

# Effect of Film Irregularities on Sunscreen Efficacy

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**Abstract** □ The effect of distortion of a uniform film on its opacity has been calculated for a simple step film model. Nonuniform distribution of sunscreen films on skin and of the absorber within the film would account for large discrepancies between naively predicted efficacy and that observed clinically.

**Keyphrases** □ Film irregularities—effect on sunscreen efficacy, opacity □ Sunscreens—effect of film irregularities, opacity

Cosmetic sunscreen products are effective in protecting the user from sunburn by absorbing injurious UV radiation, but it is well known that their performance is not nearly as good as would be predicted from the absorption spectra of their active ingredients. Spectra of strongly absorbing materials are usually measured at weight concentrations of ~0.001% in transparent solvents like water or ethanol in a cuvette with an optical path length of 1 cm. A sunscreen on the skin contains several percent of the absorber in a film with an average thickness of ~0.002 cm. The fact that such lengthy extrapolation of spectrophotometric data leads to predictions of efficacy far greater than those obtained in clinical measurements is occasionally ascribed to misapplication or even to a failure of the physical laws underlying spectrophotometry. More often it is ascribed to vehicle effects and to skin topography.

In this paper the average opacity of a simple model film is calculated as a function of its departure from uniform thickness and chemical homogeneity. It is suggested that plausible irregularities can account for discrepancies of many orders of magnitude between naively predicted and observed sunscreen efficacy.

## BACKGROUND

The pharmacological measure of sunscreen efficacy, the sun protection factor (SPF), is the factor by which the product allows the time of exposure to sunlight to be increased before a given degree of sunburn occurs. For example, someone who suffers a slight sunburn after 20-min exposure could remain in sunlight of the same intensity for 40 min wearing an ointment with an SPF of 2 before suffering the same slight burn.

The equivalent physical definition is:

$$\text{SPF} = \frac{\int (S \times A) \cdot d\lambda}{\int (S \times A \times T) \cdot d\lambda} \quad (\text{Eq. 1})$$

where  $S(\lambda)$  is the intensity of sunlight under standardized conditions of altitude, latitude, time of day, etc. (usually replaced in clinical practice with the more accessible and intense emission spectrum of a solar simulator);  $A(\lambda)$

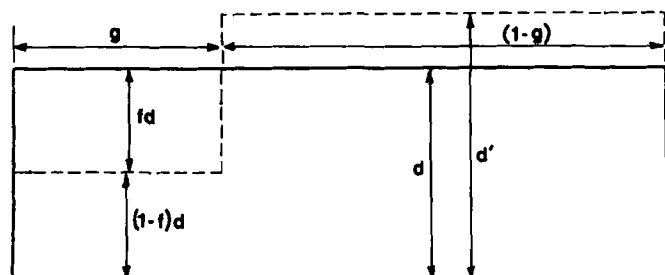


Figure 1—Step film geometry: cross section of a rectangular slab of unit width.

is the skin sensitivity or action spectrum, the reciprocal of the energy per unit area of exposed skin producing a standard degree of burn (usually the minimum perceptible erythema); and  $T(\lambda)$  is the fractional transmission of the sunscreen.

In both integrals the lower limit is ~290 nm because the function,  $S(\lambda)$ , is negligibly small in the standard solar spectrum at lower wavelengths. The upper limit is the wavelength above which the action spectrum,  $A(\lambda)$ , is so small that the product  $S \times A$  is negligible. From our own experience with sunscreens, we take this limit as ~350 nm but its exact location is immaterial in the discussion that follows.

Since the dimensions of  $S$  in Eq. 1 are energy  $\times$  area<sup>-1</sup>  $\times$  time<sup>-1</sup> and those of  $A$  are erythema  $\times$  energy<sup>-1</sup>  $\times$  area, and since  $T$  is the dimensionless ratio of transmitted to incident intensity, both the numerator and denominator have "dimensions" of erythema per unit of time. For a given degree of erythema, this reduces to the time ratio of the pharmacological definition.

