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Journal of the Society of Cosmetic Chemists

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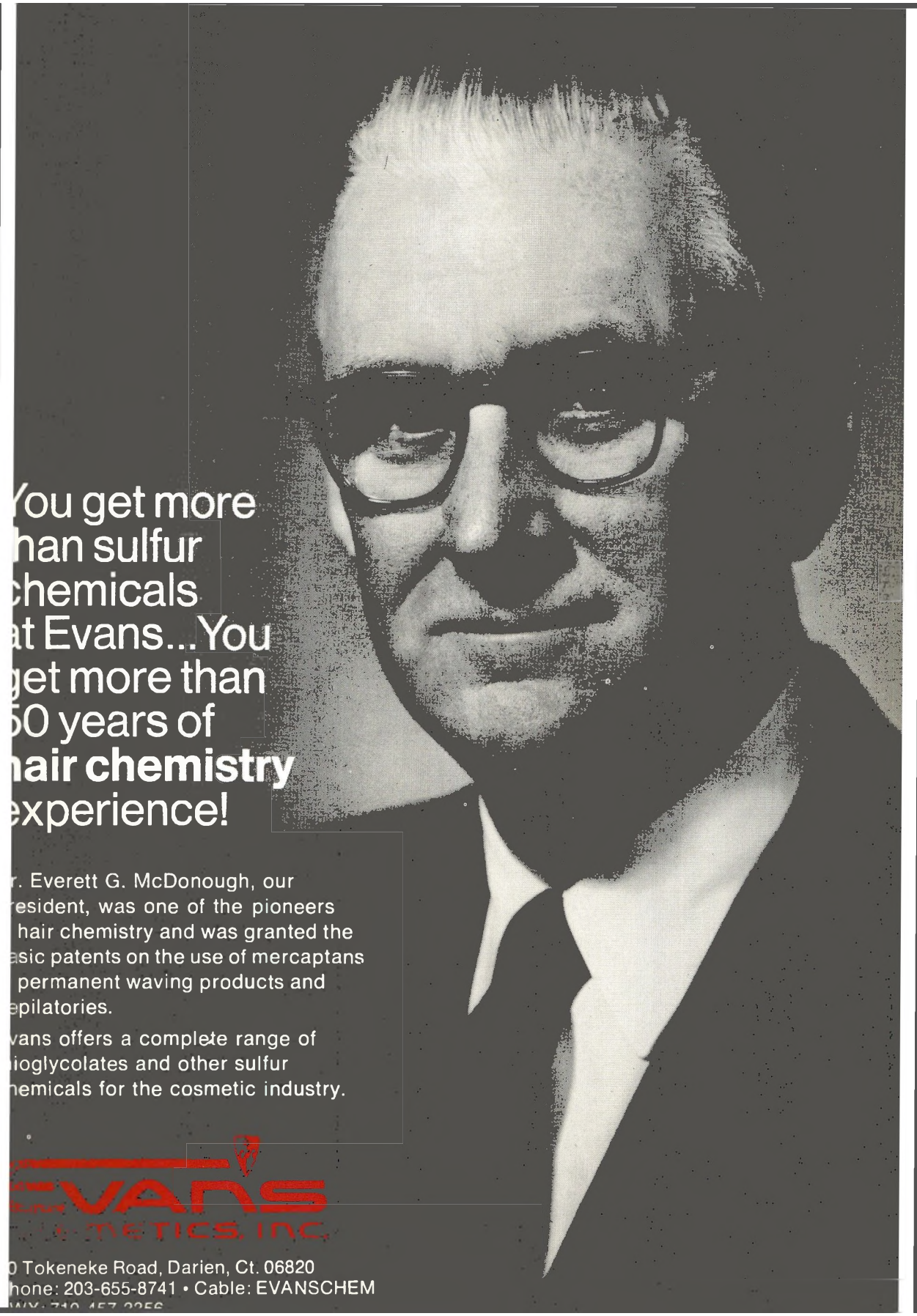

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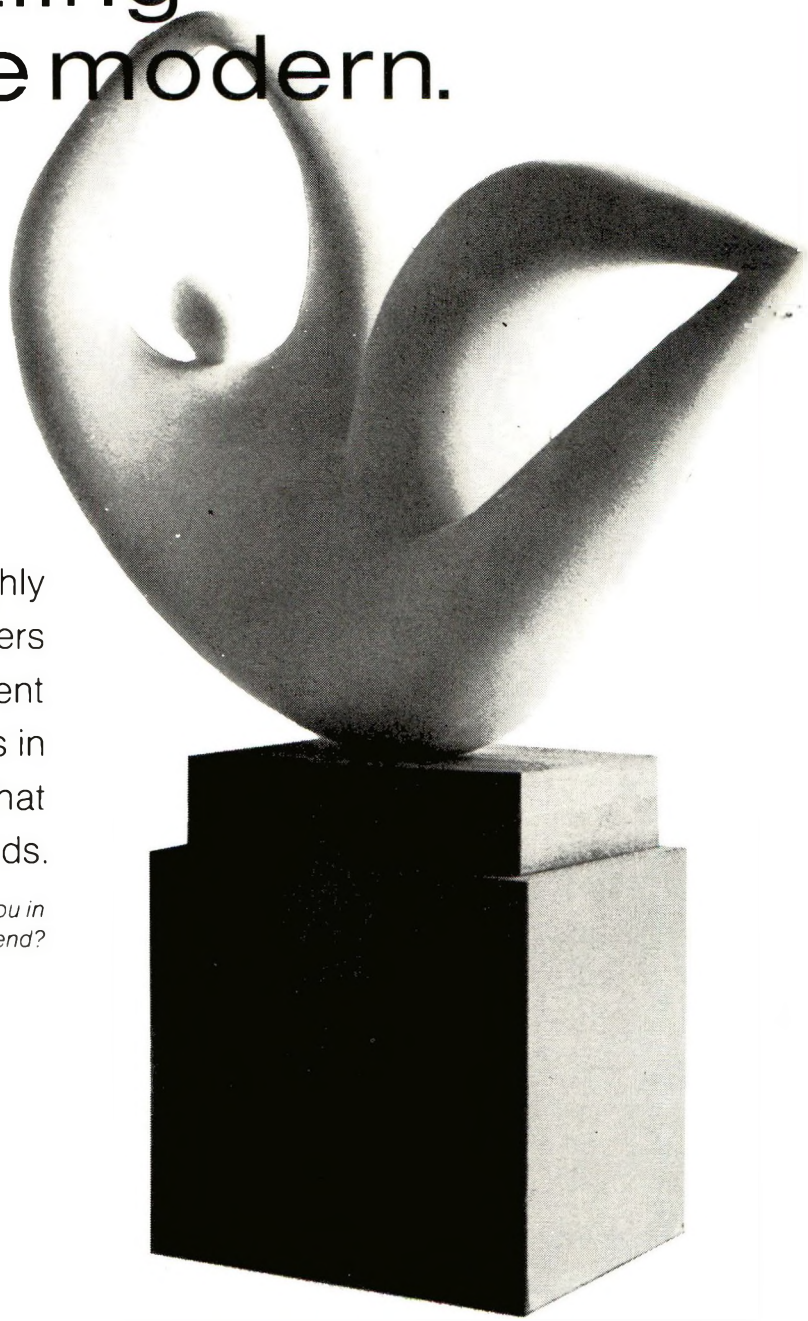

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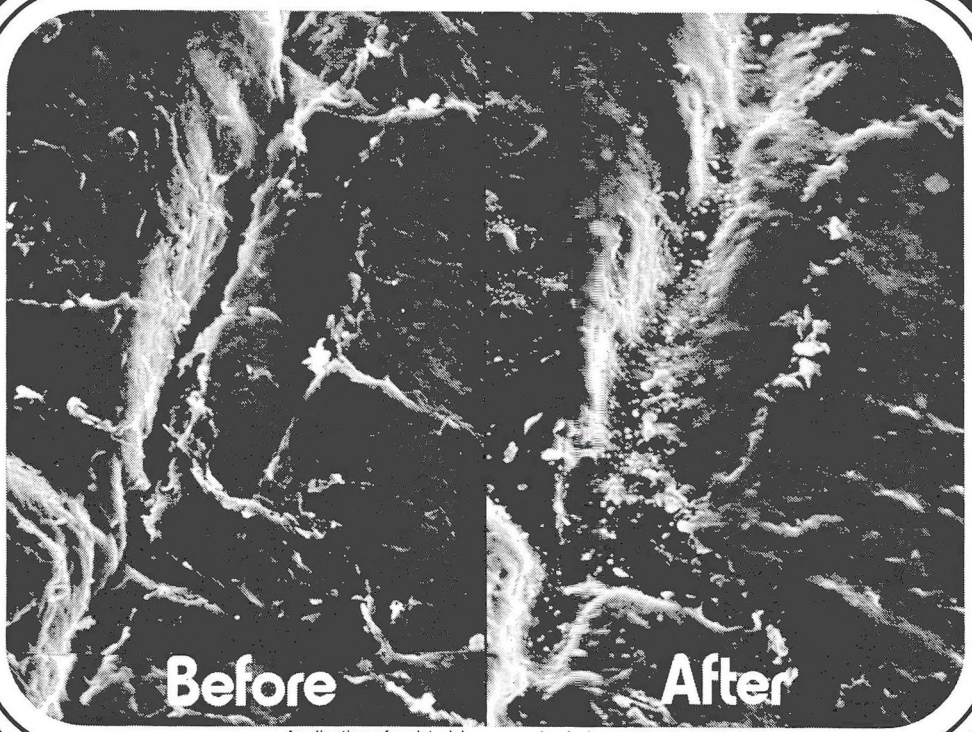

