Evaporation of sunscreen films: how the UV protection properties change.

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ABSTRACT

We have investigated the evaporation of thin sunscreen films and how the light absorption and the derived sun protection factor (SPF) change. For films consisting of solutions of common UV filters in propylene glycol (PG) as solvent, we show how evaporation generally causes three effects. Firstly, the film area can decrease by dewetting leading to a transient increase in the average film thickness. Secondly, the film thins by evaporative loss of the solvent. Thirdly, precipitation of the UV filter occurs when solvent loss causes the solubility limit to be reached. These evaporation-induced changes cause the UV absorbance of the film to decrease with resultant loss of SPF over the time scale of the evaporation. We derive an approximate model which accounts semi-quantitatively for the variation of SPF with evaporation. Experimental results for solutions of different UV filters on quartz, different skin mimicking substrates, films with added nanoparticles, films with an added polymer and films with fast-evaporating decane as solvent (instead of slow evaporating PG) are discussed and compared with model calculations. Addition of either nanoparticles or polymer suppress film dewetting. Overall, it is hoped that the understanding gained about the mechanisms whereby film evaporation affects the SPF will provide useful guidance for the formulation of more effective sunscreens.

KEYWORDS: sunscreen, evaporation, spectrophotometry, precipitation, wetting, sun protection factor

1. INTRODUCTION

Sunscreen films are applied to skin to protect it from the harmful effects of solar UV radiation in the UVB (290-320 nm) and UVA (320-400 nm) wavelength ranges. Sunscreen formulations commonly contain one or more chemical UV filters which absorb light and/or one or more "physical" filters which are generally small oxide semiconductor particles which absorb, scatter and reflect light. Common formulation types include solutions, particle dispersions and emulsions, both water-in-oil (w/o) and oil-in-water (o/w). Sunscreens are spread on the skin at application extents of 1-2 mg cm⁻² which correspond to initial mean film thicknesses of 10-20 μ m.

The sun protection factor SPF of a sunscreen film is defined by

$$SPF = \frac{med_{with \, sunscreen}}{med_{without \, sunscreen}}$$
1

where med is the minimum erythema dose of sunlight to induce erythema (sunburn) and the subscripts indicate with or without the sunscreen. SPF is most reliably measured *in vivo* but can be estimated *in vitro* by measuring the diffuse optical transmittance T of the sunscreen film as a function of wavelength λ . The estimated SPF is derived from *in vitro* measurements of T(λ) according to

$$SPF = \frac{\int_{290}^{400} E(\lambda)S(\lambda)d\lambda}{\int_{290}^{400} E(\lambda)S(\lambda)T(\lambda)d\lambda}$$
2

where $E(\lambda)$ is the erythema action spectrum and $S(\lambda)$ is the spectral irradiance of terrestrial sunlight under defined conditions¹⁻⁵. The functions $E(\lambda)$ and $S(\lambda)$ are available in the literature¹ (see Figure S1) and so spectrophotometric measurement of $T(\lambda)$ for a sunscreen film allows the estimation of SPF. For sunscreen films which both scatter and absorb light, the diffuse transmittance must be measured using an integrating sphere with detector acceptance angular range of $\pm 90^{\circ}$ since all light scattered at scattering angles less than or equal to 90° is transmitted through the film. However, for non-scattering films such as the films consisting of molecular solutions used here, the diffuse transmittance is equal to the specular transmittance recorded using a standard UV/vis spectrophotometer. In this work, the films used are non-scattering and hence specular transmittance measurements enable derivation of the SPF according to equation 2. In equation 2, the wavelength integration limits correspond to the combined UVB and UVA range; other wavelength ranges can be used to estimate alternative SPF values corresponding to the UVB or the UVA ranges⁴. Values of the SPF quoted here are estimated according to equation 2 and thus correspond to a combined UVB and UVA protection factor.

SPF estimation based on *in vitro* measurements are more convenient and less expensive than *in vivo* measurement. However, the reliability of *in vitro* estimates can be compromised by several processes, which can cause the sunscreen film to change over the typical exposure time of a sunscreen film, i.e. a few hours (although we note that reapplication of sunscreen every 2 hours is commonly recommended by manufacturers). Timedependent SPF values mean that SPF values based on *in vitro* measurements at a single time (e.g. corresponding to the initial sunscreen film properties) will not give an accurate estimate of the total, time-integrated protection over a time period. Time-dependent SPF values can result from three processes. Firstly, light exposure may causes photochemical changes in the

sunscreen film thereby changing the film optical transmittance properties; there is an extensive literature on these effects⁶⁻⁹. Secondly, the sunscreen film may change due to water immersion, for example when bathing. Sunscreen stability with respect to water immersion has been discussed and can be specified¹⁰. The focus of the work described here relates to a third process: how sunscreen films change as a result of evaporation of the volatile film components and how the changes affect the optical transmittance properties of the film and the derived SPF. There is little discussion of this process in the literature; Beyer et al. measured evaporative mass loss and SPF values for two commercial sunscreen formulations (one containing organic UV filters and one containing inorganic UV filters) of undisclosed overall compositions¹¹. Both sunscreen creams (probably emulsions) clearly contained involatile solvent components since the film masses remained constant after 30 min at approximately 30% of their original values. For these incompletely evaporating films, evaporation caused no change in UV transmission measured in vitro. The SPF measured in vivo decreased by 25% over 8 h when test participants performed no activity and was similar for both sunscreen types. In the present study, we shall show that sunscreen film evaporation can cause large changes in SPF in vitro and the aim of the work is to elucidate the mechanisms of how film evaporation can impact SPF.

This paper is organised as follows. Following the experimental section, in section 3.1 we first discuss the behaviour during evaporation of films consisting of solutions of several common molecular UV filters spread onto a quartz plate substrate. The solvent used for these studies is propan-1,2-diol (propylene glycol abbreviated to PG). The main reason for this solvent choice is that the evaporation of a thin film of PG is slow enough (several hours) to enable the range of measurements used here to be made during the evaporation. However, we note that this solvent choice is not based only on experimental convenience; PG is a common ingredient of many sunscreen formulations. In sections 3.2 and 3.3, we investigate how the addition of semiconductor oxide particles (used as "physical" UV filters) and a polymer affects the film evolution during evaporation. In section 3.4, we show how substrates other than smooth quartz, selected to attempt to mimic skin more closely, affect the sunscreen film evaporation behaviour. Finally, the main conclusions are summarised.