For convenience, we define a protection factor for monochromatic radiation as:

$$\begin{aligned} \text{MPF}(\lambda) &= \frac{S(\lambda) \times A(\lambda)}{S(\lambda) \times A(\lambda) \times T(\lambda)} \\ &= 1/T(\lambda) = P(\lambda) \end{aligned} \quad (\text{Eq. 2})$$

where  $P(\lambda)$  is the opacity of the film. This definition is used rather than the more cumbersome Eq. 1 in the discussion that follows. For the most part, the notation of wavelength dependence is dropped, but we emphasize that MPF is a strong function of the wavelength and that it is not simply related to the SPF except in special cases (e.g., where the transmission is a constant, independent of wavelength, as might be true of a dispersion of an opaque, reflective solid like aluminum powder; in this case  $\text{SPF} = P$ ). The extension of conclusions regarding the effect of sunscreen film irregularities on MPF to that on SPF is discussed below where appropriate.

The opacity of a cosmetic sunscreen is given, in the first approximation, by the absorption spectrum of the active ingredient as measured in dilute solution in a transparent solvent expressed according to the Beer-Lambert law:

$$P(\lambda) = \left( \frac{I_0}{I} \right)_\lambda = 10^{k(\lambda)Cd} \quad (\text{Eq. 3})$$

where  $I_0$  and  $I$  are the intensities of incident and transmitted light,  $k(\lambda)$  is the absorptivity in units corresponding to those of the concentration,  $C$ , and the path length  $d$ .

Although the concentrations and path lengths in applied sunscreens differ by several orders of magnitude from those used in spectrophotometry, there are no obvious grounds for suspecting that the opacities will not be related according to Eq. 3. There are no known exceptions to Lambert's law relating opacity to path length through homogeneous bodies, and marked deviations from Beer's law (the concentration effect) are usually attributable to gross physicochemical departures from simple molecular solutions, such as ionization or complexation, which are not likely to occur with the absorbers used in sunscreens at either very high or very low concentrations. Nevertheless, sunscreen efficacy as predicted from spectrophotometry using Eq. 1, assuming a film thickness corresponding to the application level, is usually higher, sometimes by several orders of magnitude, than the SPF value measured clinically. The following calculations show that seemingly plausible deviations from uniformity of film thickness or of distribution of the absorber can account for these discrepancies.

## DISCUSSION

**Opacity of Step Films**—Figure 1 shows the cross section of a uniform, homogeneous film of thickness  $d$  of a solution of concentration  $C$  of an absorbing solute whose absorptivity in the transparent medium is  $k$ . The broken lines show what we call a step film, produced by removing a fraction ( $f$ ) of the uniform film over a fraction ( $g$ ) of its area and redepositing it uniformly over the remaining area. The average intensity of light transmitted by the step film is:

$$I_s = gI_1 + (1-g)I_2 \quad (\text{Eq. 4})$$

**Table I—MPF (Opacity) of Step Films Derived from a Uniform Film of Opacity 10**

$f^a$	Fraction of Area Depleted, $g$					
	0.1	0.3	0.5	0.7	0.9	1.0
0.1	9.968	9.882	9.740	9.464	8.728	7.943
0.3	9.680	8.934	8.011	7.267	5.568	5.011
0.5	9.023	7.267	5.749	4.476	3.513	3.162
0.7	7.976	5.392	3.837	2.844	2.216	1.995
0.9	6.626	3.743	2.478	1.797	1.398	1.258
1.0	5.893	3.066	1.980	1.428	1.111	1.000

<sup>a</sup> Depth fraction.

