DESIGN OF COSMETIC SUN SCREENS

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WITHIN THE last two decades our knowledge of ultraviolet screens has made it possible to offer to the public suntan preparations which will effectively prevent painful sunburn and at the same time permit adequate tanning. Any material exposed to radiant energy will absorb, reflect or transmit that energy to a varying degree which depends upon both the nature of the incident energy and the nature of the material. It is the function of the cosmetic sun screen to absorb as completely as possible the sun's erythematogenic ultraviolet radiation while it transmits a maximum of all the other wavelengths of the sun's radiation. Very few chemicals come close to meeting this ideal situation.

Radiant energy is classified in a broad electromagnetic spectrum. Perhaps the simplest way of considering this energy is that in the absence

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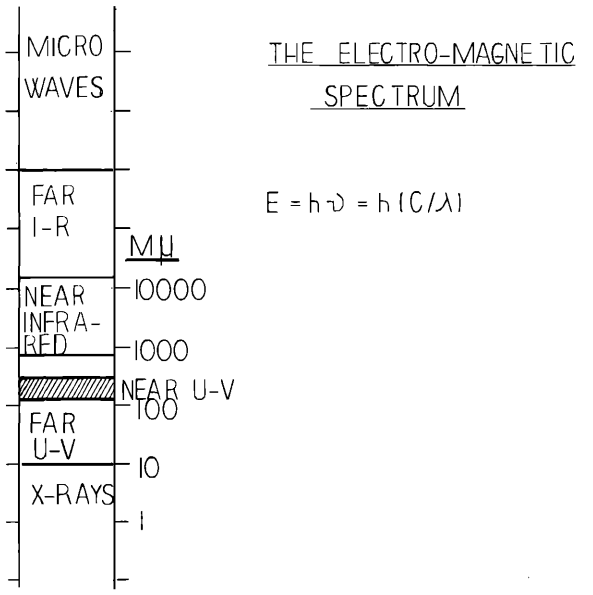
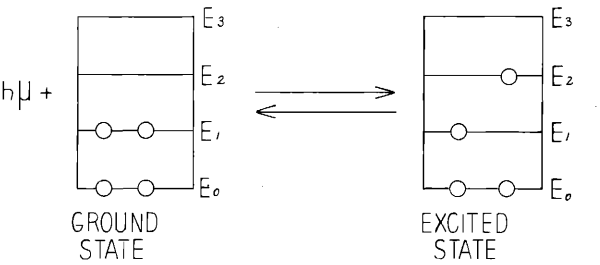


of matter it is propagated as a wave form. But when it is absorbed it is in the form of discrete packets—photons—whose energy is a function of the wavelength of the wave form. The relationship between energy and wavelength is expressed by the general equation

$$E = h\nu = h(c/\lambda) \tag{1}$$

where
E = energy in ergs
h = Plank's constant, 6.6242×10^{-27} erg-second
ν = frequency, per second
λ = wavelength, centimeters, and
c = velocity of electromagnetic radiation, 3×10^{10} cm./sec.



PHOTON-ATOM INTERACTION

When atoms are excited by heat or electrical energy their electrons are raised through one or more steps of a possible series of energy levels, E_1, E_2, E_3, etc., which may be stable, or may revert to a lower level, or even to the ground state with liberation of the absorbed energy. For every drop in energy level, the difference in the energy content of the atom is in the form of monochromatic radiation of frequency such that, for a drop from E_2 to E_1

$$\Delta E = E_2 - E_1 = h\nu \tag{2}$$

This radiation forms the *emission spectrum* of the atoms characteristically shown in an electric arc or in a flame test.