2. EXPERIMENTAL

2.1 Materials. The full chemical names, abbreviations used here, common tradenames and sources of the three UV filters used are as follows. 4-*tert*-butyl-4'-methoxy dibenzoyl methane (AVB, Avobenzone, Sigma-Aldrich, pharmaceutical secondary standard) was used as received. *Iso*-pentyl p-methoxycinnamate (MC, Neo Heliopan E1000) and diethylamino hydroxybenzoyl hexyl benzoate (DHHB, Uvinul A Plus) were kindly donated by the industrial sponsor (GSK) and used as received. The chemical structures and UV absorption spectra in the solvent used here are shown in Figures S2 and S3. Squalane (Sigma-Aldrich, 99% purity) was columned over neutral aluminium oxide (Merck) to remove any polar impurities. Propan-1,2-diol (PG, Sigma-Aldrich, >99%), n-decane (TCI Europe, >99%) and poly-diallyldimethylammonium chloride (poly-DADMAC, Sigma-Aldrich, average relative molar mass 200-350 kDa, supplied as a 20 vol% aqueous solution, >99.5% purity) were used as received.

Titanium dioxide (Sigma-Aldrich, a mixture of rutile 20 wt% and anatase 80 wt%, 21 nm primary particle size), Cerium oxide (Sigma-Aldrich, nanopowder, < 25 nm primary particle size), Zinc oxide (Sigma-Aldrich, primary particle size in the range 60-300 nm) and Tungsten VI oxide (US Research Nanomaterials Inc., 60 nm primary particle size) were used as received. Fumed silica particles of primary particle diameter 10-30 nm (but containing

aggregates of larger sizes) which were hydrophobised to different extents by chemical reaction of the surface silanol groups with dichlorodimethylsilane (DCDMS) were provided by Wacker-Chemie (Germany). Two silica particle samples with different hydrophobicities (containing 100% and 35% unmodified SiOH surface groups) were used here without additional purification. Vitro skin, with surface roughness $P_a = 12 \mu m$ measured using Bruker DektakXT stylus profiler with a 12.5 mm radius stylus, was obtained from IMS Inc. Keratin from wool (TCI Europe), lignoceric acid (TCI Europe, >96%) cholesterol (Sigma Aldrich, >99%), chloroform (VWR Chemicals, 99%) and N-acylphytosphingosine C18:1 (ceramide III, Evonik) were used as received.

2.2 Methods. UV/vis spectra of all UV filters dissolved in PG were measured using a Unicam UV3 UV/vis double beam spectrophotometer for a range of concentrations and path lengths. This instrument reports absorbance values derived from specular transmittance measurements. For each sample, the measured data of absorbance versus wavelength was converted to molar extinction coefficient versus wavelength. It was found that the molar extinction coefficients did not change significantly with either concentration or path length (i.e. all solutions followed the Beer-Lambert law) and values from individual runs were averaged to obtain the final spectra shown in Fig S3.

Equilibrium solubilities at 32° C of the different UV filters in PG and other solvents were determined by adding an excess of each UV filter to 10 ml of the solvent in a sealed glass vessel. The samples, stirred using a magnetic stirrer, were left to equilibrate within a water bath at 32° C for seven days. The stirring was stopped and excess solute phase allowed to separate under gravity for 3 hours. Samples of the saturated solution supernatant phase were removed, accurately diluted with solvent and the concentration determined from absorption measurements. The final values of the solubilities (Table 1) were the average of four measurements and are estimated to be accurate within approximately $\pm 10\%$.

Film preparation and evaporation studies were made as follows. Approximately 11 µL (approximately 12 mg) of the liquid film material was deposited on a substrate (a quartz plate unless noted otherwise) with dimensions of 4.5 x 1.25 cm using an Eppendorf pipette. The sample was spread using the pipette tip as evenly as possible over an initial surface area of a few cm^2 to produce a film of initial mean thickness of a few tens of μm . The typical film application was 2-3 mg cm⁻², similar to the recommended standard sunscreen application dosage of 2 mg cm⁻². The substrate plus film was placed on a Linkam Peltier heating stage set to skin surface temperature of 32°C and allowed to evaporate in the open lab air. At timed intervals during the evaporation, the film mass was recorded using a Denver instruments balance (accurate to +0.2 mg), the film area and presence/appearance of precipitated crystals were recorded by optical microscopy and the film absorption spectrum measured. Optical micrographs were obtained using an Olympus BX51 transmission microscope equipped with an Olympus DP 70 digital camera. Low magnification micrographs of the films were analysed using ImageJ software to determine the film perimeter and derive the total film area. High magnification images of selected films containing precipitated crystals were also recorded.

UV-vis spectra of the films were measured at room temperature (approximately 20°C) using a Unicam UV3 UV/vis double beam spectrophotometer which was oriented vertically to enable the sample films to be placed horizontally in fixed measurement positions. This spectrophotometer records the *specular* optical transmittance; any *diffuse* transmittance is not recorded. The position and area (1.6 cm x 0.20 cm = 0.32 cm²) of the illuminated region on

the sample was measured and kept constant for all samples. All film + substrate spectra were initially measured using only air in the reference beam of the spectrophotometer. The reference spectrum of the sunscreen film lacking the UV filter on the relevant substrate was measured separately (using only air in the reference beam). The substrate reference spectrum was subtracted from the film + substrate spectrum to obtain the final spectrum of the film alone. For a PG film on quartz, the absorbance values of the substrate reference spectrum were generally small (around 0.05) relative to the absorbance values of the sunscreen film (around 0-2) and hence subtraction of the substrate reference spectrum was a relatively small correction. For the vitro skin and keratin/lipid substrates, the substrate absorbance values were of similar magnitude to the film absorbances. In these cases, subtraction of the final spectrum of the final spectrum of the film alone.

Films on vitro skin as substrate were prepared by first cutting a sample of vitro skin to the same size as the quartz plate, taping it by the edges to the quartz plate and then spreading the film on the vitro skin surface. Keratin-lipid films containing 80.0 wt% keratin, 6.7 wt% cholesterol, 6.7 wt% lignoceric acid and 6.7 wt% ceramide III in the final dry film were made as follows. 0.16 g total mass of the three lipids (comprising equal masses of cholesterol, lignoceric acid and ceramide III) were initially added to 5 ml of chloroform at 50°C and the solution was left under stirring until all lipids were fully dissolved. Keratin powder with particle diameters in the range 2-5 μ m (0.64 g) was added and the dispersion was left to stir for a further 30 min at 50°C to give an opaque dispersion of keratin particles in a solution of the mixed lipids. 15 mg of this keratin–lipid dispersion was spread on a quartz plate using an Eppendorf pipette tip to cover an area of 2.06 cm². Evaporation of the chloroform solvent was complete within a minute or so to leave a dry, opaque-white film containing 3.0 mg of keratin plus lipid. From the film mass and area, the average thickness of the keratin-lipid film was estimated to be approximately 15 μ m.