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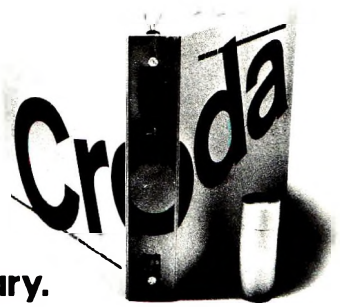

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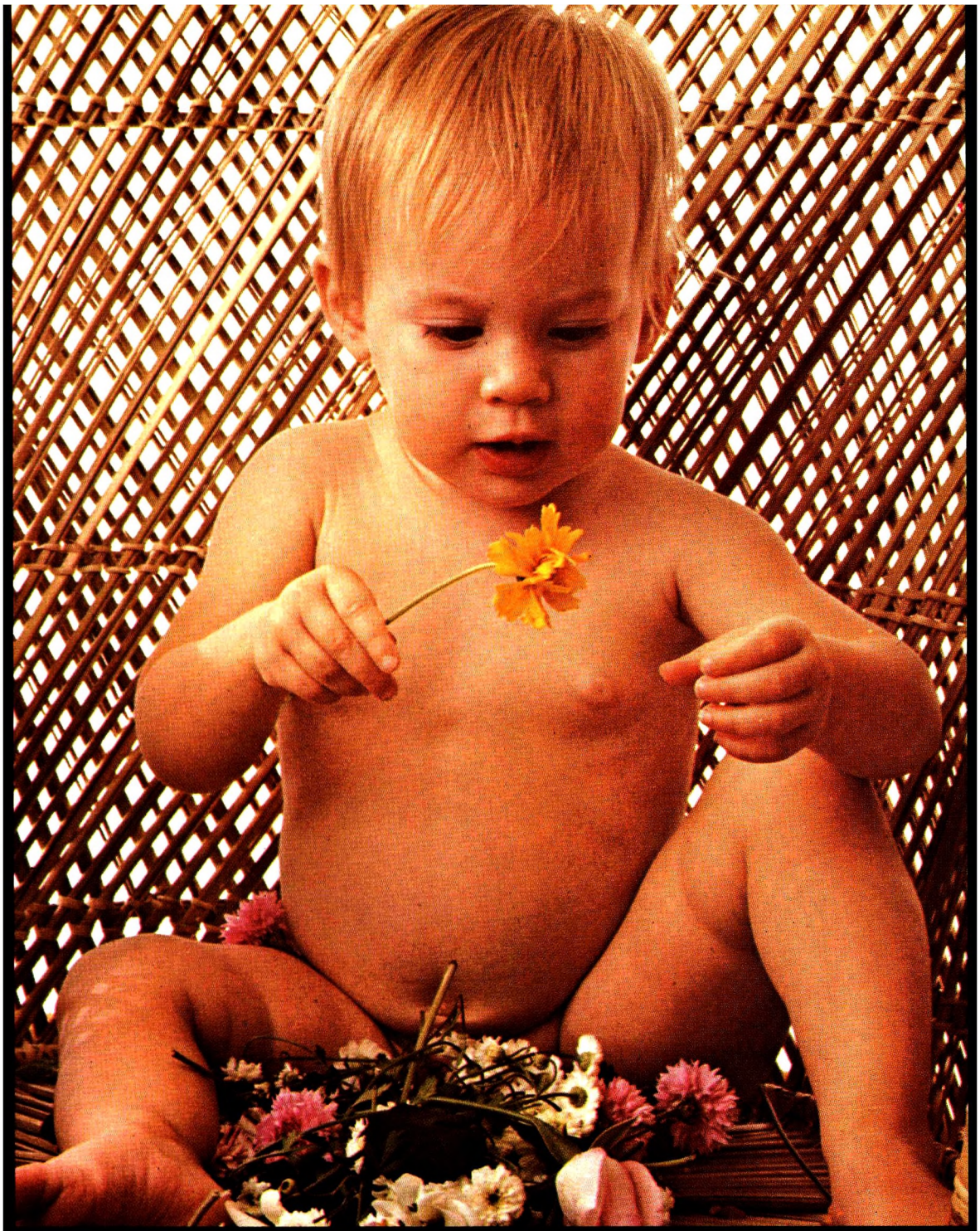

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SYNOPSES FOR CARD INDEXES

The following synopses can be cut out and mounted on 3 × 5 index cards for reference, without mutilating the pages of the Journal.

A method for the study of emotional sweating: Richard P. Quatrale, Karla L. Stoner, and Carl B. Felger. *Journal of the Society of Cosmetic Chemists* **28,** 91 (March 1977)

Synopsis—Methodology for the study of emotionally induced sweating, as well as for the routine conduct of human antiperspirant test panels, wherein the stress mode is emotional rather than thermal, has been developed. To stimulate emotional sweating, virtually on command, the word association list is used most successfully on a variety of subjects. Alternative methods such as mental arithmetic and electric shock are also useful, but only on certain subjects. To collect and measure the amount of emotional sweat output from the axillae, absorbent Webril pads, as customarily used in thermal stress studies, have been found quite suitable when studying groups of subjects simultaneously.

It has been determined that the capacity for the average individual to sweat under emotional stress is very high, and the volume of perspiration substantially exceeds that generally produced by subjects under thermal stress. On the average, for panelists studied to date, emotionally stimulated sweat output is about 550 mg/axilla/10 min at ambient temperature (70°F). By comparison (presumed), emotionally quiescent subjects have an output of about 250–300 mg/axilla/10 min under thermal stress (100°F). One of the more important aspects of this new methodology is that the high sweat output is achievable in these subjects for at least as long as 5 consecutive days. Thus emotional sweating test panels using product application and measurement protocols established for routine thermal studies are now possible.

PH-changes on infant skin following application of sunscreening emulsions—a quantitative evaluation: Udo-Angresius Hoppe, Hans-Joachim Kopplow, and Hans-Wilhelm Kreysel. *Journal of the Society of Cosmetic Chemists* **28,** 103 (March 1977)

Synopsis—Variations of pH in the stratum corneum following the application of different fluid O/W emulsions have been studied on healthy skin of 24 one to eight-year old children of both sexes. The pH of the tested emulsions was 6.6 and 8.5 respectively. As proven by statistical analysis these emulsions induced highly significant shifts of pH on the treated skin areas for a period of three hours after application. It has been demonstrated with the aid of the Kolmogorow-Smirnow test that the frequency distribution of the pH values may be described by a Gaussian distribution, i.e. the proton concentration of children's skin exhibits a logarithmic normal distribution. The pharmaco-kinetics of the pH shifts caused by the different emulsions may, with a high degree of statistical safety, be represented by Bateman functions. The regression-equations of these functions quantitatively describe the absorption and elimination processes. From the dermatological point of view the weakly acidic emulsion appears preferable to the alkaline one because the induced pH-shift on the treated skin is less pronounced.

Determination of vitamin E in cosmetic products by gas-liquid chromatography (GLC): E. Patricia Sheppard and Martin J. Stutsman. *Journal of the Society of Cosmetic Chemists* **28**, 115 (March 1977)

Synopsis—Vitamin E is being incorporated into an increasing number of Cosmetic Products. Because some adverse reactions have been reported following the use of some of these products, a method for isolating and determining vitamin E in cosmetics has been developed. The vitamin E analogs investigated, *d*-α-tocopherol and *d*-α-tocopheryl acetate, were added to vanishing cream, shampoo, and bath oil at 3 use levels. After preparation of these samples, the compounds were determined by gas-liquid chromatography (GLC) using a glass column packed with Gas-Chrom Q coated with SE-30. Dotriacontane was selected as the internal standard for quantitative measurement. *d*-α-Tocopherol and *d*-α-tocopheryl acetate were well resolved from dotriacontane, with relative retentions of 0.81 and 0.92, respectively. The recoveries of *d*-α-tocopheryl acetate ranged from 93 to 103 per cent with an average and standard deviation of 98 ± 5 per cent. Recoveries of *d*-α-tocopherol ranged from 91 to 102 per cent with an average and standard of 97 ± 3.5 per cent.

Factors affecting the penetration of light through stratum corneum: James L. Solan and Karl Laden. *Journal of the Society of Cosmetic Chemists* **28**, 125 (March 1977)

Synopsis—Light transmission values were obtained for isolated guinea pig stratum corneum exposed to water vapor, water, and organic liquids. Several of the variables involved, such as equilibration time, wavelength of light and refractive index of the liquids were examined. Increasing the relative humidity of the atmosphere surrounding the tissue resulted in a slight increase in light transmission, which was wavelength dependent. Immersion in water or other liquid produced a substantial increase in transmission. This effect increased with the refractive index of the liquid, reached maximum at the refractive index of stratum corneum, and then decreased.