When light passes through an absorbing medium, the reverse process takes place: the energy is absorbed and results in raising the energy levels of the electrons in the absorbing medium. This absorption of specific frequencies causes gaps to appear in the spectrum of the original light source which are shown as dark absorption lines at those wavelengths which are absorbed:

$$\Delta E = E_1 - E_2 = h(c/\lambda) \tag{3}$$

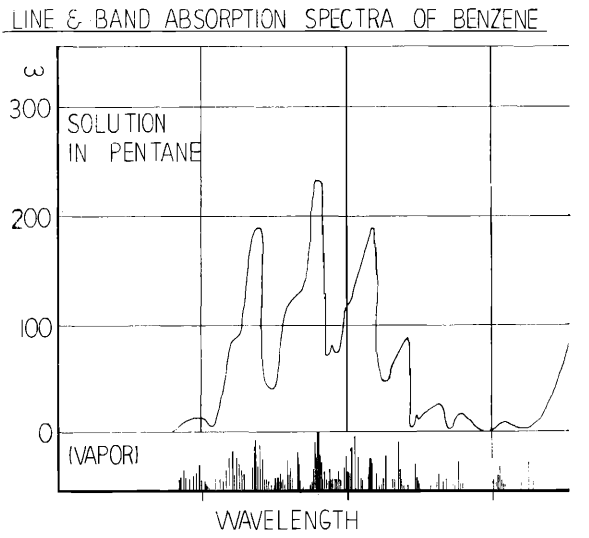
The absorption of energy by molecules is more complex than atomic absorption, especially if the molecules are in the condensed liquid or solid states, or in solution. The total energy content of a molecule is made up of electronic bonding energy and kinetic energy. The latter has both vibrational and rotational components:

$$E = E_{\text{bonding}} + (E_{\text{vibrational}} + E_{\text{rotational}}) \quad (4)$$

$E_{TOTAL} = E_{BONDING} + (E_{VIBRATIONAL} + E_{ROTATIONAL})$

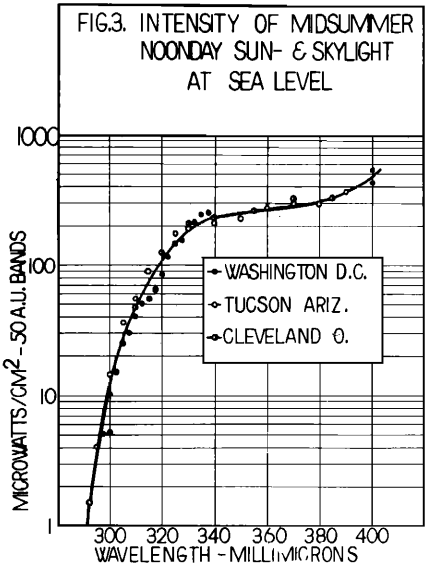
ENERGY	KCAL/GM-MOLE	RADIATION
BONDING	200	FAR U-V
	100	NEAR U-V
	50	VISIBLE
VIBRATIONAL	5	NEAR I-R
ROTATIONAL	0.5	FAR I-R

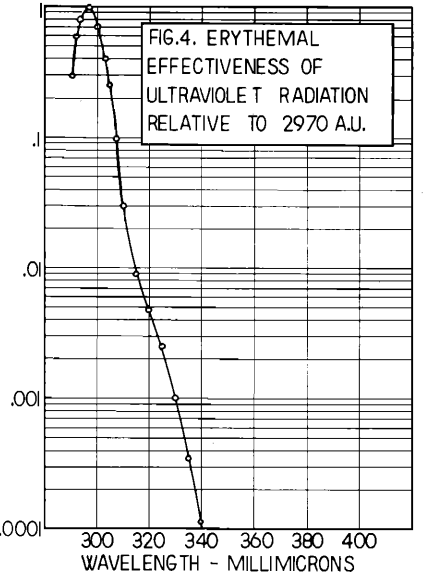
Quantitatively, the electronic bonding energies are the largest, and the vibrational energies are greater than the rotational energies. Thus bonding energies are associated with absorption bonds in the ultraviolet and visible regions (200 kcal./mole in the far ultraviolet, 100 kcal./mole in the near ultraviolet, 50 kcal./mole in the visible range. Vibrational changes are of the order of 5 kcal./mole, in the near infrared, and rotational changes are of the order of 0.5 kcal./mole, in the far infrared.



It is important to note that absorption can take place only if the photon corresponds to the difference in energy between two possible energy levels of the molecule. The change from one such permissible level to the other is termed an *electronic* transition.