For films containing particles, dry particles were added (by mass) into 5 ml of the required solvent and dissolved UV filter. The particles were dispersed by sonication using a Branson Digital Sonifier 450 (400W) operating at 40% power in a duty cycle of 1 sec pause every 2 sec for a total run time of 5 min. Films containing poly-DADMAC were prepared by addition of the required amount of poly-DADMAC aqueous stock solution to PG containing the required amount of dissolved UV filter, followed by stirring at 800 rpm for 24 h to obtain a final transparent solution. It should be noted that PG films containing poly-DADMAC also contained minor amounts of water originating from the polymer stock solution.

Particle sizes of the powder samples were estimated from transmission electron microscopy (TEM) images obtained using a JEOL 2010 High Resolution TEM instrument operating at 200 kV. Images were collected using a Gatan 64 megapixel US4000 camera with Digital Micrograph software. The samples were dispersed in ethanol prior to their deposition on carbon-supported copper grids and they were left to evaporate in the open lab air under ambient temperature conditions.

Contact angles of drops of PG and decane on the quartz substrate in air were measured at 32°C using a Kruss DSA 10 instrument.

3. **RESULTS AND DISCUSSION**

3.1 Evaporation of solutions of UV filters in PG. Figure 1 shows the visual appearance of a film of 8 mM AVB in PG spread onto a quartz plate. As evaporation proceeds, the film is seen to shrink in surface area, presumably as a result of both loss of PG by evaporation and/or dewetting of the quartz plate. Evaporative loss of the PG solvent causes the concentration of the involatile AVB solute to increase and exceed its solubility (14 mM, Table 1). AVB precipitation within this film was first observed after 150-180 minutes of evaporation. The area illuminated in the spectrophotometric measurements of the drying film is superimposed on the images of Figure 1.

Figure 2 shows the measured mass of film remaining as a function of evaporation time and the total film area estimated from the images of Figure 1. As discussed in ref. 12, the rate of mass loss by evaporation of a liquid is limited by the rate of diffusion of vapour molecules across a "stagnant" gaseous layer immediately above the liquid surface. Within this stagnant vapour layer, a steady-state gradient in vapour concentration is formed rapidly; the vapour concentration corresponds to the equilibrium vapour pressure at the liquid surface and decreases to zero at the upper surface of the stagnant vapour layer. Under these conditions, the steady-state rate of liquid mass loss by evaporation is given by equation 3.

$$-\frac{dm}{dt} = \frac{MADPf}{hRT_e}$$
3

where m is the mass of the film remaining, t is time, M is the relative molar mass of the evaporating liquid, A is the liquid surface area, D is the diffusion coefficient of the vapour through air, P is the equilibrium vapour pressure of the liquid, h is the thickness of the stagnant vapour layer, R is the gas constant and T_e is the absolute temperature. The parameter f is a factor which is dependent primarily on the geometry of the evaporation setup. Under the evaporation conditions used here, h and f are not known but are approximately constant within and between runs. Hence, the evaporation rate is proportional to the liquid surface area A. From Figure 2, it can be seen that, as A shrinks, the evaporation rate (equal to -dm/dt) decreases with the result that the plot of film mass m versus time is concave in shape. Also shown in the mass loss plot of Figure 2 is the predicted film mass m^{*} and time t^{*} at which the AVB concentration is predicted to increase to a value equal to its equilibrium solubility, corresponding to the onset of AVB precipitation. The value of m^{*} is estimated according to

$$m^* = \frac{m_0 [AVB]_0}{S_{AVB}} \tag{4}$$

where m_o is the initial film mass (0.0117 g), $[AVB]_o$ is the initial concentration of AVB (8 mM) and S_{AVB} is the equilibrium solubility of AVB in PG (14 mM, Table 1). Hence, m^{*} is estimated to be 0.0067 g and (from the mass loss plot) t^{*} is 190 minutes. This estimate is in reasonable agreement with the time range (150-180 minutes) at which precipitated crystals of AVB are first observed.

The measured values of film mass and total film area can be combined to derive the (time-dependent) average film thickness d (= m/ ρ A where ρ is the film density, taken to correspond to pure PG which is 1.027 g cm⁻³ at 32°C¹³). From Figure 2, it can be seen that, during the evaporation, the film initially shrinks in area by dewetting from the quartz plate surface which causes it to initially thicken, despite ongoing evaporative mass loss. In the later stages, loss by evaporation dominates and eventually thins the film to almost zero. It should be emphasised that the film thicknesses estimated here are *average* values; the film is

probably somewhat thicker at the edges and thinner in the middle as dewetting is likely to "push" material to the film edges. In addition to the total film area, Figure 2 also shows the fraction of the area illuminated during spectrophotometric measurements (the red rectangles in Figure 1). Finally, we note that the evaporation and dewetting behaviour of this film of 8 mM AVB in PG is not significantly different to that of a film of pure PG (Figure S4). Repeat measurements for films of 8mM AVB in PG were found to be reproducible in their mass and total area loss behaviour within about 10%. However, the variation of the fraction of film area illuminated was observed to be more variable between repeat runs since this depends on the pattern of dewetting adopted by each individual film relative to the fixed illuminated area.

Figure 3 shows how the UV/vis spectrum of the film changes during the evaporation process. It can be seen that the spectral absorbance initially (over the first 120 minutes of evaporation) increases in magnitude whilst maintaining the shapes of the absorbance peaks. At longer times, the spectral peaks "flatten" in shape and the spectral absorbance decreases progressively to values in the range 0.015-0.2 and almost independent of wavelength. The initial absorbance increase arises from the initial thickening of the film due to dewetting causing shrinkage of the total film area and film thickening. The later absorbance decrease and peak "flattening" is due to the combined effects of (i) incomplete coverage by the film of the illuminated area and (ii) the precipitation of AVB from solution.

As shown in the lower plot of Figure 3, we have calculated the evolution of the AVB spectrum during evaporation using a model based on the following considerations and assumptions. For a film containing a concentration c of dissolved AVB which has uniform thickness d and which completely covers the area illuminated in the spectrophotometer, the (wavelength dependent) absorbance is given by the Beer-Lambert law.

$$Abs = -log_{10}T = \varepsilon cd 5$$

where T is the (wavelength dependent) light transmittance and ε is the (wavelength dependent) molar extinction coefficient of AVB (see Fig. S3). Equation 5 is valid for plane parallel light incident normal to the film and non-scattering films, i.e. the transmittance is equal to the specular transmittance and contains no significant diffuse contribution. When the fraction of the illuminated area covered by the film A_f is less than unity, the measured absorbance is equal to the negative log of the illuminated area average of the transmittance, i.e.

$$Abs = -log_{10} \{ A_f 10^{-\varepsilon cd/A_f} + (1 - A_f) \}$$
6

Equations related to equation 6 have been developed to account for the light absorption properties of thin sunscreen films of non-uniform thickness.^{14,15} Equation 6 is valid when (i) the illumination light intensity is uniform across the illuminated area and (ii) the film thickness is uniform. Neither of these conditions are fully met by the experimental setup used here and so equation 6 is expected to yield only an approximate prediction of the measured absorbance changes resulting from A_f decreasing below unity. Inspection of equation 6 shows that the effect of A_f decreasing below unity is that Abs is reduced and larger absorbance values are reduced more than smaller values. Thus, when $A_f < 1$, the absorbance peaks in the spectra are "flattened", as seen in the spectra of Figure 3. This peak "flattening" provides a distinctive and easily observable feature which indicates film dewetting leading to A_f decreasing below unity.