The effect of fiber diameter on the cosmetic aspects of hair: Naling E. Yin, Roy H. Kissinger, William S. Tolgyesi, and Ellyn M. Cottington. *Journal of the Society of Cosmetic Chemists* **28**, 139 (March 1977)

Synopsis—Most cosmetic aspects of a head of HAIR depend on the physical characteristics of the hair mass. In turn, the hair mass characteristics are determined (directly or indirectly) by the properties of its individual fiber components. Among fiber properties, diameter is of great significance. It influences hair body, tangling, combing, and resistance to damage. Both human hair and a model system using synthetic fibers were used to study the fiber diameter contribution. When these systems were assessed using combing, body, and abrasion test methods, it was found that the fiber diameter was directly related to hair body, combing ease, and abrasion resistance when all other hair or synthetic fiber properties were equal.

J. Soc. Cosmet. Chem., 28, 91–101 (March 1977)

A method for the study of emotional sweating

RICHARD P. QUATRALE, KARLA L. STONER,
and CARL B. FELGER *Gillette Research Institute,
Rockville, MD 20850*

*Received July 23, 1976. Presented Ninth IFSCC Congress,
June 1976, Boston, MA.*

Synopsis

METHODOLOGY for the study of EMOTIONALLY INDUCED SWEATING, as well as for the routine conduct of human antiperspirant test panels, wherein the stress mode is emotional rather than thermal, has been developed. To STIMULATE EMOTIONAL SWEATING, virtually on command, the WORD ASSOCIATION LIST is used most successfully on a variety of subjects. Alternative methods such as MENTAL ARITHMETIC and ELECTRIC SHOCK are also useful, but only on certain subjects. To collect and measure the amount of emotional sweat output from the axillae, absorbent Webril pads, as customarily used in thermal stress studies, have been found quite suitable when studying groups of subjects simultaneously.

It has been determined that the capacity for the average individual to sweat under emotional stress is very high, and the volume of perspiration substantially exceeds that generally produced by subjects under thermal stress. On the average, for panelists studied to date, emotionally stimulated sweat output is about 550 mg/axilla/10 min at ambient temperature (70°F). By comparison (presumed), emotionally quiescent subjects have an output of about 250–300 mg/axilla/10 min under thermal stress (100°F). One of the more important aspects of this new methodology is that the high sweat output is achievable in these subjects for at least as long as 5 consecutive days. Thus emotional sweating test panels using product application and measurement protocols established for routine thermal studies are now possible.

INTRODUCTION

Over a number of years, substantial thought and research have been devoted to the study of eccrine sweat gland function and its control. These studies have invariably drawn information from results obtained after sweating has been induced by thermal stress. The stimulation of sweating, or the relative lack thereof subsequent to application of an antiperspirant, is both conveniently achieved and controlled physically via the imposition of thermal stress coupled with elevated humidity. However, the facts have been largely ignored that such comparable hot and humid weather conditions generally exist naturally for only a few months of the year in temperate climates. These conditions are still further minimized when one considers the increasingly widespread use of climate control in homes, transportation means, and places of work. Nevertheless, the use of antiperspirants is a 'year-round' occurrence, and, disturbingly so, the

desire for increased efficacy of these agents is not infrequently voiced. The contribution to eccrine sweating by factors whose origin is emotionally generated has to date been both an unknown and ill-defined quantity and a methodologically uninvestigated phenomenon. Upon reflection of the fact that emotionally induced sweating occurs to a substantial degree in the axillae, the necessity for a method to induce and to study emotionally caused axillary sweating, which has a facility comparable to that used in thermal studies, appears highly desirable.

Attempts to estimate axillary sweat output under ambient temperature conditions have been reported (1–3). These studies, which presumably rely on the ambient emotional state of the subject for sweat production, generally require long periods of time to insure that quantities of sweat sufficient for measurement are obtained and, partially because of that requirement, these studies are difficult to control. Similarly, although reports on palmar (emotional) sweating physiology are available, studies dealing with emotional sweating in the axilla are few (3). Even for investigations of palmar sweating, the methods to stimulate the firing of the glands are frequently glossed over with abstract terms such as "mental arithmetic," "pain production using pin pricks," etc., and rarely make mention of actual sweat output, method reproducibility, universal applicability to subjects, or duration of stress.

The lack of well-defined methods for the routine stimulation of emotional sweating in human subjects might well rest on the recognition that it is difficult, at best, to emotionally stimulate a subject to sweat literally upon command. Intricate psychological factors far more involved than the placing of the individual in an environmental chamber set to 100°F and 35 per cent relative humidity (RH) are frequently in force. Nevertheless, the importance of emotional sweating and its contribution to axillary sweat output requires that appropriate methods for the routine stimulation and measurement of this emotionally derived eccrine sweat be available.

METHODS

A. GENERAL PROCEDURAL CONDITIONS

1. *Subjects:* The subjects used in these studies were volunteer employees of the Gillette Research Institute, the majority of whom were college educated with technical training in a scientific discipline. The level and background of education is not critically exclusive in subject selection. However, when that information is available to the investigator, it aids substantially in the design of emotionally stimulating protocols wherein maximized sweat response is the singular measure of success. Furthermore, it is important that the subjects have an appreciation for the intended goal of a given emotional challenge session, namely maximum sweat output of nonthermal origin in minimum time and literally "upon command" of the investigator. They must cooperate fully with the investigator to realize that goal. Cooperation includes not only the subjects' self-motivation under the investigator's guidance, but also a clear recognition that they will be occasionally subject to badgering, verbal barrage, and deliberately embarrassing situations which are inconsistent with their normal life's routine and relationships. Without these essential ingredients, successful emotional sweat stimulation cannot be expected.

2. *Environment and time:* A small quiet room, which is free from outside noise and distraction and thus permits concentration is an important prerequisite. The major testing

reported herein has been conducted at ambient temperature (70°F) and 20–25 per cent RH. Conversely, it has been suggested that the mental trauma of exposure to a hot room in itself causes some level of emotional sweating (3).

Initial considerations suggested that the time of day might materially detract from a subject's capacity for response. It would presumably be prudent, then, to forego testing immediately after lunch or late on Friday afternoons. Such apprehensions have only occasionally been fulfilled, however. The important factors are the subject's emotional state at the time of test, his willingness to cooperate, and, to a very substantial degree, the investigator's own capability and attitude at the time.

B. METHODS FOR STIMULATING EMOTIONAL SWEATING

It has been our experience that an appropriately chosen emotional stimulus, if sufficiently intense to evoke sweating, will cause the glands to fire immediately. Effectively sustaining that stimulus will result in continuous high sweat output. A representative example of these characteristics of sweating response to an emotional stimulus, as obtained with electronic hygrometry instrumentation coupled to a strip chart recorder, is presented in Fig. 1. The methods evaluated in these studies for stimulating emotional sweating are described below.

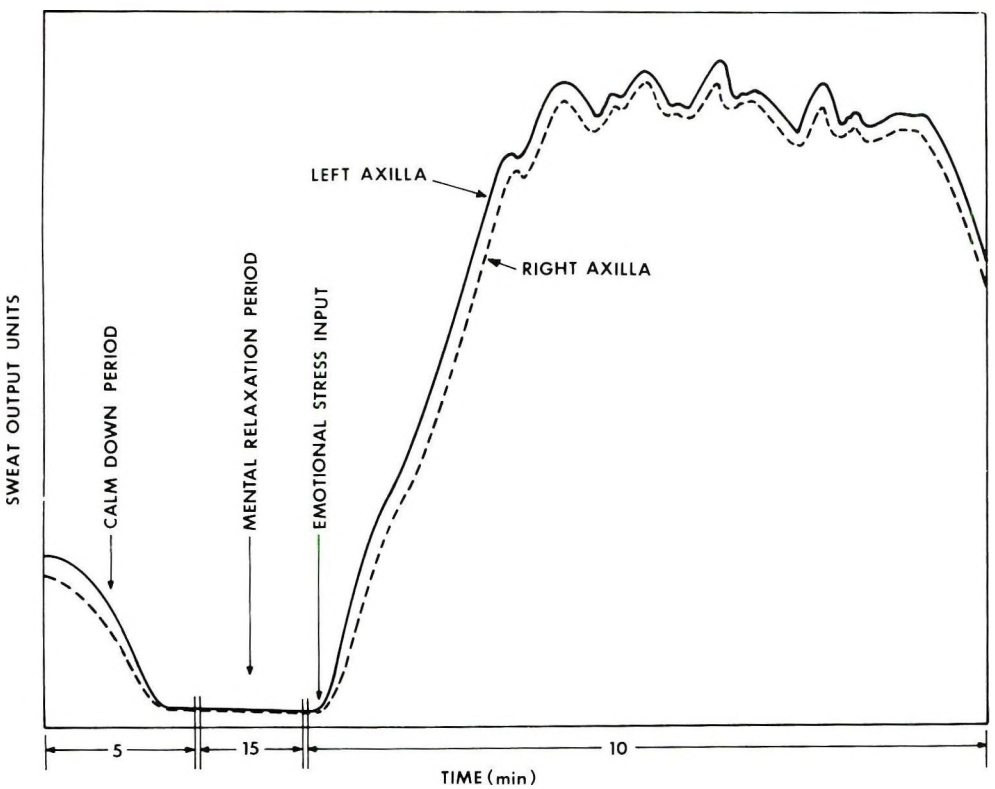

Figure 1. Hygrometric recording of the characteristics of an emotional sweating course for a representative individual

1. *Mental arithmetic:* The requiring of a subject to perform tasks in arithmetic without benefit of pencil, paper, or unlimited time has been successful, in our experience, in stimulating both axillary and palmar emotional sweating in a number of subjects. The mental arithmetic method whose use was first reported by Kosaka (4), has been mentioned frequently as a means for emotional stimulation, but it has never been described. In our hands, for administering this type of stimulus, the investigator reads to the subject the steps in the mathematics problem in a cadence, which is designed to be just rapid enough for each individual so that the subject is constantly fighting to keep up in order to obtain the correct answer. Recitation of the steps too slowly diminishes stimulus intensity. Alternatively, too rapid a progression through the steps of the problem usually loses the subject altogether, and consequently no stimulus at all is administered.