Each transition gives rise to an absorption line of very narrow, though finite, width; and for each such electronic transition, there is a progression of closely spaced absorption lines corresponding to different possible combinations of vibrational and rotational levels belonging to the same two electronic levels. In complex molecules, the number of possible combinations of vibrational and rotational levels are so great that the linear fine structure is blurred. In solutions, and in the condensed states, vibrations and rotations are blurred still further by solute-solvent interactions and by molecular association of the close-packed molecules. This gives rise to a diffuse absorption band which is observed in place of the system of discrete absorption lines.





WAVELENGTH-MU	ENERGY-KCAL/GM-MOLE
280	103.2
290	99.4
297.5	96.9
315	91.4
320	90.4

Braude (1) points out that the absorption maximum for a given molecule corresponds to the most probable transition, and the value of $\lambda_{max.}$ is one of the most characteristic parts of the absorption curve. For a cosmetic sun screen, the location of the absorption maximum should therefore correspond to those wavelengths of sunlight which have a major erythemal effect on human skin. Solar radiation is known to extend in a continuous band throughout the entire electromagnetic spectrum. Were it not for the absorption of the lower wavelengths by our atmosphere, which absorbs virtually all radiation of wavelengths shorter than 290 millimicrons (mμ), it is doubtful that life, at least as we know it, would have been possible on Earth. At any rate, the major erythemal wavelengths penetrating the atmosphere to sea level extend from about 290 to 315 mμ. From equation 1 it is calculable that these wavelengths correspond to transition energies of 91.4 to 99.4 kcal./gm.-mole. At the wavelength of maximum erythemal effectiveness, 297.5 mμ, the corresponding transition energy is 96.9 kcal./gm.-mole. A transition with ΔE of 90.4 kcal./gm.-mole will have an absorption maximum at 320 mμ, a region where absorption is undesirable because it impedes tanning. At the other end of the erythemal range, a transition energy of 103.2 kcal./gm.-mole results in an absorption maximum at 280 mμ, too low to be cosmetically useful.

It becomes apparent from these figures that the allowable transitions that will result in a useful cosmetic sun screening fall within an exceedingly narrow range of energy requirements. It is not surprising then that few molecular species have been found which will serve satisfactorily as screens for human use.

The extent of the absorption of any particular wavelength depends further on the molecular geometry of the molecules. The quantitative measure of completeness of absorption is given by the molecular extinction coefficient, $\epsilon_{max.}$, which is defined by the equation:

$$\epsilon_{max.} = (O.D./cl) = (100/\%T)/cl) \qquad (5)$$

where
$O.D.$ = optical density = log $(100/\%T)$
$\%T$ = per cent transmission
c = concentration of the screen, gm.-moles/liter, and
l = thickness of the absorbing layer, in centimeters.

The value of $\epsilon_{max.}$ is as characteristic of a molecular species as is the value of $\lambda_{max.}$.

The absorption coefficient, $\epsilon_{max.}$, is determined by the transition probability, in the statistical sense. That is: when a photon of radiant energy strikes a molecule, what is the statistical probability of absorption of the photon? This transition probability is given approximately by Braude (1) as

$$P = 6.9 \times 10^3 \epsilon_{max.}/N \times a = 1.15 \times 10^{-20} \times \epsilon_{max.}/a \quad (6)$$

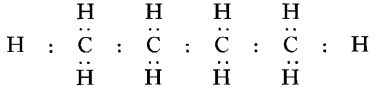
where
N = the Avogadro number, 6.06×10^{23}, and
a = the chromophore area, centimeters squared.

The chromophore area is that part of the molecule within which a given photon must strike in order that interaction and absorption shall occur. In complex molecules this area is generally much smaller than the total cross-sectional area, and includes only those atoms and bonds which are concerned in the transition.