The final aspect of the model concerns the effects of AVB precipitation. During the course of the evaporation of the solvent from the film, the dissolved AVB concentration c increases as solvent is lost until the time t^{*} at which c is equal to the AVB solubility (see equation 4). Individual crystals of precipitated AVB are expected to absorb light strongly since the localised concentration of AVB within the crystals is high and the molar extinction coefficient for AVB within the crystal is expected to be similar in magnitude to that for AVB in dilute solution¹⁶. However, the contribution from the crystals to the overall, measured film absorbance is expected to be highly localised within the small crystals of which only a fraction will lie within the illuminated area and will occupy only a very small fraction of the illuminated area, as seen in the representative optical micrographs of the precipitated AVB crystals shown in Fig. S5. From the form of equation 6, when the illuminated area fraction of the crystals is vanishingly small, their contribution to the overall measured absorbance tends to zero. For the model calculations used here, we assume that the crystals have negligible contribution to the overall film absorbance, i.e. in a film containing a concentration c of dissolved UV filter plus precipitated filter, only the *dissolved* UV filter molecules contribute to the overall absorbance estimated using equations 5 and 6. This latter model assumption is implemented in the calculations by taking

$$c = \frac{c_0 m_0}{m}$$
 for times less than or equal to t^{*} and 7
 $c = S_{AVB}$ for times greater than t^{*}

The middle plot of Figure 3 shows the evolution of the AVB spectrum with evaporation time calculated according to this model using the separately measured values of AVB extinction coefficient (Fig. S3), film mass, average thickness and A_f (from Figure 2). It can be seen that the model correctly captures (i) the initial increase in absorbance with retention of the spectral peak shapes and (ii) the longer time absorbance decrease and "flattening" of the peaks. However, we note that the magnitudes of the calculated and measured absorbance values do show significant differences. These discrepancies are likely to be due to the simplifying model assumptions (i.e. uniform illumination light intensity and uniform film thickness) not being fully valid. Overall, it is concluded that the simple model developed here correctly accounts *semi-quantitatively* for the main features of the behaviour of these films during evaporation. The quantitative accuracy of the modelling could be improved (albeit at the cost of sacrificing the model's simplicity) by explicit incorporation of the non-uniformity of the film thickness and light illumination intensity.

In addition to the AVB/PG films on quartz described in detail above, we have made similar measurements for DHHB (solubility = 28 mM) and MC (solubility = 435 mM) films in PG. AVB and DHHB are both solids and precipitate as crystals whereas MC is liquid and separates as a second liquid phase. For each UV filter, both the measured and calculated absorbance spectra can be converted to SPF using equation 2 to yield plots of measured and calculated SPF versus evaporation time. Such plots provide a convenient means to summarise the results of evaporation runs for the different films as shown in Figure 4. For highly soluble UV filters such as MC in PG, the loss of SPF with evaporation is primarily a result of film dewetting rather than precipitation of the molecular filter. In the case of MC which separates as a liquid, the dried films show small residue liquid spots of MC which is consistent with the observed loss of SPF. If the residual liquid MC formed a very thin spread liquid film, retention of the SPF would be expected. As noted above, measurements of the time variation of the mass loss, total film area and derived average film thickness are all reproducible but the variation in illuminated area fraction A_f is more variable since it depends on the exact pattern of dewetting for each individual run. Hence, the results of Figure 4 are specific to each individual run to some extent. In addition, the quantitative accuracy of the calculated variation of SPF is limited owing to the simplifying assumptions of uniform illumination and film thickness. Despite these important caveats, it can be seen in Figure 4 that the key features of the evaporative behaviour of the different UV filter solution films are successfully captured.

Figure 4 demonstrates how the SPF of sunscreen films vary strongly with time due to evaporation and that the changes can be semi-quantitatively modelled. The time scale over which these evaporation-driven changes occur is controlled by the time required for the solvent evaporation. In the case of the relatively slowly evaporating solvent PG, the film SPF values change over a long time scale of several hundred minutes which allows the detailed measurements shown here. For sunscreen films containing other solvents, evaporation-driven SPF changes will occur on the timescale dictated by the evaporation rate of the solvent used. From equation 3, for films of different liquids of the same surface area and measured under the conditions used here, the mass loss rate by evaporation is proportional to the factor MDP. Comparing values for PG (M = 76.09 g mol⁻¹ and P = 50.8 Pa at $32^{\circ}C^{17}$) and water (M = 18.015 g mol⁻¹ and P = 4746 Pa at 32°C¹²) and estimating (based on the data given in ref. 12) that D is approx. 3 times larger for water than for PG enables us to estimate the evaporation rate of water is approximately 66 times faster than for PG films of the same area. This relative rate estimate is in reasonable agreement with experiment. We have measured that a film of water shows complete evaporation in 10 minutes compared with 690 minutes required for complete evaporation of an identical PG film, i.e. the water film evaporates approximately 69 times faster than the PG film of similar surface area.

We have checked whether the loss of film absorbance seen in Figures 3 and 4 for slowly evaporating PG films is also observed for fast evaporating films. Water is a common ingredient of sunscreen films and, from data in ref. 17, the evaporative mass loss rate per unit surface area is predicted to be approximately 66 times faster than for PG. Consistent with this prediction, we have measured that a water film of initial average thickness of 50 µm is completely lost by evaporation after only 10 minutes. However, water cannot be used to illustrate the effect of fast solvent evaporation of a sunscreen film since the UV filters used here are not sufficiently soluble in water. For this reason, films of 8 mM AVB in n-decane were chosen for this study. From data in ref. 17, the evaporative mass loss rate per unit surface area for decane is predicted to be approximately 7 times faster than PG. As seen in Figure S6, the decane film evaporation is complete within approximately 20 minutes and the onset of AVB precipitation occurs at after 13 minutes. From Figure S7, the absorbance spectrum reduces to that of just the quartz plate reference after 20 minutes evaporation. The film residue after this time consists of small particles of precipitated AVB and some circular drops which may be highly concentrated drops of AVB in decane for which evaporation is incomplete owing to their small surface area. Although there are differences in the appearance of the evaporated film residues for slow and fast evaporating systems, the major effect of evaporation is the almost complete loss of AVB absorbance in either slow or fast evaporating systems. Only the time scales for this absorbance loss differ between the slowlyevaporating PG films and the fast evaporating decane films.