Usually, a given stimulus session will consist of from 4 to 7 problems, 2 or 3 of which are short and read quickly, with the subject being prodded for the answer within 5 to 8 sec. The remainder of the problems are longer, read somewhat more slowly, and require that the subject continually solve correctly each step in order to arrive at the final answer. Examples of each type of problem are presented below.

a. *Short problems*
   i. Multiply 11 × 3 × 4,
      Divide by 12, then multiply by 1/2,
      Now add 3/4—Answer?
   ii. Add 47, 19 and 136,
      Now subtract 78—Answer?

b. *Long problem*
   i. Take 3 times the number of ounces in a pound, add 2,
      take its reciprocal, and convert it to a decimal,
      now multiply it by 10, then square it,
      add 15.26, then divide it by 5,
      now multiply it by 100, subtract the square of 12,
      and sum the digits,
      then subtract 8, add 5, and cube it,
      now divide by 10, then subtract 5.6,
      multiply it by 5/8,
      now subtract 1-1/4, then add 17 to it,
      then subtract 3-3/4, now add 39,
      sum the digits, multiply it by 5/6 and
      give the answer.

A nominal reward for the correct solution to the problem frequently encourages the efforts of the subject. It is generally a good practice to permit everyone to earn a reward from time to time in order to encourage continued participation. On the other hand, when the last several steps of a long problem are read so rapidly that the answers are just beyond a subject's grasp, his frustration at having come a long way for naught adds additional emotional stimulation.

Mental arithmetic for stimulating emotional sweating in those individuals, who are both willing and capable of cooperating is a powerful tool. Furthermore, it can be used

successfully against a group of about 3 subjects. In so doing, the factor of competition, wherein individuals are struggling against each other to be first with the correct answer and thus earn the reward, provides a still stronger level of stimulation. However, care in the selection of group participants must be exercised so that each member has relatively the same facility and talent for problem solving.

2. *Electric shock:* A person's fear of receiving even a mild electric shock has been used as a means of producing emotional sweating in a small number of subjects. Generally, the procedure has been to have the subject supine with the electrodes attached to one of his ankles. The subject's head is elevated so that he can easily watch a clock having a second hand. He is told that at every half-minute interval, ±5 seconds, over the course of 10 min, there is the possibility that the investigator will administer a shock. Out of 20 total possible instances, usually about 7 to 12 shocks are actually given. When a water sensing instrument is used to follow axillary emotional sweating, the recorder tracing provides a graphic display of increased sweat output just as the clock's second hand is approaching the point where the possibility of receiving a shock exists.

In most of the few subjects, where electric shock has been used for stimulating emotional sweating, the sweat response has been good, perhaps equal in intensity to that produced by the mental arithmetic technique. There have been some subjects, however, who apparently do not fear electricity and thus do not sweat. On the other hand, a number of subjects seemingly have so substantial a fear of it that they have refused to participate.

Permutations on the electric shock theme such as administering a punitive shock when the subject fails to provide the correct answer to a mental arithmetic problem, have been explored briefly. The results of those experiments have not indicated the promise of a still better method for stimulating emotional sweating, however.

3. *Word association list:* In order to be able to emotionally stimulate virtually any individual to sweat so that an unlimited subject pool for testing is available, alternative methods more widely applicable than mental arithmetic or electric shock are desirable. It was brought to our attention that in the psychology literature there is described a number of laboratory means for creating stress and anxiety in human subjects. Because emotional sweating is one physiological manifestation of anxiety, consideration was directed to those anxiety-causing methods as candidates for stimulating emotional sweating. The one method, which appeared to be least complicated and most easy and rapid to administer to any individual, was the Word Association List and this method, as we have now modified and varied it, has been used extensively. The method involves the recitation of a list of words by the investigator to the subject. When each of these words is spoken, the subject must respond quickly (about 5 sec) with an associative word, for example, investigator—"table;" subject response—"chair." The word list, as used by us, is designed so that a number of those words, about 40–70 per cent, are neutral and can be expected to provoke no particular feeling or emotional response from the subject. Interspersed among the neutral words, however, are charged words—words which conjure up in the subject's mind emotional connotations associated with such feelings on the subject's part as pleasure, repulsion, sympathy, prejudice, anxiety, and embarrassment. Categories of these charged words may be easily designed and chosen so as to obtain maximum impact for a given subject type (housewife, college student, professional, etc.) or a given group of subjects. Charged

word categories (with examples) used for emotionally stimulating subjects in our studies have included job (supervisor, unemployment); school or studies (hour exam, tuition); money (car payment, inflation); pleasant (sunshine, vacation); unpleasant (cancer, vomit), double meaning (screw, rubber); religion, politics and personalities (Bar Mitzvah, Good Friday, Watergate, Martin Luther King, Lee Harvey Oswald, Raquel Welch); and embarrassment (pap smear, proctoscope, virgin). An example of a Word Association List is presented below.

Word Association List

1. silicone injection
2. swimming pool
3. extensive foreplay
4. grandmother
5. chapped lips
6. children's hospital
7. Rocky Mountain oysters
8. pig
9. "Where would you least want to have gangrene?"
10. group therapy
11. inexpensive
12. cherry
13. prostate problems
14. harmony
15. Bar Mitzvah
16. psychiatrist
17. hair in the bathtub
18. Disneyland
19. mercy killing
20. Joe Namath
21. bidet
22. stardust
23. Haley's M.O.
24. rubber band
25. incompetent midwife
26. morass
27. loan shark
28. antonym—to blot dry
29. robin—redbreast

The Word Association List has been a successful means for stimulating emotional sweating in approximately 75 per cent or more of the randomly selected subjects to whom it has been presented. Its intensity level is from mild to moderate for most subjects when they are challenged individually, as compared to the high level for those individuals who do respond when mental arithmetic is employed. However, it has invariably been found to evoke intense emotional sweating when it is used on a group of subjects simultaneously. A group of 5 subjects has been found best, although the method can work well with as few as 3 or as many as 8. However, the use of more than 5–6 subjects in a group is usually not practical, mainly because the rhythm of the stimulus input is unbalanced. In these groups, it is highly desirable that both males and females be present. Attention to such subtle details as the placing of chairs close together and in a manner such that the participants must look at each other also contributes to a successful session. In the recitation of the words to the subjects, one rotates the order of subject responses so that each individual, in turn, has the opportunity to respond first and by the same token, all individuals at one time or another are the last to respond. In this fashion, and coupled with the important stipulation that no subject can repeat a previously used response, even neutral words take on a "semi-charged" stimulatory effect. It has been frequently obvious in our experience, that subjects "4" and "5" were thinking of the same response, but with "4's" use of it, added pressure was brought on "5" and while he was stumbling and searching for an alternative, his particular stress would be further compounded by the investigator's chiding and goading him to hurry up. The number of words used is variable. Generally, for a group of 5 subjects, about 25 words are sufficient to provide 10 min worth of emotional stress.

In sessions where successive days of stress inducement are required, and all panelists have come to know each other well, the placing of the individuals in different subgroups each day is helpful. In so doing, the individual does not have the opportunity to become relaxed in the presence of familiar coparticipants and an atmosphere of novelty is maintained. A given group of 5 subjects on a given day will usually and quite rapidly develop its own "personality." The investigator must be attuned to this and must attempt to create and foster a "group electricity" drawing the more shy and reticent personalities into participation while permitting the more boisterous types to mentally "run loose." It is imperative that each individual is forced to interact with and relate to his coparticipants. Initially, our approach had been to maintain rigid control over decorum in the sessions, and to discourage idle chatter among the subjects. However, as gauged by the single most important endpoint, the amount of sweat produced, such control has appeared unimportant and, in fact, it may be detrimental to the goal's attainment. The successful investigator might more aptly be described as an instigator, a panel moderator, an aggravator, and a catalyst. He must be alert and adaptable during every moment of these sessions, questioning, ridiculing, badgering, feigning shock, or embarrassment at responses and using one subject in the group against the other as the situation momentarily arises.

Some variations of the Word Association List have been employed, particularly against groups of subjects, to stimulate or maintain mental anxiety. For the most part, these have been in the form of questions wherein one individual's response is governed by his predecessor's response. For example, individuals might be required, in turn, to name a flower with the provision that whatever flower he names begins with a letter of the alphabet which is subsequent to, but not necessarily immediately following, that which his predecessor named. The alphabet is considered nonending, with a-b-c following x-y-z. "Skips" of more than 5–8 letters (e.g., daffodil–rose) should not be permitted because individuals can thereby take the pressure off themselves. This method's effectiveness resides in spontaneously and unexpectedly removing a given subject's planned response. For example, if subject 1 says "lily," subject 3 may plan on saying "orchid," but when subject 2 says "petunia," subject 3's response is disallowed and he must instantly search for another. By the panel moderator's usual goading, insistence on rapid response and staccato tempo, anxiety is produced.