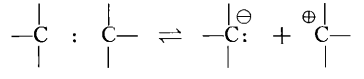
The values of $\epsilon_{max.}$ for high intensity electronic bands are of the order of 10^4 to 10^5, and chromophore areas of the order of 10^{-15} to 10^{-16} cm.^{2}, or 1 to 10 square Angstrom units. This corresponds to transition probabilities of approximately unity. In such a case it is said that the transition is *allowed* and occurs whenever a photon of the proper energy strikes the appropriate part of the molecule.

In order to use these generalizations in the design of new sun screening compounds, it would be necessary to predict the transition energies associated with specific atomic and molecular groupings. An approach to this can be made through our knowledge of the electronic structures of organic compounds.

Mineral oils have from time to time been used as sun screens. These oils are predominantly saturated paraffin hydrocarbons. The electronic bonds in such compounds are formed by pairs of electrons in covalent bonds. For example in butane:

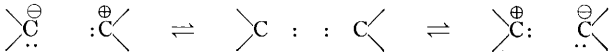


The absorption of energy in the erythemal range is known to involve electronic shifts. The most probable shifts in saturated compounds involve the complete ionization of the molecule, brought about through bond rupture:



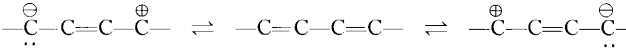
The probability of such an ionization is extremely small, and we find that extinction coefficients for hydrocarbons in the near ultraviolet and the visible range are close to zero. These transitions are not allowed by the molecular structure. This class of compounds does not absorb in the erythemal range, and whatever doubtful value they may have cannot be due to their sun screening activity.

For unsaturated compounds, another type of electronic transition is possible. One pair of the two pairs of electrons forming the double bond may resonate between two possible structures:



This type of transition requires about 170 kcal./gm.-mole for a single olefinic group, and corresponds to an absorption at 170 mμ, in the far ultraviolet. At this point the $\epsilon_{max.}$ is high and the transition probability is about 1.0.

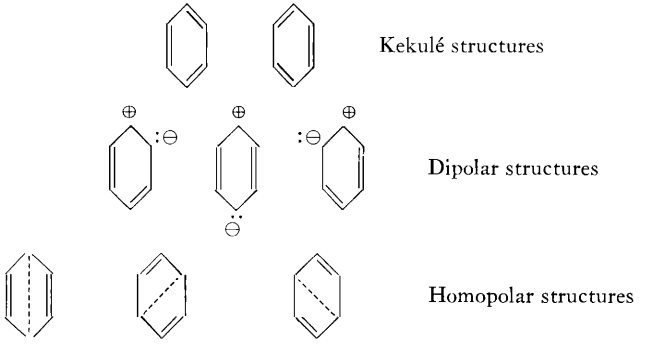
As the unsaturated structures increase in length, i.e., there are greater numbers of unsaturated bonds in the molecule, the ionic and homopolar resonance structures contribute more and more to both the ground state and excited states of the molecule. This results in the lowering of the potential energy levels of both the ground and the excited states with respect to the unconjugated system. But since the contribution of resonance structures is greater in the excited than in the ground state, the energy level of the former is lowered more than that of the latter. The transition energy therefore is reduced and the absorption bands are displaced to longer wavelengths (bathochromic shift).



As the number of conjugated double bonds in the resonating system increases, this shift of $\epsilon_{max.}$ to longer wavelengths continues, as shown in Table 1.

TABLE 1—ABSORPTION MAXIMA OF CONJUGATED UNSATURATES OF THE SERIES $(—C=C—)_n$

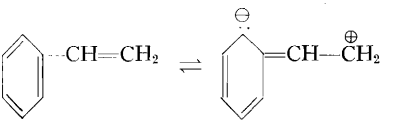
n	$\lambda_{max.}$	$\epsilon_{max.}$	Color
1	170.0	15,000	Colorless
2	217.0	21,000	Colorless
3	258.0	35,000	Colorless
4	310.0	42,000	Pale Yellow
5	328.0	51,000	Yellow (Vitamin A)
11	472.0	170,000	Red
15	528.0	150,000	Violet



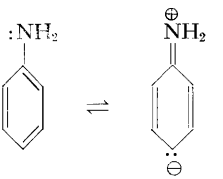
The instability of the conjugated polyolefins toward oxidation and polymerization makes them unsuitable for use as sun screens. However, the aromatic compounds constitute a very stable series of conjugated double bond structures. The conjugated system of alternating single and double bonds permit resonance structures to contribute largely to the molecular structure. For benzene there are a large number of possibilities shown on bottom of page 104.