For these films spread on smooth quartz substrates, film dewetting and area shrinkage is observed for films containing either PG or decane as solvent and it is also observed that liquid residues of MC form dewetted, isolated spots rather than a coherent thin spread film after solvent evaporation. The observed film dewetting occurs despite the contact angles for drops of the materials on smooth quartz being close to zero. The measured values at 32°C

are: PG: static, advanced = 11°, static, receded = 9°; decane: static, advanced = 0°, static, receded = 0° and MC: static, advanced = 15°, static, receded = 10°. It appears that the tendency of a film to dewet is not controlled solely by the contact angles; it is likely that substrate surface roughness also affects whether or not pinning of the three phase contact line and suppression of dewetting occurs. In addition, it is likely that capillary forces resulting from the tendency of the film liquid-air surface to resist localised curvatures higher than the surface capillary length (equal to $(\gamma/\rho g)^{1/2}$ where γ is the liquid-air tension, ρ is the liquid density and g is acceleration due to gravity) also play a role. For the liquid films considered here, the capillary lengths are much larger (of the order of a mm or so) than the film thickness and hence are likely to lead to non-uniform film thicknesses in addition to promoting dewetting. The stability, dynamics and dewetting of thin liquid films is a highly complex subject and the reader is referred to ref. 18 for a comprehensive review.

3.2 How added particles affect the film evaporation. Sunscreen formulations commonly contain a combination of dissolved, molecular UV filters and inorganic, semiconductor filters in the form of small particles. Hence it is of interest to see how film evaporation is affected by the presence of small particles. In Figure 5, we compare the evaporation behaviour of 8 mM AVB in PG films with and without 0.1 wt% of four different semiconductor particles and two types of silica particle; one hydrophilic (unmodified silica with 100 % surface SiOH groups) and one hydrophobic (35 % surface SiOH with 65% modified with DCDMS). Although there are some quantitative differences between the different particles, the main effect of particle addition is to decrease the extent of film area contraction by dewetting. Because the rate of PG solvent evaporation is proportional to the film area, the higher film area causes the evaporation rate to be faster in films containing particles. The variation of average film thickness is the result of two competing effects: film area contraction by dewetting causes film thickening whereas film mass loss causes film thinning. In the absence of particles, rapid initial film area contraction with relatively slow mass loss causes the film to initially thicken with eventual thinning only at long evaporation times. In the cases of TiO₂ and hydrophilic (100 %SiOH) silica particles, mass loss dominates over area contraction and progressive film thinning is observed from time zero. The remaining particles show intermediate behaviour. In addition to the measurements shown in Figure 5, the variation of the fraction of illuminated area covered by film (A_f) was also determined. Because the area contraction was relatively small for the particle films, A_f remained equal to unity over all (or almost all) of the evaporation period for all particle films.

The effects of addition of 1 wt% of the same particles was also determined (but is not shown here); the variation of film mass, area and average thickness was similar to that of films with 0.1 wt% particles. However, the higher concentration of the particles caused strong light absorption and scattering by the particles within the films which complicates the measurement and unambiguous interpretation of the comparison of the evolution of the optical absorption properties of the AVB within the films with and without particles. For this reason, the evolution of the film absorption spectra was determined only for films containing 0.1 wt% of particles for which the total light extinction is dominated by the absorption due to AVB. Figure 6 shows the spectral changes occurring during evaporation of a film containing 8 mM AVB plus 0.1 wt% TiO₂ in PG and the (separately measured) absorbance contribution arising from the TiO₂ particles. For this film, A_f remains equal to 1 during the time period measured and precipitation of the AVB occurs after approximately 100 minutes. The spectra can be compared to those of the corresponding no added particle film shown in Figure 3. For films with and without particles, the absorbance peak initially increases due to film thickening and concentration of the AVB by solvent loss. It can be seen that the initial

absorbance increase is much less in the case of the particle-containing film since film thickening by film area contraction is suppressed. For the particle-containing film, the decrease in absorbance at longer evaporation times is reduced since A_f remains equal to 1 for this film and the loss of absorbance is due solely to AVB precipitation. Consistent with this conclusion, it can be seen that the characteristic peak "flattening" which occurs when $A_f < 1$ observed in Figure 3 is not observed in Figure 6.

Using the model described above with inclusion of the separately measured absorbance contribution of the particles (assumed to remain constant during the evaporation), the film spectra have been calculated. Although the calculated spectra are only approximate due to the simplifying assumptions of uniform film thickness and illumination, the model calculations and derived SPF are in reasonable agreement with experiment. The light absorption and its evolution during evaporation for AVB/PG films containing the other particle types (not shown) is similar to that seen here for the TiO₂-containing films. Overall, it is concluded that particle addition suppresses film dewetting. This suppression of dewetting probably occurs by a mechanism of particle deposition around the edge of the evaporating film which aids "pinning" of the three phase contact line. The suppression of dewetting of films of the hydrophilic liquid PG is more effective for the hydrophilic silica particles compared to otherwise identical particles which have been partially hydrophobised. There is an extensive literature on the evaporation of liquid films containing particles¹⁹⁻²² which discuss how the complex interplay of evaporation-induced liquid flow patterns, particle-particle, particle-substrate and particle-liquid surface interactions control the final pattern of particle deposition in the dried film residue which can include so-called "coffee ring", spot and uniform types of deposition. Although these complex effects may affect the UV absorbance properties of the semiconductor particle UV filters, they are not of prime relevance in considering the absorbance of the molecular UV filter (AVB) considered here. Focusing on this aspect, the main effect of particle addition observed here is suppression of dewetting; this is consistent with the observation in ref. 19 that contact line pinning is much stronger in the presence of added particles.

3.3 How polymer addition affects the film evaporation. As seen in Figures 7 and 8, the addition of 1 or 5 wt% poly-DADMAC polymer suppresses film dewetting similarly to the effect of particles. As a result, the rate of evaporative mass loss is increased and the average film thickness shows only a progressive decrease. The fractional illuminated area A_f is 1 for almost all of the evaporation period and so, as seen for the particle-containing films, the optical absorbance shows only a small initial increase followed by a progressive decrease due solely to AVB precipitation. Because $A_f = 1$, no absorbance peak "flattening" is observed. In order to model the spectra, we have estimated the points at which AVB is expected to precipitate based on the assumption that the minor amounts of water present and the polymer do not significantly affect the solubility of the AVB. Calculated and measured spectra and the derived SPF are in reasonable agreement. Hence, although the polymer effectively suppresses the film dewetting, it does not stop or significantly delay the AVB precipitation and consequent loss of absorbance and SPF.