**Table II—MPF (Opacity) of Step Films Derived From a Uniform Film of Opacity 1000**

$f^a$	Fraction of Area Depleted, $g$					
	0.1	0.3	0.5	0.7	0.9	1.0
0.1	968.0	893.4	801.1	686.5	556.8	501.1
0.3	662.5	374.3	247.8	179.7	139.8	125.8
0.5	264.8	103.6	63.18	45.17	35.13	31.62
0.7	76.24	26.41	15.88	11.34	8.825	7.943
0.9	19.77	6.648	3.990	2.850	2.216	1.995
1.0	9.958	3.332	1.999	1.428	1.111	1.000

<sup>a</sup> Depth fraction.

**Table III—MPF (Opacity) of Step Films Derived From a Uniform Film of Opacity 1,000,000<sup>a</sup>**

$f^b$	Fraction of Area Depleted, $g$					
	0.1	0.3	0.5	0.7	0.9	1.0
0.1	845,676	632,295	472,560	357,309	279,098	251,188
0.3	145,403	52,501	31,689	22,641	17,609	15,848
0.5	9,958	3,332	2,000	1,428	1,111	1,000
0.7	630.8	210.3	126.1	90.13	70.10	63.09
0.9	39.81	13.27	7.962	5.687	4.423	3.981
1.0	10.00	3.333	2.000	1.428	1.111	1.000

<sup>a</sup> A 20- $\mu$ m thick film of an absorber solution whose molar extinction coefficient is 30,000 L · mol<sup>-1</sup> · cm<sup>-1</sup> reaches this opacity at a concentration of 0.1 mol/L; for octyl dimethyl *p*-aminobenzoate (Escalol 507 brand of padimate O) this corresponds to a weight concentration ~2.8%. <sup>b</sup> Depth fraction.

where  $I_1$  and  $I_2$  are the intensities of light transmitted by the depleted and augmented areas. These are given by the Beer-Lambert law as:

$$I_1 = I_0 \cdot \exp_{10} [-kCd(1 - f)] \quad (\text{Eq. 5})$$

$$I_2 = I_0 \cdot \exp_{10} \left[ -kCd \left( \frac{fg}{1 - g} + 1 \right) \right] \quad (\text{Eq. 6})$$

where  $I_0$  is the intensity of the light normally incident on both areas. In Eqs. 5 and 6 the expressions in parentheses are the factors by which the thickness of the film is changed; the expression in Eq. 6 can be derived by equating the volumes removed,  $fd \times ga$ , and redeposited,  $(d' - d) \times (1 - g)a$ , where  $a$  is the area of the film. The average opacity of the step film,  $P_s$ , as a function of  $f$  and  $g$ , is given by combining Eqs. 3-6:

$$P_s = P_c \left[ g \cdot \exp_{10} (kCdf) + (1 - g) \cdot \exp_{10} \left( \frac{-kCdfg}{1 - g} \right) \right]^{-1} \quad (\text{Eq. 7})$$

where  $P_c$  is the opacity of the uniform parent film.

Tables I-III give the calculated opacities of the step films derived from uniform films of opacities 10, 1000, and 1,000,000. The most obvious feature of these tables is that all the calculated average opacities are less than that of the uniform parent film. It might have been expected that for some range of values of the distortion factors  $f$  and  $g$ , the increase in opacity of the area on which the film thickness is increased would more than offset the loss of opacity of the depleted area. This is not so in any case: the distorted film is always less opaque.

Another disturbing feature of the behavior of the model is the dependence of the relative loss in opacity on the opacity of the parent film: for any set of values of  $f$  and  $g$ , the greater the opacity of the parent film, the greater the relative decrease in opacity. For example, at  $f = g = 0.9$  (removal of 90% of the film over 90% of the area) uniform films of opacities 10, 1000, and 1,000,000 are degraded to step films with respective opacities of 14%, 0.22%, and 0.00044% of those of the parent films.

The same behavior can be viewed in terms of the absorption spectrum of the active ingredient. Note that according to Eq. 7 the ratio of step film opacity,  $P_s$ , to that of the uniform film,  $P_c$ , depends on the wavelength, because for a given film distortion (fixed values of  $f$  and  $g$ ) the ratio is the reciprocal of the sum of two terms which vary exponentially with  $k$ , the absorptivity. In this view, film distortion has its greatest relative effect at the absorption

maxima where the absorber is expected to be most effective; distortion blunts the spectrum of the absorber.