With this method, any number of alternatives for "flower," such as men's given names, edible animals which live in water, vegetables, states of the United States, Shakespearean plays, etc., may be used. The limitations of the topics and the various ways in which they can be effectively used are set only by the investigator's imagination.

Of the several methods described above, the Word Association List has been the most useful. It is easy and rapid to administer to any subject and it provides a powerful stimulus for emotional sweating for the greatest number and variety of subjects. Equally important is the aspect that it can be applied to a number of subjects simultaneously.

C. METHODS FOR MEASURING EMOTIONAL SWEAT OUTPUT

Two methods for measuring the sweating response to emotional stress have been examined.

1. *Electronic hygrometry instrumentation:* A number of ways for measuring sweating using instrumentation which is sensitive to the presence of water have been explored through the years. These various means have been reviewed by Bakiewicz (5). One of the more recently devised instruments, which has been used in these studies, was developed by Dobson and Slegers (6). The instrument was found to be a highly sensitive and useful research tool, particularly for the study and characterization of individual emotional sweating patterns. Through it, several important parameters of the course of emotional sweating were revealed early in these studies. First, despite the absence of a deliberate emotional stimulus, an individual generally exhibits some level of sweating at the beginning of the test period which is higher than his subsequently determined ambient unstimulated level. Second, in order to begin a controlled emotional stimulus period at the point where the subject is as mentally unstimulated as possible, an initial 20-min calm-down period is necessary. During this calm-down period, subjects will exhibit, on average, an ambient sweat rate of about 0.2–0.3 μl/min/0.75 in. Third, upon administration of an effective emotional stress stimulus, sweating greatly increases immediately. Fourth, even in the most responsive individuals, it is difficult for the investigator to maintain an effective emotional stimulus for much longer than 10 min. These characteristics are illustrated in Fig. 1.

Although the water-sensing instrument provided valuable information about events occurring during an individual subject's emotional sweating course, it has been found wanting for routine sweat output measurements. These shortcomings are founded partly in its need for time for regular instrument calibration, but principally because one can simultaneously obtain data from only as many subjects as instrumental set-ups are available.

2. *Sweat-absorbent axillary pads:* The use of tared absorbent Webril®*pads, which are held in place in the axillae by the subject during the emotional stress period, has been adopted directly from thermal stress studies (7, 8). In those studies, it is customary to use 4 × 7 in. pads throughout the several (usually 4) 20-min collection periods. (Generally, sweat pads from the first two 20-minute periods are discarded because of erratic sweating rates (9).) In these studies, the subjects first wash and blot dry their axillae. Then, as found necessary in the water-sensing instrumentation studies described above, a 20-min calm-down period follows. During this time, the subjects sit quietly with the 4 × 7 in. pads held in their axillae. These pads are discarded. For the immediately subsequent emotional stress period, which lasts for 10 min, a substantially smaller pad measuring 2 × 4 in.is placed directly in the center of the axillary vault. This pad size, chosen initially so as to minimize tare weight in the event that small volumes of sweat were obtained, is quite adequate for the valid and reflective collection and measurement of emotional sweat excretion. To determine sweat output, the pads are retrieved from the axillae, placed in sealable plastic bags† and subsequently reweighed. As is known from thermal studies, this method is rapid and reliable and, most important, it permits obtaining data from a number of subjects simultaneously.

*Kendall Co., Fiber Prod. Div., Walpole, MA.

†Ziploc® Bags, The Dow Chemical Co., Indianapolis, IN.

RESULTS AND DISCUSSION

The utility and the value of a method for stimulating and measuring emotional sweat output depends on first, that protocol's capability to generate meaningful amounts of axillary sweat output from subjects during a short period of time, and second, the protocol's demonstrable effectiveness in generating those substantial sweat volumes repeatedly when used against the same subjects on a daily basis.

Using the Word Association List method for 10 min daily on 5 consecutive days against the same 20 subjects (groups of 5 each), the following sweat output amounts for untreated axillae, as collected via absorbent pads, were obtained (Table I).

Table I
Emotional Sweat Output From Untreated Axillae

Subject	$\bar{x} \pm$ SD (mg) Daily	
	Right	Left
1	502 ± 149	447 ± 131
2	795 ± 248	741 ± 288
3	350 ± 84	262 ± 72
4	1411 ± 215	1561 ± 192
5	763 ± 204	871 ± 249
6	906 ± 239	742 ± 243
7	914 ± 117	1051 ± 136
8	367 ± 131	438 ± 139
9	492 ± 201	485 ± 180
10	340 ± 86	352 ± 92
11	1097 ± 120	1179 ± 146
12	716 ± 126	481 ± 157
13	348 ± 76[a]	369 ± 21[a]
14	854 ± 76	743 ± 216
15	243 ± 76	99 ± 15
16	497 ± 273	302 ± 171
17	206 ± 117	340 ± 136
18	148 ± 92	211 ± 37
19	241 ± 53	217 ± 87
20	111 ± 55	80 ± 64

[a]Average for 4 days only.

Table II
ANOVA of Data in Table I

Source of Variation	DF	SS	MS
Replication	19	30.7310	1.6174
Sides (left vs. right)	1	0.0722	0.0722
Residual error	19	1.6219	0.0854

Table III
Total Daily Sweat Output (mg/axillae) For a Group of 20 Subjects

Monday	19,276 mg
Tuesday	21,513 mg
Wednesday	23,701 mg
Thursday	22,353 mg
Friday	23,458 mg (19 subjects only)
Average daily output per subject: ~ 1100mg	

The data in Table I indicate that there is a very high average daily sweat output volume by most of the 20 subjects. This volume, averaging 1100 mg/subject, is especially underscored when one considers the collection conditions of ambient temperature and 10-min collection periods. By contrast, in thermal stress studies, where collection conditions employ 100°F temperature and a 20-min collection period, representative sweat outputs corrected to a 10-min collection period are in the order of 500–600 mg/subject. Furthermore, an analysis of variance of these data in Table I, as calculated by the SSEM method of Wooding and Finklestein (2), has shown that the average residual mean squares error for the 5 days is 0.0854 (Table II). With the commonly used thermal stress procedure for stimulating sweat output, mean squares errors of 0.03 to 0.05 are not infrequently observed. Comparatively, the use of emotional stress has introduced a larger variance into the estimation of sweat output. This observation is not entirely unpredictable if one considers the uncontrollable factors involved in stimulating an excited emotional state. While continued experience with this procedure would be expected to reduce this variance somewhat, the variance observed to date does not preclude its usefulness in estimating sweat output and the effects of substances, such as antiperspirants, on the eccrine sweat gland.

The apprehension that sustained high levels of emotional stress and sweating might not be maintainable in subjects for 5 consecutive days is completely abrogated when one considers the sweat output for the entire group of 20 subjects through the course of this study (Table III). In fact, the highest daily output might well have been realized on the last day had one subject not been absent.

The data in Table I, and the implications thereof, dramatize several important points. First, as has been recently summarized by Shelley and Hurley (10), a number of investigators have observed and commented upon the contribution of emotional stress to axillary sweating. Those authors, themselves, have suggested that the lack of effectiveness of an antiperspirant might be due to its being washed away from its site of action in the sweat gland by emotionally derived sweating. As seen from the data presented above, the need for considering the copious sweating, which can originate from emotional stress when undertaking antiperspirant efficacy testing, is now clear. Second, a method for testing antiperspirant efficacy against this type of sweating may be available.

SUMMARY

Several methods were examined for their ability to stimulate emotional sweating in humans. One of these methods, mental arithmetic, was found to be a powerful stimulus *per se*, but only for some subjects. A second method, the Word Association List, was

found to be at least equally as powerful as mental arithmetic, but more important, it could be used successfully against approximately 75 per cent of the subjects studied.

For the actual measurement of emotional sweat output, 2 methods were examined. One of these, a water sensing instrument, was sophisticated, sensitive, and accurate for quantitating minute volumes of sweat output, but was impractical for obtaining data from subjects simultaneously. Alternatively, sweat absorbent Webril pads, as routinely used in axillary thermal stress studies, were found quite suitable for collecting and measuring emotionally stimulated axillary sweat.

Through the use of the Word Association List method for sweat stimulation and the axillary absorbent pad for sweat collection, it was found that a panel of 20 subjects in groups of 5 could be induced to sweat emotionally for 5 consecutive days. Emotional sweat output was, in fact, very high, averaging 550 mg/10 min/collection pad in the axilla each day at ambient temperature as compared to 250–300 mg/10 min/pad seen under thermal stress. Thus the substantial contribution of emotional sweating to axillary sweating has now been established, and, more important, a method to test the efficacy of antiperspirants for controlling this heavy sweating is now available.