3.4 Evaporation of films on different substrates. It is convenient to measure the film properties on smooth quartz plates as this enables easy measurement of the film absorption properties. However, the smooth quartz surface does not mimic either the roughness or the surface energy properties (which, in turn, affect the wetting behaviour of liquids placed on the surface) of real skin. For this reason, we have examined the behaviour of films of 8 mM AVB in PG on two alternative substrates: vitro skin and films of keratin plus lipids.

Vitro skin is a commercial polymer sheet of undisclosed composition with a surface roughness of 12 µm, designed to mimic the roughness of real skin. For the experiments discussed here, the 8 mM AVB in PG solution was gently spread on the rough vitro skin surface which was supported by taping it by its edges to a quartz plate. Figure 9 shows the film mass, area and average thickness as the film evaporates. It can be seen that the film area remains constant during evaporation because the rough vitro skin surface completely prevents dewetting. As a consequence of the maintenance of the high film area, the films evaporation is more rapid than for the film on a smooth quartz plate and $A_f = 1$ throughout the evaporation. UV absorption spectra of the film and the vitro skin substrate are shown in Figure 10 where it can be seen that the vitro skin alone reduces light transmittance strongly, particularly at wavelengths below 300 nm. In addition, the high wavelength extinction due to the vitro skin changes depending on whether the rough polymer film is wet or dry. The higher extinction seen for dry vitro skin is likely to be due to increased light scattering or reflection from the rough surface. This effect complicates the separation of the absorbance due to the AVB/PG film alone from that due to the sum of extinction due to the film plus the vitro skin substrate. For this reason, Figure 10 shows the spectral changes during only the first 120 minutes of evaporation. For this time period, we assume that the extinction of the vitro skin is that of the wet substrate and that this remains approximately constant. With this assumption, the spectrum of the film alone is obtained by subtraction of the wet vitro skin reference from the measured spectrum of the film + substrate. From Figure 10, it can be seen that the absorbance due to AVB decreases progressively with evaporation without any "flattening" of the peaks. This is consistent with the A_f remaining equal to unity throughout and the loss of absorbance occurring solely as a result of AVB precipitation. The measured variation of SPF due to the film alone (i.e. derived from the measured film + substrate spectrum minus the substrate spectrum) is again in reasonable agreement with calculation.

The second alternative substrate, designed to approximately mimic the chemical composition of the outermost, stratum corneum layer of skin²³⁻²⁶, consisted of a film of 80 wt% keratin particles mixed with 20 wt% of lipids deposited onto a smooth quartz plate and was prepared as described in the experimental section. This substrate has a matt white appearance and scatters and/or reflects light strongly. Drops of 8 mM AVB in PG placed on this substrate were partly imbibed into the porous substrate film and thus the initial film area was relatively low and the initial average films thickness correspondingly high (Figure 11). As a result of the substrate porosity, the liquid film initially spreads within the porous keratinlipid film and *increases* its area with a corresponding reduction in average film thickness. At longer times, evaporation then progressively reduces the film area and average thickness. The illuminated area fraction A_f drops below 1 after approximately 80 minutes and the onset of AVB precipitation occurs at 130 minutes. Hence, the absorbance due to AVB is expected to initially decrease slightly due to film thinning and, after 100-120 minutes, to decrease more rapidly due to the combined effects of A_f decreasing below 1 and precipitation of the AVB. The measured and calculated spectra of the film plus substrate are shown in Figure 12. Optical extinction of the substrate alone is high (approximately 1.8 absorbance) due to light scattering and/or reflection which causes two difficulties with the spectral measurements and their interpretation. Firstly, the combined optical extinction of the substrate plus the AVB film exceeds the reliable range of the spectrophotometer. Secondly, because the liquid film does not lie on top of the porous substrate but rather soaks into it, the liquid film transmittance cannot be easily de-convoluted from the transmittance of the substrate alone. The high light scattering of the film-soaked substrate is very likely to include a multiplyscattered, diffuse component in the overall transmittance of the overall film. The

spectrophotometer used here measures the *specular* transmittance from which the reported absorbance is derived. Thus, the measured (specular) absorbance values are likely to overestimate the true optical extinction of the film. Despite these additional caveats, the calculated spectra of the film plus substrate and the SPF due to the film alone (i.e. following subtraction of the optical extinction due to the substrate alone) successfully capture the main features of the measured plots.

4. CONCLUSIONS AND OUTLOOK

We have demonstrated how the evaporation of thin films of liquid sunscreens changes their UV absorption and derived SPF values by three main mechanisms. Firstly, film dewetting with area shrinkage causes thickening of the film and increases the film absorbance and SPF. Secondly, film dewetting so that the illuminated area is not fully covered leads to loss of absorbance and SPF with a characteristic "flattening" of the spectral absorbance peaks. Thirdly, evaporation of the solvent in the film increases the concentration of the UV filter to a value above its solubility and causes precipitation of the UV filter molecules. Because the precipitated UV filter species contribute virtually zero to the overall spectral absorbance, precipitation results in loss of SPF. Based on these mechanisms, we have developed a simple model which successfully, semi-quantitatively accounts for the variation of SPF with evaporation time using no adjustable parameters. We have measured and successfully modelled the behaviour of films of solutions of different UV filters in PG on smooth quartz. Addition of either small solid particles or polymer suppresses the dewetting of these films but does not inhibit the precipitation. Dewetting of the films is also suppressed by using a rough vitro skin surface instead of smooth quartz but does occur for films spread on a porous substrate of keratin and lipid.

The conclusions and insights from this study provide important and useful guidance for sunscreen formulators seeking to optimise their performance. In addition to consideration of numerous factors which include overall SPF, photochemical factors such as photostability, photosensitization and possible photocatalysis, stability with respect to water immersion, cost, consumer acceptability and ease of manufacture, we have shown here that it is also important to optimise factors relating to film evaporation. Firstly, choice of the solvent components of a sunscreen strongly influences the time scale over which the evaporationdriven variation of SPF occurs. It happens over several hours for slowly-evaporating liquids such as PG but takes minutes for faster evaporating solvents like water or decane. Secondly, the solubilities of the UV filters used (relative to their initial concentrations) controls the time at which precipitation and resultant loss of SPF occurs. Finally, we have shown that the film wetting/dewetting properties can be strongly influenced by additives such as particles or polymers. However, it is important to note that further work needs to be done using substrate surfaces which better mimic the surface of skin in terms of wettability^{27,28} and roughness. In addition, further work is required to examine the evaporation behaviour of more complex (but commonly used) types of sunscreen formulations, particularly emulsions. We are currently investigating these two avenues of further research.