In Tables I-III the bottom row, where  $f = 1.0$ , shows the result of completely removing part of the film. Even if only 10% of the area is so depleted ( $g = 0.1$ ), the step film opacity drops to  $\leq 10$  as would be expected from ordinary experience: if the parent film were a metallic foil of virtually infinite opacity, a few pin pricks would degrade it into an imperfect screen transmitting a fraction of incident light equal to the areal fraction of the holes, as is the case, to four significant figures in the bottom row of Table III.

The right-hand column of each table illustrates Lambert's Law relating opacity to thickness over the entire area of the film ( $g = 1.0$ ). Removal of 90% of the film ( $f = 0.9$ ) reduces the opacity to the tenth root of that of the parent film—from 1,000,000 to 4.0 for example, as seen in Table III.

If the geometry of sunscreens on human skin corresponds to large values of  $f$  and moderate-to-large values of  $g$ , then the values of MPF( $\lambda$ ) predicted according to Eq. 7, and, by inference, of SPF itself, will be very modest compared with those predicted on the assumption of a uniform film.

The dependence of step film opacity on absorber concentration as given by Eq. 7 is illustrated in Fig. 2 where the opacity of the uniform film,  $P_c$  is also shown for comparison. The opacities for a given combination of  $f$  and  $g$  are plotted on semilogarithmic graphs against the log<sub>10</sub> of the opacity of the uniform parent film, which, according to Eq. 3, is proportional to the concentration  $C$  for fixed  $k$  and  $d$ . In all cases, the curve is more or less concave down, near the origin ( $C = 0, P = 1$ ) and then becomes nearly log-linear at high concentration. The latter occurs when the second term in Eq. 7 becomes negligible compared with the first (when the transmittance of the augmented area is negligible compared with that of the depleted area):

$$\log P_s = \log P_c - \log g - kCdf \quad (\text{Eq. 8})$$

or, since  $\log P_c = kCd$ :

$$\log P_s = (1 - f)kCd - \log g \quad (\text{Eq. 9})$$

which corresponds to a straight line with the slope reduced by a factor of  $1 - f$  relative to that of  $\log P_c$  against  $C$ , and with an intercept of  $-\log g$  (as shown by extrapolation in a few cases).

For  $f = 0.9$ ,  $P_s$  or MPF appears to increase linearly with absorber concentration over the range covered in Fig. 2C, as can be seen from the linear plots