ACKNOWLEDGMENT

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Quantitative Auswertung von p_H-Änderungen der Kinderhaut nach Applikation von Sonnenschutzemulsionen

UDO-ANGRESIUS HOPPE*, HANS-JOACHIM KOPPLOW*, HANS-WILHELM KREYSEL**

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Synopsis—p_H-Changes on Infant Skin Following Application of Sunscreening-Emulsions—a Quantitative Evaluation. — Variations of p_H in the stratum corneum following the application of different fluid O/W emulsions have been studied on healthy skin of 24 one to eight-year old children of both sexes. The p_H of the tested emulsions was 6.6 and 8.5 respectively. As proven by statistical analysis these emulsions induced highly significant shifts of p_H on the treated skin areas for a period of three hours after application. It is been demonstrated with the aid of the Kolmogorow-Smirnow test that the frequency distribution of the p_H values may be described by a Gaussian distribution, i. e. the proton concentration of children's skin exhibits a logarithmic normal distribution. The pharmaco-kinetics of the p_H-shifts caused by the different emulsions may, with a high degree of statistical safety, be represented by Bateman functions. The regression-equations of these functions quantitatively describe the absorption and elimination processes. From the dermatological point of view the weakly acidic emulsion appears preferable to the alkaline one because the induced p_H-shift on the treated skin is less pronounced.

I. Einführung

Die Beschreibung einer kosmetischen Wirkung sollte immer unter zwei Voraussetzungen erfolgen.

1. Definition der kosmetischen Wirkung nach objektiven Gesichtspunkten und unter phänomenologischer Betrachtungsweise; Berücksichtigung der physikalischen und biochemischen Parameter und Dimensionen zur Be-

* Zentrale Forschung/Biophysik Beiersdorf AG — Hamburg
** Universitätshautklinik — Hamburg

stimmung dieser Wirkung unter der Maxime, den Effekt möglichst praxisnahe beschreiben zu können und Aufbau von geeigneten Meßsystemen mit entsprechender Datensammlung.

2. Datenauswertung und Zukunftsforschung.

Die meist sehr kleinen kosmetischen Effekte mit kontrollierenden, regulierenden und schützenden Funktionen lassen sich im Verhältnis zur Gesamtleistung der lebenden Haut nur sehr schwer vom Untergrundrauschen separieren, weil im Gegensatz zur Arzneimittelwirkung die Beeinflussung eines gesunden Zustandes in einem stark streuenden, individuell sehr variationsfähigen System untersucht werden soll. Betrachtet man den Aufwand, mit dem die starken Arzneimittelwirkungen nachgewiesen werden, d. h. das Überführen des kranken Zustandes in einen Bereich, der als der normale gilt, dann ist leicht einzusehen, wie schwer es ist, die kleinen kosmetischen Wirkungen mit einer großen statistischen Sicherheit nachzuweisen. Es handelt sich nicht nur um das Problem, Signale aus der sich laufend verändernden lebenden Haut herauszufiltern, sondern es ist auch ein Problem angewandter Zukunftsforschung, weil es gilt, eine Aussage mit großer statistischer Sicherheit über ein Ereignis zu machen, das der Verbraucher bei der Anwendung eines kosmetischen Präparates in einer unbestimmten Zukunft an sich selbst erlebt. Nach den Gesetzen der mathematischen Statistik bedeutet dies, daß mit einer Sicherheit von mehr als 95 % (entsprechend einer Irrtumswahrscheinlichkeit von weniger als 5 %) die Häufigkeitsverteilung aller Werte der behandelten Situation sich signifikant von der analogen Häufigkeitsfunktion der unbehandelten Hautsituation unterscheidet. Dieses scharfe Kriterium gibt die Sicherheit an, mit der das gefundene Ergebnis bei der Wiederholung der Versuche in einer fernen Zukunft reproduzierbar ist. So kann zum Beispiel das biologische Ereignis „Tod" für ein größeres Kollektiv mit größter Wahrscheinlichkeit nach der Weibull-Verteilung vorausberechnet werden. Ähnliche Gesetzmäßigkeiten gelten auch für andere, nicht so bedeutende Wirkungen. Daher ist die Lösung solcher Probleme meist nur mit Computerhilfe möglich. Es ist selbstverständlich, daß alle Meßwerte mehr Informationen liefern können als die sogenannten Mittelwerte, die als Zusammenfassung der biologischen Antwort häufig eine Aussage verbergen.

3. Problem

In dieser vergleichenden Untersuchung soll der Einfluß von 2 Emulsionen auf die Haut-p_H-Werte für eine spezielle Kinderaltersgruppe von ca. 1—8 Jahren beschrieben werden.

Als Emulsionsbasis wurden unter der Bezeichnung A (acid) eine nichtionogene O/W-Emulsion mit polyäthoxylierten Fettsäureestern (p_H von A: 6,6) und unter der Bezeichnung B (basic) eine ionogene O/W-Triäthanolammoniumstearat-Emulsion (p_H von B: 8,5) ausgewählt. Es sollte lediglich die dermatologische Eignung der beiden Emulsionstypen in Abhängigkeit von p_H-Wert untersucht werden. Über das Ausmaß der Lichtschutzwirkung soll eine zweite Studie angefertigt werden.

II. p_H-Werte auf Kinderhaut

Über die p_H-Werte der menschlichen Haut ist nach den Arbeiten von HEUSS (1) und MARCHIONINI (2) viel publiziert worden. Eine Dissertation über das Thema „Zur Alkalineutralisation von Kindern und Kleinkindern" wurde von RINDERMANN (3) vorgelegt. Die unterschiedlichen p_H-Werte der Haut werden im wesentlichen auf die Wechselwirkung von organischen Carbonsäuren (Milchsäure, Kohlensäure, Pyrrolidoncarbonsäure, Urocaninsäure etc.) mit verschiedenen Basen (Na^+, K^+, NH_4^+ etc.) zurückgeführt. Aminosäuren und Peptide puffern das geschilderte komplexe Gemisch ab; HERRMANN, IPPEN, SCHÄFER (4). Über die Inhaltsstoffe des Schweißes gibt das Buch von FIEDLER (5) erschöpfend Auskunft.

Im physikochemischen Sinn gilt der p_H-Wert nur für reine, verdünnte wäßrige Lösungen. Aus diesem Grund bedeutet eine Messung des „negativen Logarithmus der Wasserstoffionenkonzentration" in dem Wasser-Lipid-Film der Hautoberfläche eine grobe Vereinfachung. Hinzu kommt, daß Wasserstoffionen oder Protonen kleine Elementarteilchen sind, die unmeßbar schnelle Reaktionen ausführen können. Demzufolge zielt im Zuge der geschilderten Vereinfachung die Frage auf das Protonengefälle von langsamen bzw. übergeordneten Reaktionen.

1. Alters- und Geschlechtsverteilung

Die Untersuchung wurde an 24 hautgesunden Kindern (10 Mädchen und 14 Jungen) im Alter von 1—8 Jahren an den ventralen Seiten der Unterarme durchgeführt. Die Kinder unterlagen keiner Selektion (Zufallsauswahl). Die Altersverteilung ist in *Abb. 1* dargestellt. Nach dem KOLMOGOROW-SMIRNOW-Test waren Alter der Jungen ($\bar{x}$ = 4,7 a; s = 1,56 a) und Mädchen ($\bar{x}$ = 4,8 a; s = 2,11 a) normal verteilt. Die Superposition der beiden Einzelverteilungen ergab die dargestellte Häufigkeitsverteilung des Lebensalters, das im Maximum bei 4,7 Jahren lag. Der jüngste Proband war 1,8 und der älteste 8,1 Jahre alt.

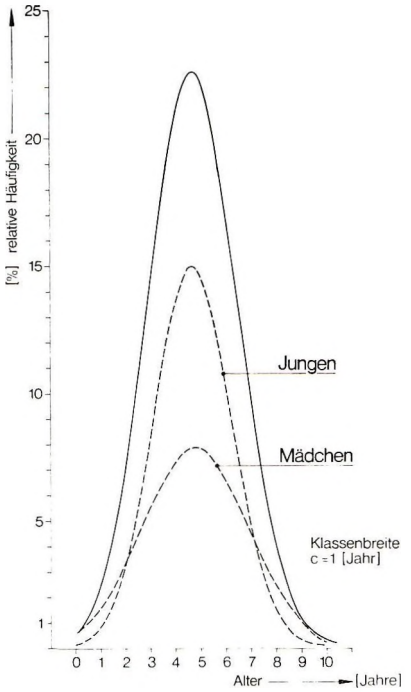

Abbildung 1

Altersverteilung der Kinder

2. Auftragsgewohnheiten

Die Präparate A und B wurden im Doppelblindversuch durch eine Betreuerin auf die Unterarme mit dem Finger appliziert. Auch diese Mengen lassen sich nach dem erwähnten KOLMOGOROW-SMIRNOW-Test durch eine Gauß'-sche Normalverteilung beschreiben. Zwischen den Mittelwerten der aufgetragenen A- und B-Emulsionen lagen nach dem t-Test (nach STUDENT) keine signifikanten Unterschiede vor. Beide Auftragsmengen ließen sich zusammenfassen. Der Mittelwert betrug $\bar{x} = 410$ mg/Unterarm; Standardabweichung $s = 25$ mg/Unterarm. Wegen der unterschiedlichen Größenverhältnisse wurde auf eine Ausmessung in cm^2 verzichtet.

3. Meßapparatur

Die p_H-Messungen wurden ausschließlich mit Glaselektroden, die neben der zentralen Glasmembran auf 4 Seitenarmen die Diaphragmen einer Bezugselektrode aufwiesen (6) durchgeführt, so daß ein guter Kontakt auf der Hautoberfläche gewährleistet war. Die Elektroden wurden, um Verschmutzung durch Lipide und Emulgatoren auszuschließen, zwischen den Messungen im Ultraschallbad gereinigt.