ASSOCIATED CONTENT

Figure S1. Reference erythema action spectrum $E(\lambda)$ (upper plot) and spectral irradiance of terrestrial sunlight $S(\lambda)$ corresponding to midday midsummer sunlight for latitude 40°N, solar zenith angle 20° and ozone layer thickness equal to 0.305 cm. (From: B.L. Diffey and J. Robson, J. Soc. Cosmet. Chem., 1989, **40**, 127-133.)

- Figure S2. Molecular structures of the UV filters.
- Figure S3. Spectra of the UV filters in PG.
- Figure S4. Evolution of film mass, total film area and average film thickness and fraction with evaporation time for a film of pure PG spread on quartz.
- Figure S5. Overall appearance and representative optical micrograph of the film residue following 690 minutes of evaporation of 8 mM AVB in PG on a quartz plate. The film region in the micrograph corresponds to the centre of the illuminated area indicated by the red rectangle.
- Figure S6. Variation of film mass, area and average thickness during evaporation of a film of 8 mM AVB in decane spread on quartz. The fraction of illuminated area covered by film (A_f) was equal to 1 throughout the evaporation.
- Figure S7. Upper: Spectra of film of 8 mM AVB in decane spread on quartz at the start and end of complete evaporation. Lower: optical micrograph of the film residue within the illuminated area after 20 minutes evaporation.

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REFERENCES

- 1. Diffey, B.L.; Robson, J. A New Substrate to Measure Sunscreen Protection Factors throughout the Ultraviolet Spectrum. *J. Soc. Cosmet. Chem.*, **1989**, *40*, 127-133.
- Diffey, B.L.; Tanner, P.R.; Matts, P.J.; Nash, F.J. In vitro Assessment of the Broadspectrum Ultraviolet Protection of Sunscreen Products. *J. Amer. Acad. Dermatol.*, 2000, 43, 1024-1035.
- 3. Osterwalder, U.; Herzog, B. Sun Protection Factors: World Wide Confusion. *Brit. J. Dermatol.* **2009**, *161*, 13-24.
- 4. Schmalwieser A.W.; Wallisch, S.; Diffey, B. A Library of Action Spectra for Erythema and Pigmentation. *Photochem. Photobiol. Sci.*, **2012**, *11*, 251-268.
- 5. Moyal, D.; Alard, V.; Bertin, C.; Boyer, F.; Brown, M.W.; Kolbe, L.; Matts, P.; Pissavini, M. The Revised COLIPA in vitro UVA Method. *Int. J. Cosmetic Sci.*, **2013**, *35*, 35-40.
- 6. Herzog, B.; Wehrle, M.; Quass, K. Photostability of UV Absorber Systems in Sunscreens. *Photochem. Photobiol.*, **2009**, *85*, 869-878.
- 7. Stanfield, J.; Osterwalder, U.; Herzog, B. In vitro Measurements of Sunscreen Protection. *Photochem. Photobiol. Sci.*, **2010**, *9*, 489-494.
- 8. Shaath, N.A. Ultraviolet Filters. *Photochem. Photobiol. Sci.*, **2010**, *9*, 464-469.
- 9. Kockler, J.; Oelgemoller, M.; Robertson, S.; Glass, B.D. Photostability of Sunscreens. *J. Photochem. Photobiol. C*, **2012**, *13*, 91-110.
- 10. U.S. Department of Health and Human Services, Food and Drug Administration, Center for Drug Evaluation and Research (CDER), Guidance for Industry. Labeling and Effectiveness Testing: Sunscreen Drug Products for Over-The-Counter Human Use — Small Entity Compliance Guide, December **2012**.
- 11. Beyer, D.M.; Faurschou, A.; Philipsen, P.A.; Hoedersdal, M.; Wulf, H.C. Sun Protection Factor Persistence on Human Skin during a Day without Physical Activity or Ultraviolet Exposure. *Photodermatol. Photoimmunol & Photomed.*, **2010**, *26*, 22-27.
- 12. Beverley, K.J.; Clint, J.H.; Fletcher, P.D.I. Evaporation Rates of Pure Liquids Measured using a Gravimetric Technique. *Phys. Chem. Chem. Phys.* **1999**, *1*, 149-153.
- 13. George, J.; Sastry, N.V. Densities, Dynamic Viscosities, Speeds of Sound, and Relative Permittivities for Aater + Alkanediols (propane-1,2- and -1,3-diol and butane-1,2-, -1,3-, -1,4-, and -2,3-diol) at Different Temperatures. *J. Chem. Eng. Data*, **2003**, *48*, 1529-1539.
- Ferrero, L.; Pissavini, M.; Doucet, O. How a Calculated Model of Sunscreen Film Geometry can Explain In vitro and In vivo SPF Variation. *Photochm. Photobiol Sci.*, 2010, 9, 540-551.
- 15. Herzog, B.; Osterwalder, U. Simulation of Sunscreen Performance. *Pure & Appl. Chem.*, **2015**, 87, 937-951.
- 16. The peak (Naperian) absorption coefficients of solid films of organic UV/visible dyes used in solar cell applications are in the range 2-3 x 10^5 cm⁻¹. (From: Hoppe, H.; Sariciftci, N.S. Organic Solar Cells: an Overview. *J. Mater. Res.* **2004**, *19* 1924-1945.) These values are of similar magnitude to the values calculated for the UV filters used here. For AVB as an example, the concentration of AVB in the solid is approx. 3 M and its peak molar extinction coefficient at 361 nm is 3.4×10^4 M⁻¹ cm⁻¹. Hence, if the molar extinction remains the same in solution and solid state, the peak (Naperian) absorption coefficient is $2.3 \times 3.4 \times 10^4 \times 3 = 2.3 \times 10^5$ cm⁻¹. This is similar in magnitude to the values measured for organic solar cell films.