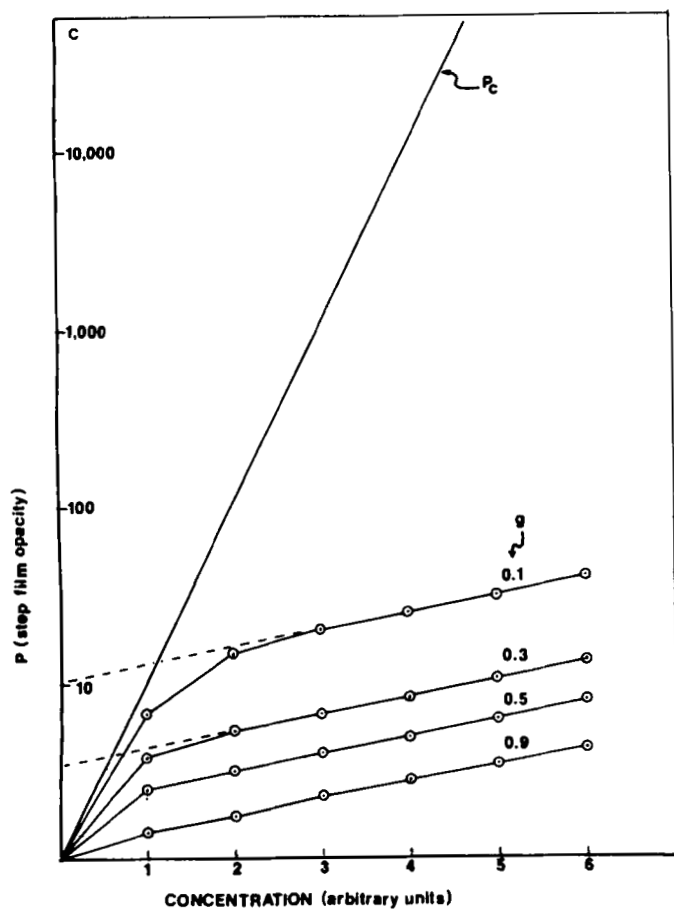
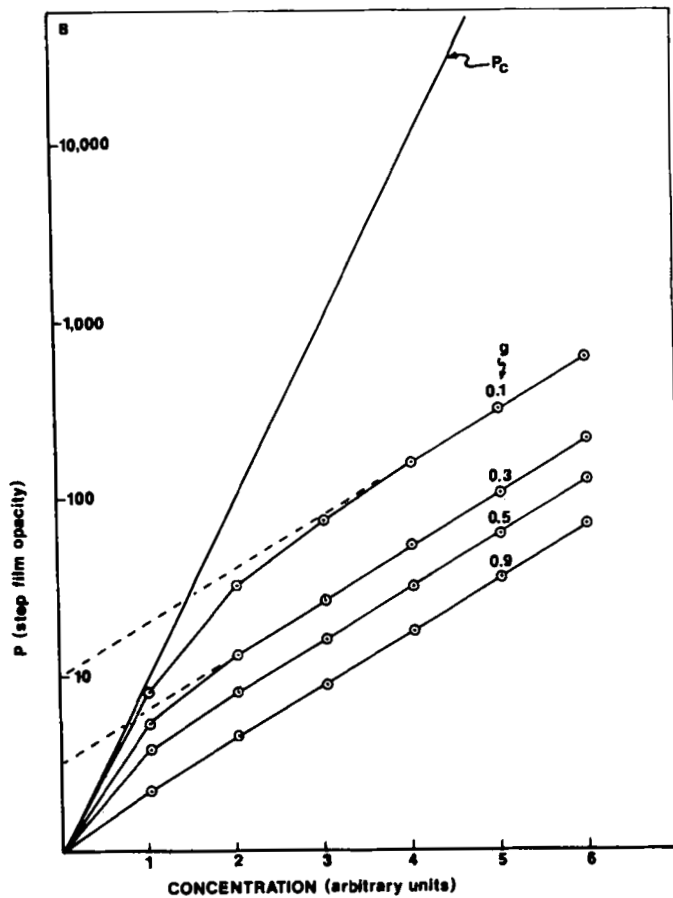
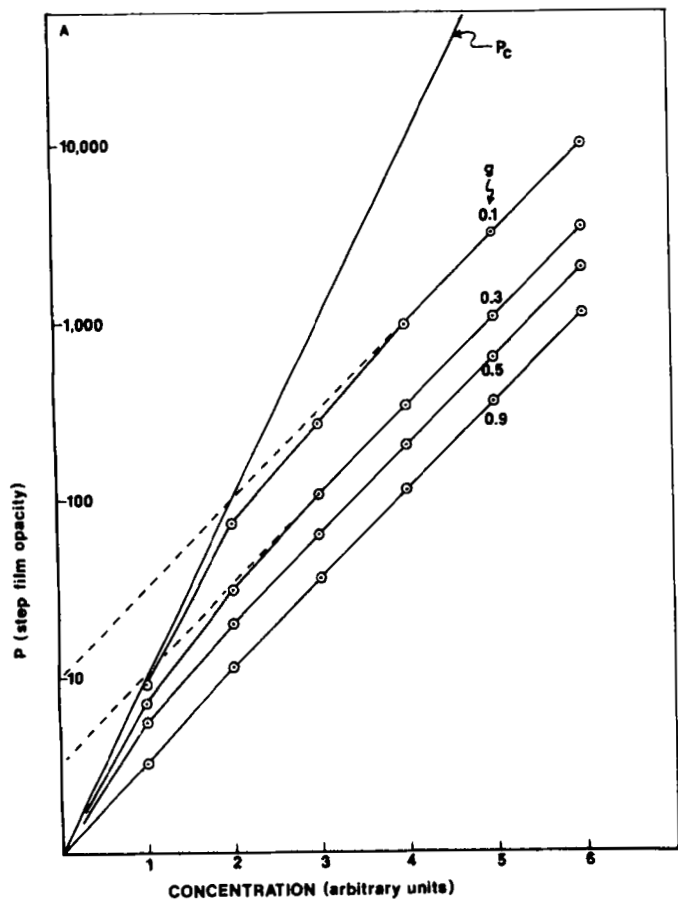