Die Anzeige erfolgte durch ein digitales p_H-Meter auf 2 Stellen nach dem Komma (kommerzielles Gerät). Um eine einwandfreie Datensammlung und statistische Analyse zu gewährleisten, wurde durch Umbau an den digitalen Ausgang (BCD) ein Drucker angeschlossen, der durch eine selbstgefertigte, programmierbare Zeiteinheit gesteuert wurde. Nach längeren Vorversuchen hatte sich folgendes Intervall sehr bewährt: pro Meßsituation wurden 1 Minute lang, jeweils im 6-Sekunden-Abstand, 10 Haut-p_H-Werte erfaßt und ausgedruckt. Auf diese Weise wurden 480 p_H-Werte der unbehandelten Unterarm-Innenseiten (links und rechts) gewonnen. Wegen der großen Anzahl von Einzelwerten wurde ein χ^2-Test auf Normalverteilung durchgeführt. Die p_H-Werte erstreckten sich vom $p_H = 4{,}46$ bis $p_H = 6{,}25$ und ließen sich mit größter Näherung durch eine Normalverteilung beschreiben. Der Mittelwert der unbehandelten kindlichen Haut lag bei $p_H = 5{,}354$, und die Standardabweichung betrug $s = 0{,}348$ (p_H-Einheiten).

In gleicher Weise wurden die p_H-Werte nach Behandlung mit den Emulsionen A und B registriert. Zu folgenden Zeiten wurden Messungen vorgenommen: 5, 10, 20, 30, 45, 60, 80, 90 und 160 Minuten nach Behandlung. Von jedem Präparat wurden zu den angegebenen Zeitpunkten 240 Einzelwerte gemessen, wobei bemerkt werden muß, daß der Meßvorgang jeweils eine Minute dauerte. Eine solche Momentaufnahme ist in *Abb. 2* dargestellt.

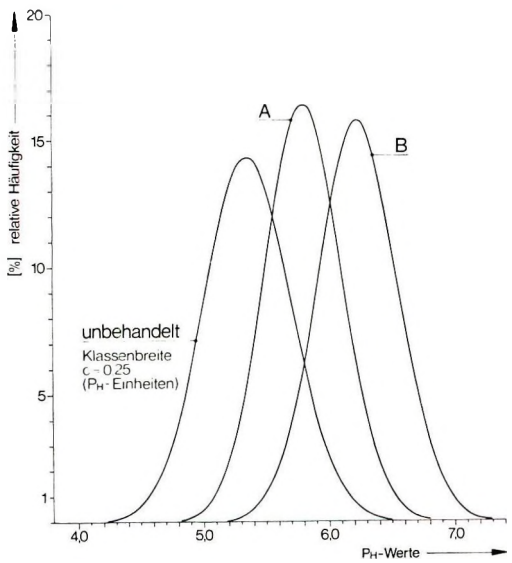

Abbildung 2

p_H-Werte-Verteilung 30 Minuten nach Applikation der O/W-Emulsion A und B auf Kinderhaut

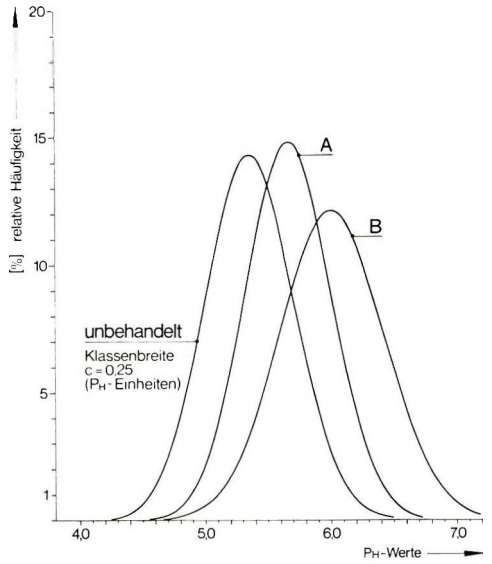

Abbildung 3

pH-Werte-Verteilung 60 Minuten nach Applikation der O/W-Emulsion A und B auf Kinderhaut

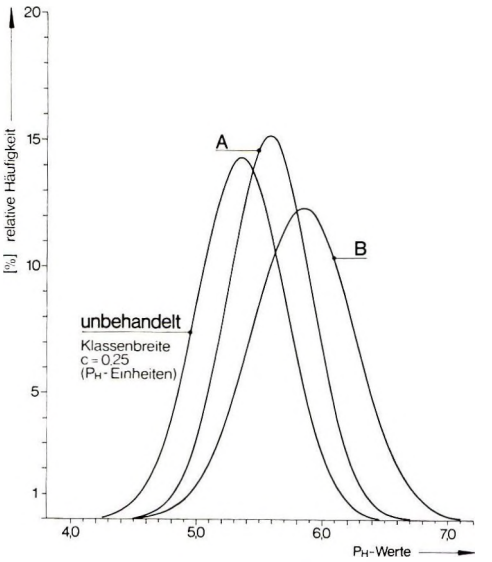

Abbildung 4

pH-Werte-Verteilung 90 Minuten nach Applikation der O/W-Emulsion A und B auf Kinderhaut

Zwischen den unbehandelten und den durch die Emulsionen A und B erzielten p_H-Verteilungen liegen nach 30 Minuten hochsignifikante Unterschiede vor. Auch die p_H-Wert-Verteilungen nach A- und B-Applikation unterscheiden sich mit einer statistischen Sicherheit, die größer ist als 99,9 %, voneinander. Im Zuge der Zeit nach der Behandlung bewegen sich die durch A und B hervorgerufenen Verteilungen langsam in Richtung zur unbehandelten Situation. *Abb.* 3 stellt das Ergebnis 60 Minuten nach der einmaligen Applikation dar. Immer noch liegen zwischen allen Verteilungen hochsignifikante Unterschiede vor.

Die Situation läßt nach 90 Minuten *(Abb. 4)* eindeutig den zeitlichen Ablauf in Richtung zur unbehandelten Haut erkennen; hochsignifikante Unterschiede zwischen den Verteilungen herrschen nach wie vor.

4. *Kinetik einer kosmetischen Wirkung*

Bei der Betrachtung natürlicher Fließgleichgewichte (steady state) geht man von vereinfachten Modellen aus, wie es z. B. in *Abb.* 5 dargestellt wurde. Dieses Grundmodell sieht ein Applikationskompartiment vor, aus dem mit der Geschwindigkeitskonstanten k_1 die Invasion des Wirkstoffes in das Meß-

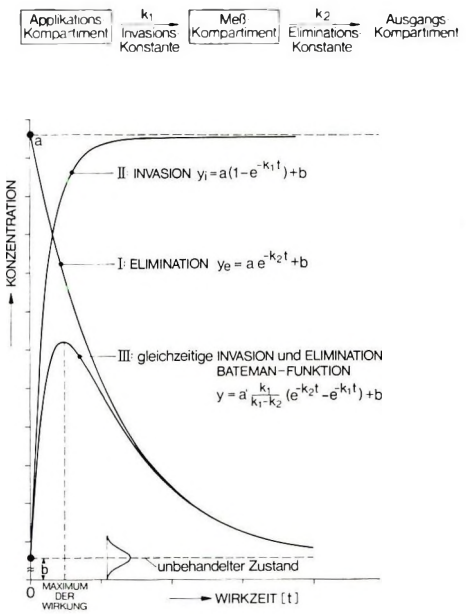

Abbildung 5

Verlauf einer konzentrationsabhängigen, biologischen Wirkung

kompartiment erfolgt. Aus dem Meßkompartiment wird mit der Geschwindigkeitskonstanten k_2 der Wirkstoff in ein hier nicht zu berücksichtigendes Ausgangskompartiment eliminiert. Dieses Modell hat den großen Vorteil, gleichzeitig Invasion und Elimination als Prozesse erster Ordnung zu betrachten. Die Superposition der beiden Terme, die die Elimination und die Invasion beschreiben, wird BATEMAN-Funktion genannt. Sie wurde ursprünglich für die Beschreibung des radioaktiven Zerfalls von einer Muttersubstanz in eine ebenfalls radioaktive Tochtersubstanz von BATEMAN entwickelt. Diese Gleichung hat inzwischen eine fundamentale Bedeutung in der Pharmakinetik erlangt, weil hiermit quantitativ die „Auseinandersetzung zwischen Organismus und einverleibtem Pharmakon" beschrieben werden kann (7). Die *Abb. 5* zeigt die reine Elimination eines Wirkstoffes (I), die reine Invasion (II) und den gesamten kinetischen Vorgang (III). Mit der Wahl dieses mathematischen Modells für die Kinetik des p_H-Ablaufs nach Applikation der Emulsionen A und B auf Kinderhaut wurde intuitiv der wichtigste Schritt vollzogen. Mathematisch werden BATEMAN-Funktionen vorzugsweise durch Analogrechner bestimmt, in denen elektrische Entladungsvorgänge Elimination bzw. Invasion simulieren. Um die BATEMAN-Funktion als Regressionsgleichung aus den vielen hundert Meßdaten mit einem Digitalrechner zu ermitteln, ist großer mathematischer Aufwand erforderlich. Es müssen zunächst Hilfsfunktionen berechnet werden, die anschließend mit Hilfe des Iterationsverfahrens optimiert und in die BATEMAN-Funktionen umgerechnet werden. Die Güte der Anpassung wird mit Hilfe des Bestimmtheitsmaßes B geprüft. Bei 100 % Übereinstimmung der Merkmalswerte mit der vorgegebenen Funktion wird B = 100 %. Dies wird natürlich bei streuenden Werten niemals erreicht. Nach JOHN (8) können Regressionsrechnungen mit einem Bestimmheitsmaß von 80 % und mehr als hinreichend genau bezeichnet werden.