- 17. Stull, D.R. Vapor Pressures of Pure Substances: Organic Compounds. *Ind. Eng. Chem.*, **1947**, *39*, 517-540.
- 18. Craster, R.V.; Matar, O.K. Dynamics and Stability of Thin Liquid Films. *Rev. Mod. Phys.*, **2009**, *81*, 1131-1198.
- 19. Deegan, R.D.; Bakajin, O.; Dupont, T.F.; Huber, G.; Nagel, S.R.; Witten, T.A. Capillary Flow as Cause of Ring Stains from Dried Liquid Drops. *Nature*, **1997**, *389*, 827-829.
- 20. Bhardwaj, R.; Fang, X.; Somasundaran, P.; Attinger, D. Self-assembly of Colloidal Particles from Evaporating Droplets: Role of DLVO Interactions and Proposition of a Phase Diagram. *Langmuir*, **2010**, *26*, 7833-7842.
- 21. Anyfantakis, M.; Baigl, D. Manipulating the Coffee-ring Effects: Interactions at Work. *ChemPhysChem.*, **2015**, *16*, 2726-2734.
- 22. Anyfantakis, M.; Geng, Z.; Morel, M.; Rudiuk, S.; Baigl, D. Modulation of the Coffee-ring effect in Particle/Surfactant Mixtures: the Importance of Particle-interface Interactions. *Langmuir*, **2015**, *31*, 4113-4120.
- 23. Wertz, P.W. The Nature of the Epidermal Barrier: Biochemical Aspects. *Adv. Drug Delivery Rev.*, **1996**, *18*, 283-294.
- 24. Wertz, P.W.; van den Bergh, B. The Physical, Chemical and Functional Properties of Lipids in the Skin and other Biological Barriers. *Chem. Phys. Lipids*, **1998**, *91*, 85-96.
- 25. Madison, K.C. Barrier Function of the Skin: "la raison d'etre" of the Epidermis. *J. Inv. Dermatol.*, **2003**, *121*, 231-241.
- 26. Boncheva, M. The Physical Chemistry of the Stratum Corneum Lipids. *Int. J. Cosmetic Sci.*, **2014**, *36*, 505-515.
- 27. Mavon, A.; Redoules, D.; Humbert, P.; Agache, P.; Gall, Y. Changes in Sebum Levels and Skin Surface Free Energy Components following Skin Surface Washing. *Colloids Surf. B*, **1998**, *10*, 243–250.
- 28. Lerebour, G.; Cupferman, S.; Cohen, C.; Bellon-Fontaine, M.N. Comparison of Surface Free Energy between Reconstructed Human Epidermis and In situ Human Skin. *Skin Res. Technol.*, **2000**, *6*, 245–249.

	Solubility data at 32°C		
UV absorbers	Solvent	Solubility/mM	Solubility/wt.%
AVB	PG	14	0.42
AVB	water	0.0003	0.00009
AVB	decane	54	2.29
DHHB	PG	28	1.07
MC	PG	435	10.4
MC	water	0.15	0.0037

Table 1.Solubilities of the UV filters in PG and other solvents at 32°C.

Figure 1. Evolution of the total area of a liquid film of 8.00 mM AVB in PG on a quartz plate substrate with evaporation time. Each time step image includes a ruler with a mm scale on the left hand side (for scale) and the quartz slide with the liquid film on the right hand side. The red rectangle superimposed on each quartz slide image shows the area illuminated in the absorbance measurements. Only images covering the first 300 minutes of evaporation are shown here; similar images were obtained up to 690 minutes.



Figure 2. Evolution of film mass, total film area, average film thickness and fraction of illuminated area covered by the film with evaporation time for a film of 8 mM AVB in PG. In the film mass plot, the dashed lines indicate film mass m^{*} and time t^{*} at the point at which the AVB concentration equals its solubility.



Figure 3. Measured (upper plot) and calculated (middle plot) evolution of the film spectrum with evaporation time for a film of 8 mM AVB in PG. The lower plot compares the measured and calculated peak absorbance variation with evaporation time.



Figure 4. Measured and calculated variation of the SPF (290-400 nm wavelength range) with evaporation time for films of different UV filters in PG spread on quartz.



Figure 5. Variation of film mass, total area and average thickness (each normalised with respect to the time zero values) for films containing 8.00 mM AVB in PG on quartz with and without added particles. In the mass plot, the horizontal dashed line shows the normalised film mass at which precipitation of AVB is expected.



Figure 6. Upper plot: Evolution of the measured spectrum (versus air reference) of the film containing 8 mM AVB plus 0.1 wt% TiO₂ particles in PG with evaporation time. For this evaporating film, the illuminated area remains fully covered by the film during evaporation and precipitation of the AVB occurs after approximately 100 minutes evaporation. The dashed line shows the spectrum (versus air reference) of a PG film of the same initial thickness containing only 0.1 wt% TiO₂. Middle plot: Calculated spectra for this film. Lower plot: Comparison of measured and calculated SPF versus evaporation time.



Figure 7. Variation of mass, area and average thickness for films containing 8 mM AVB in 100 wt% PG (denoted "zero polymer"), 7.6 mM AVB in 1 wt% p-DADMAC, 4 wt% water and 95 wt% PG (denoted "1 wt%") and 6 mM AVB in 5 wt% p-DADMAC, 20 wt% water and 75 wt% PG (denoted "5 wt%"). The horizontal and vertical lines indicate the estimated points at which AVB will precipitate.



Figure 8. Upper plot: Evolution of the measured spectrum (versus air reference) with evaporation time of a film containing 7.6 mM AVB in 1 wt% p-DADMAC, 4 wt% water and 95 wt% PG. For this film, the illuminated area fraction $A_f = 1$ for 200 minutes before decreasing to zero by 300 minutes. The onset of AVB precipitation occurs at approximately 100 minutes. Middle plot: Calculated spectra. Lower plot: Comparison of measured and calculated SPF versus evaporation time.



Figure 9. Variation of film mass, area and average thickness for films of 8 mM AVB in PG spread by gentle finger "smearing" onto vitro skin. In the mass plot, the dashed lines indicate the point at which the AVB precipitates.



Figure 10. Upper plot: Evolution of the measured spectrum (versus air reference) with evaporation time of a film containing 8 mM AVB in PG on vitro skin. The dashed and dotted lines show the separately measured spectra (versus air reference) of wet and dry vitro skin. For this film, the illuminated area fraction $A_f = 1$ and the onset of AVB precipitation occurs at 51 minutes. Middle plot: Calculated spectra. Lower plot: Comparison of measured and calculated film SPF versus evaporation time.



Figure 11. Variation of film mass, area, average thickness and A_f for films of 8 mM AVB in PG spread onto the keratin/lipid film supported on a quartz plate. In the mass plot, the dashed lines indicate the point at which the AVB precipitates.



Figure 12. Upper plot: Evolution of the measured spectrum (versus air reference) with evaporation time of a film containing 8 mM AVB in PG on a keratin/lipid substrate. The dashed line shows the separately measured spectra (versus air reference) of the keratin/lipid substrate. The absorbance scale is limited to 3.3 as measured values greater than this are unreliable due to the detector sensitivity. For this film, the onset of AVB precipitation occurs at 121 minutes. Middle plot: Calculated spectra. Lower plot: Comparison of measured and calculated film SPF versus evaporation time.



Table of Contents/Abstract Graphic



Residue after evaporation of a decane/AVB sunscreen film on a quartz surface.