Figure 2—Opacity of step films with depth fractions of (A),  $f = 0.5$  (B),  $f = 0.7$ , and (C)  $f = 0.9$ .

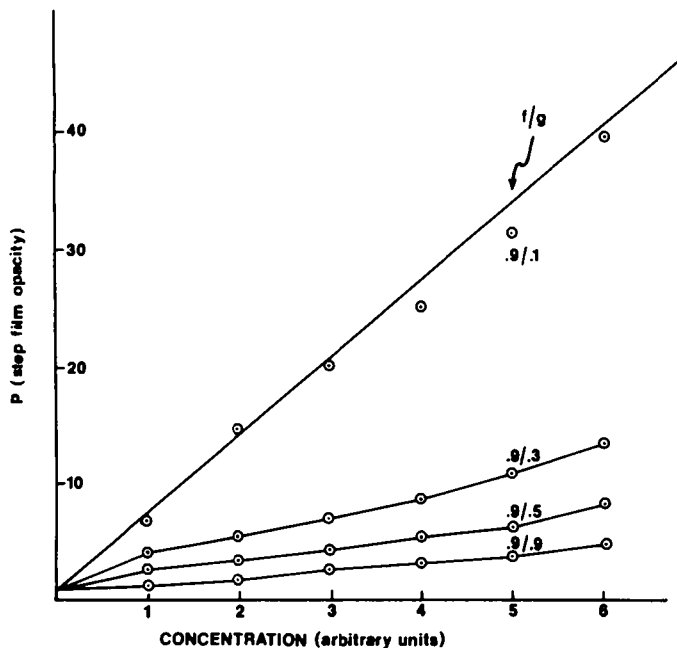


Figure 3—Opacity of step films: linear plots against absorber concentration in arbitrary units.

in Fig. 3. For  $f = 0.7$  and  $0.5$ , similar plots are distinctly concave up. We take this as an indication that high values of  $f$  apply to sunscreens on skin because in our clinical measurements SPF values increase roughly in proportion to absorber concentration rather than exponentially, as might be expected from Eqs. 2 and 3.

**Opacity of Nonhomogeneous Films**—The effect of nonuniform distribution of the absorber on the opacity of a film of uniform thickness can be treated in the same fashion as that of nonuniform thickness of a homogeneous film. The vertical dimension in Fig. 1 can be taken as a measure of absorber concentration by replacing  $d$  and  $d'$  with  $C$  and  $C'$ , and deriving Eqs. 5 and 6 from conservation of the mass of absorber rather than film volume. Equation 7 follows identically; it is now immaterial whether the parameter  $f$  refers to the extent of transfer of the bulk of the film or to relocation of the absorber (except that the result of bulk transfer follows with certainty from Lambert's law while that of relocation of the absorber assumes that Beer's law applies with the same absorptivity,  $k$ , in both parts of the film; the latter is certainly not exact for some kinds of nonhomogeneity, such as recrystallization of the absorber).