For benzene, $\lambda_{max.}$ for the polar structures occurs at 180 mμ and at 200 mμ, in the far ultraviolet.

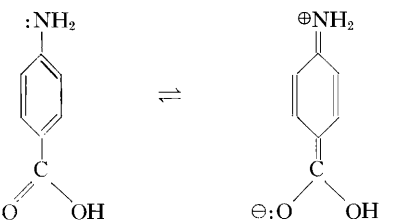
As the length of the resonating structures is increased, again there is an increase in $\lambda_{max.}$. This may be accomplished by such structures as styrene. Styrene shows maximum absorption at 244 mμ.



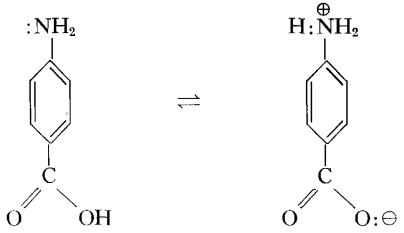
The addition of certain other groups to the benzene ring also results in increasing resonance possibilities. Thus the substitution of an amino group for a hydrogen also has a bathochromic effect. Aniline has its absorption maximum at 230 mμ.



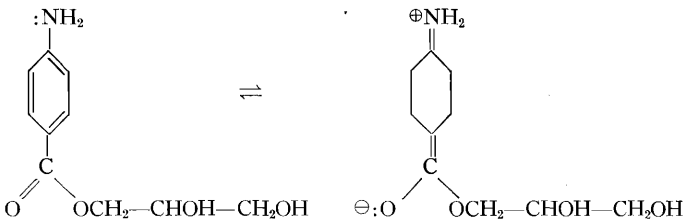
Further lengthening of the chromophore results in materials useful as cosmetic sun screens. The introduction of a carboxylic group para to the amino group in aniline shifts the absorption maximum to 290.0 mμ.



In this case, the contribution of the indicated transition is not a maximum because of the competing contributions of other, more probable structures:

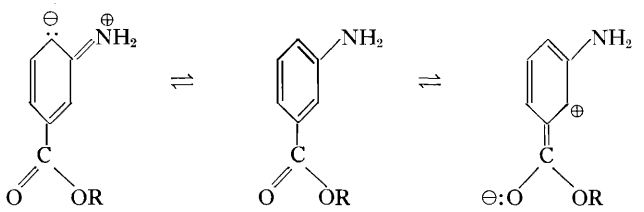


This ionization prevents the desired transition by bonding the unshared electron pair of the nitrogen atom in the ammonium ion, so that the quinoidal resonance structure cannot be formed. Thus, PABA is a relatively poor sun screen, and the absorption coefficient is low. However, when ionization is prevented by esterification of the carboxylic group, the quinoidal resonance is no longer impeded. The major electronic transition in glyceryl-*p*-aminobenzoate is shown in the following scheme.



Here the absorption maximum is at 297.5 mμ, which corresponds exactly to the erythematogenic maximum of sunlight. To compare effectiveness, more than a 15 per cent concentration of PABA is required to equal the screening efficiency of 2 per cent glyceryl-*p*-aminobenzoate.

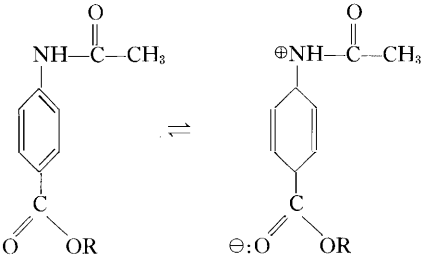
The relative positions of the polar groupings in the molecule greatly affect the energy and efficiency relationships. A change from the para to the ortho isomer in aminobenzoate esters results in a decrease in the chromophore cross-sectional area. Because of this the ortho isomers (anthranilates) are much weaker absorbers than the corresponding *p*-aminobenzoates. When the meta-aminobenzoate is tested, it is found that the peak absorption has shifted to lower wavelengths, and that the material is a very weak absorber. This is a consequence of the structure: electronic shifts involving both polar groups are not readily possible in



the meta isomer since they are located at nonconjugating positions in the molecule bottom of page 106.

