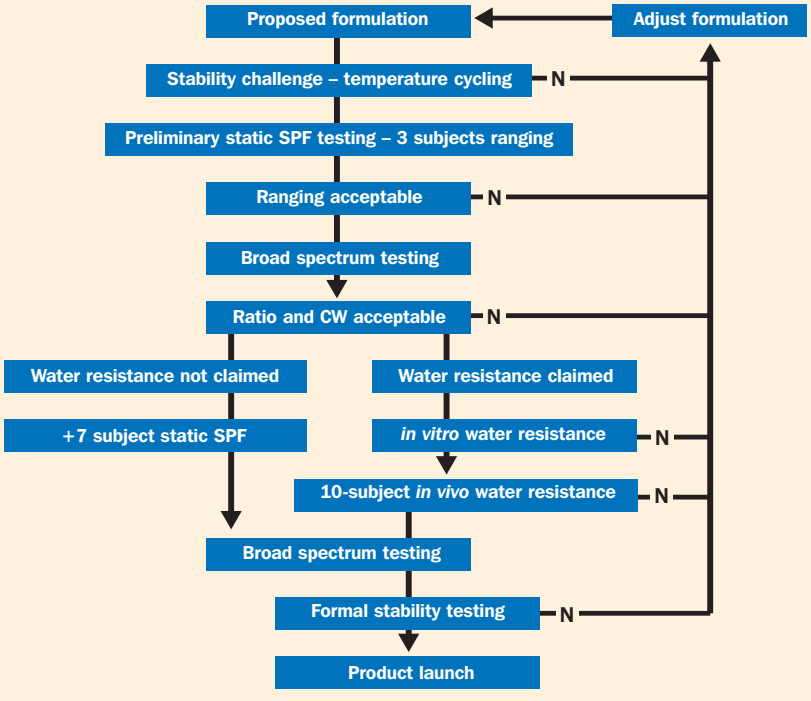

Figure 7: *Proposed flow sequence for sunscreen product development.*

● *This paper was presented at the Australian Cosmetic Chemists Conference in Adelaide and has been published in the* The Australian Journal of Cosmetic Science.

References

1 Sunscreen Standard (Proposed 2012). AS/NZS 2604.

2 *Cosmetics – Sun protection test method – determination of sunscreen SPF photoprotection* in vivo. ISO 24444; Dec 2010.

3 *Cosmetics – sun protection test method – determination of sunscreen UVA photoprotection* in vitro. FDIS ISO 24443; 2011 (E).

4 *In vitro method for the determination of the UVA protection factor and 'critical wavelength' values of sunscreen products guideline*. The European Cosmetic Toiletry and Perfumery Association. March 2011.

5 www.Colipa.eu/publications-Colipa-the-european-cosmetic-cosmetics-association/guidelines.html?view=item&id=33&catid=46.