Figures 2 and 3 can now be interpreted in terms of the transposed variables by labeling the abscissas as "thickness" rather than "concentration." They then show that nonhomogeneity frustrates the response of opacity to thickness (or product usage level) just as irregularities in thickness frustrates response to absorber concentration.

**Origins of Irregularities**—The particular geometry of the step film chosen in Fig. 1 does not enter into the derivation of average opacity. The depleted area can be broken up into any number of elements of arbitrary size and shape as seen from above (from the origin of the incident beam); only its fraction,  $g$ , enters the calculation. In fact, it is tacitly assumed in reference to sunscreens that the irregularities of thickness or concentration are distributed on a scale

of distances fine enough that the resulting pattern of burned and protected skin will be averaged when subjectively scoring the degree of erythema. The only evident physical limitation is that the irregularities be large compared with the wavelength of UV light (of the order of  $1 \mu\text{m}$ ).

The topography of human skin is an obvious source of variation in the thickness of an applied film. Any fluid which wets the skin tends to accumulate in the sulci, the furrows which unfold to spare the inelastic epidermis from tensile stress when body movements, such as making a fist, increase the contour length along the surface. Heavily dyed mineral oil moderately applied to the skin discloses a map of the sulci; very little color is seen on the plateaus (the roughly triangular areas bounded by sulci). This pattern develops spontaneously on relaxed skin as soon as rubbing is stopped, partly because surface tension reduces the pressure of the fluid under the concave surfaces over unfilled sulci and pumps it away from the plateaus (except where it wicks up into a cone at the base of each hair). Dyed petrolatum gives somewhat more uniform coverage showing the importance of viscosity in retarding the effects of capillary action. With fluid mineral oil the plateaus are well covered only at repugnantly high levels of application.

This effect could be quantified by measurements of the cross-sectional area of the sulci and the length of sulci per unit area of skin on surface replicas (like those used in scanning electron microscopic studies of skin). The product of these two would give the sulcus volume per unit area of skin, and this would indicate the fraction of the residue of a sunscreen (or any other applied fluid) "lost" by this mechanism (which might vary from subject to subject and on different parts of the body); but, even in the absence of such data it seems evident from observation of dyed mineral oil on skin that the assumption of a uniform film thickness at tolerable application levels is a poor one.

Nonhomogeneity of the sunscreen residue on the skin is another likely cause of the disappointing performance of commercial products. When a typical sunscreen lotion is rubbed out on a microscope slide, dried at room humidity, and examined at moderate magnification, it has the irregular appearance of an ordinary emulsion residue. At least two phases are usually present: one probably derived from the water phase and another from the oil phase (as can be seen when an unrubbed, thin film is examined as it dries). Except in the very unlikely event that the UV absorber partitions between these residual phases at equal opacity, the resulting film must be optically more or less similar to a slice of Swiss cheese. If two or more absorbers are present, the array of possible distortions becomes more complex, especially if the absorbers were selected to be complementary on the basis of their dilute solution spectra, but the likelihood of a near optimal distribution seems remote.

A solution of *p*-aminobenzoic acid (PABA) in alcohol is an extreme case of poor absorber distribution in the residue. On glass the residue is a crust of small well-formed crystals with a large areal fraction of voids. On skin it is a loosely held, chalky-looking deposit which can be resolved into individual crystals with a magnifier. In either case it is obvious that even if the crystals are infinitely opaque, the residue can have an opacity no greater than the reciprocal of the areal fraction of voids (as in the bottom row of Table III). This situation is probably not altered much when a glycol or an oil is added to mask the chalkiness. Since neither of these fluids is a good PABA solvent, they would be almost as transparent to harmful radiation as the voids they fill.

## CONCLUSION

The ideal sunscreen leaves a chemically and physically uniform residue on the skin. The physical form of the product as applied is not important. It may be a simple solution or a coarse emulsion but the residue after casual application should be a single continuous phase in which the absorbers are in true solution. It should tend to remain well spread on the plateaus of the skin and not accumulate in the sulci.