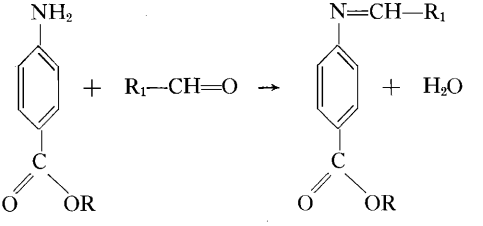
This transition is simila rto that of the simple benzoate esters, and to aniline. These considerations lead to the conclusion that the para isomers afford the optimum cosmetic screen.

Substitutions of various groups on the amino radical of the para amino-benzoates lead to considerable modification of the transition possibilities, and hence change the screening characteristics of the original chomophore. Acetylation of the amino radical greatly reduces the basic character of the nitrogen atom and hence decreases its electron-releasing tendencies. Thus the probability of the transition

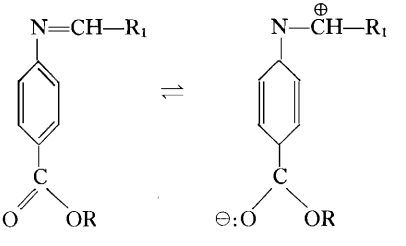


is smaller than that in the parent free amine, and requires greater energy. As a result, absorption maximum is lowered from 297.5 mμ to about 270 mμ, and resulting *p*-acetamidobenzoate ester is not a good cosmetic screen.

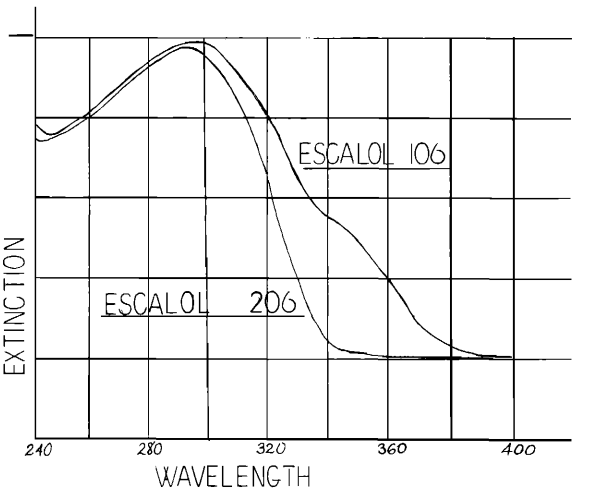
Another method of modifying the amino group is through Schiff-base formation by condensation with an aldehyde group.



The resulting aldimino structure allows a transition to occur which lies within the erythematogenic range of energy,



and the resulting activated state is resistant to oxidation. These Schiff bases are the newest development in commercially available cosmetic sun screens. Thus, ethyl-*p*-glucosylimidobenzoate is a screen (Escalol-206*) which is highly selective in its activity. To a greater extent than even the *p*-aminobenzoate esters, such compounds absorb selectively in the erythematogenic range while they are nearly completely transparent in the higher ultraviolet. They permit the most complete transmission of the tanning radiation while providing efficient protection against erythemal radiation.



Thus a 2.7 per cent concentration of Escalol 206 in a clear or emulsified lotion transmits only 7.4 per cent of the erythematogenic radiation of sunlight, and 95.6 per cent of the radiation in the so-called tanning range, above 315 millimicrons.

Reference

(1) Braude, E. H., "Chemistry of Carbon Compounds," Vol. 1A, Elsevier Publishing Co., Princeton, N. J. (1951), pp. 71–93.

* Van Dyk & Co., Inc.