5. *Quantitative Beschreibung des p_H-Ablaufs auf Kinderhaut*

Die Daten der Tabellen 1 und 2 wurden zur Berechnung der Regressionsgleichung für die aus dem Nullpunkt parallel zur Abszissenachse verschobenen BATEMAN-Funktion verwendet.

$$y = \frac{k_1 \cdot y_k}{k_1 - k_2} \left[e^{-k_2 t} - e^{-k_1 t} \right] + y_0$$

Die *Abb. 6* zeigt das Ergebnis. Wegen der zeitbeanspruchenden Rechenvorgänge wurden die BATEMAN-Funktionen für die Mittelwertverteilungen der durch die Emulsionen A und B erzielten p_H-Werte aufgestellt. Mit Bestimmtheitsmaßen von B_A = 99,8 % und B_B = 98,3 % konnten die beiden

Tabelle 1

Min	p_H	s (p_H)	N
5	5,85	0,30	240
10	5,91	0,32	240
20	5,91	0,31	240
30	5,80	0,30	240
45	5,78	0,32	240
60	5,66	0,34	240
80	5,62	0,32	240
90	5,68	0,33	240
160	5,39	0,34	240

unbehandelt ($t = 0$) $p_H = 5{,}354$; $s = 0{,}348$ (p_H)

p_H-Werte auf Kinderhaut nach Applikation der O/W-Emulsion A

Tabelle 2

Min	p_H	s (p_H)	N
5	6,32	0,35	240
10	6,39	0,35	240
20	6,40	0,33	240
30	6,23	0,32	240
45	6,22	0,34	240
60	6,02	0,41	240
80	5,89	0,37	240
90	5,87	0,40	240
160	5,42	0,33	240

p_H-Werte auf Kinderhaut nach Applikation der Emulsion B

Regressionsgleichungen berechnet werden. Die meßtechnisch erfaßbaren Invasions- und Eliminationsprozesse der p_H-Wertänderungen von Kinderhaut beschreiben quantitativ das gewissermaßen „makroskopische" Wirksamkeitsmaximum, das erst nach ca. 22—23 Minuten erreicht wird. Über die Ursachen kann man nur Vermutungen anstellen (Gleichverteilung, Pufferwirkung, Hauttopographie). Vorauseilende, sehr schnelle Reaktionen der Protonen können natürlich nicht erfaßt werden.

Berechnet man aus den angegebenen BATEMAN-Funktionen die p_H-Werte aus den Eliminationsgleichungen zum Zeitpunkt $t = 0$ bzw. aus den Invasionsgleichungen zum Zeitpunkt $t \to \infty$, so findet man für A den p_HWert =

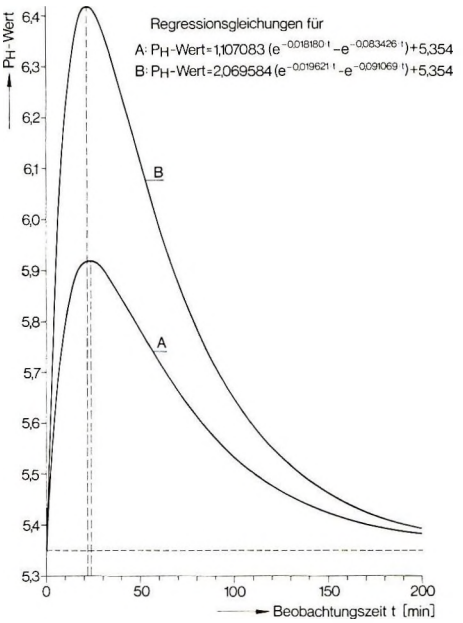

Abbildung 6

Kinetik des p_H-Ablaufs nach Applikation der Emulsionen A und B an Kinderhaut (Unterarm-ventral)

6,4 und für B den p_H-Wert = 7,4, die sehr gut mit den p_H-Werten der geprüften Emulsionen übereinstimmen, obwohl im Verlauf der Untersuchung immer nur die Wechselwirkung zur Kinderhaut gemessen wurde.

Aufgrund der p_H-Wertbelastung ist vom dermatologischen Standpunkt aus die Emulsion A bei der Anwendung an Kindern der Emulsion B vorzuziehen. Diese Aussage bezieht sich lediglich auf den p_H-Einfluß. Über das Ausmaß der Lichtschutzwirkung der beiden Emulsionen bietet diese Untersuchung keinen Hinweis.

III. Zusammenfassung

An 24 hautgesunden Kindern beiderlei Geschlechts im Alter von eins bis acht Jahren wurden die p_H-Wert-Änderungen der Hornschicht nach Behandlung mit verschiedenen O/W-Emulsionen untersucht. Die flüssigen Emulsionen, die auf die p_H-Werte von 6,6 bzw. 8,5 eingestellt waren, riefen hochsignifikante Änderungen der p_H-Situationen innerhalb der ersten drei Stunden hervor. Dies wird durch mathematisch-statistische Analysen belegt.

Es wurde gefunden, daß die Häufigkeitsfunktionen der p_H-Werte auf Kinderhaut durch GAUSS'sche Normalverteilungen nach Prüfung durch den KOLMOGOROW-SMIRNOW-Test bzw. χ^2-Test auf Normalverteilung beschrieben werden können. Für die Protonenkonzentration der Kinderhaut bedeutet dies, daß eine logarithmische Normalverteilung vorliegt.

Der gesamte pharmakokinetische Vorgang läßt sich mit großer statistischer Sicherheit durch BATEMAN-Funktionen wiedergeben, deren Regressionsgleichungen die Invasions- und Eliminitionsprozesse quantitativ beschreiben. Vom dermatologischen Standpunkt aus ist aufgrund der p_H-Wert-Verschiebung die schwach saure Emulsion der alkalischen Emulsion vorzuziehen.

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Determination of vitamin E in cosmetic products by gas-liquid chromatography (GLC)

E. PATRICIA SHEPPARD and MARTIN J. STUTSMAN *Division of Cosmetics Technology, Food and Drug Administration, U.S. Department of Health, Education, and Welfare, Washington, D.C. 20204.*

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Synopsis

VITAMIN E is being incorporated into an increasing number of COSMETIC PRODUCTS. Because some adverse reactions have been reported following the use of some of these products, a method for isolating and determining vitamin E in cosmetics has been developed. The vitamin E analogs investigated, *d*-α-TOCOPHEROL and *d*-α-TOCOPHERYL ACETATE, were added to vanishing cream, shampoo, and bath oil at 3 use levels. After preparation of these samples, the compounds were determined by GAS-LIQUID CHROMATOGRAPHY (GLC) using a glass column packed with Gas-Chrom Q coated with SE-30. Dotriacontane was selected as the internal standard for quantitative measurement. *d*-α-Tocopherol and *d*-α-tocopheryl acetate were well resolved from dotriacontane, with relative retentions of 0.81 and 0.92, respectively. The recoveries of *d*-α-tocopheryl acetate ranged from 93 to 103 per cent with an average and standard deviation of 98 ± 5 per cent. Recoveries of *d*-α-tocopherol ranged from 91 to 102 per cent with an average and standard deviation of 97 ± 3.5 per cent.

INTRODUCTION

α-Tocopherol and α-tocopheryl acetate are the analogs of vitamin E most frequently encountered in cosmetic products. α-Tocopherol is often included as an antioxidant

whereas α-tocopheryl acetate is a feature ingredient in many cosmetics, and, as such, is usually present in relatively higher concentrations.

The recent popularity of vitamin E preparations for topical application, together with reports of adverse dermatological reactions linked to cosmetics containing this vitamin (1,2), led to concern about the desirability of including these compounds in such products. Therefore, a sensitive gas-liquid chromatographic (GLC) method was developed for their determination.

Vitamin E has been determined in other commercial preparations by GLC. Pillsbury *et al.* (3) measured vitamin E in pharmaceuticals by GLC on an 8 ft glass column packed with 5 per cent SE-30 on Gas-Chrom P. Their method involved external standardization, which necessitates daily construction of standard curves. Mahn *et al.* (4) determined vitamin E in multivitamin preparations by GLC on a 4 ft copper column packed with 10 per cent SE-30 on Aeropak 30. They selected dotriacontane (a C-32 hydrocarbon) as the internal standard and thus eliminated the need for calibration curves. They observed no differences between results obtained with metal or pyrex GLC columns. However, they worked with relatively large amounts (10–15 μg), and losses of α-tocopherol due to the metal column may not have been significant. Their analysis of multivitamin creams included a preliminary separation on alumina. Subsequently, Rudy and others (5) conducted a collaborative study on a method similar to the one developed by Mahn and coworkers. The study, although showing the method to be precise, did not establish accuracy because collaborators' results could not be compared to actual amounts present.

The procedure reported here incorporates the best features of these previous methods and includes modifications to decrease the time of analysis and to accommodate the small amounts of vitamin often present in complex cosmetic mixtures. It consists of preliminary extraction of the vitamin from cosmetics with organic solvents, adsorption chromatography on alumina with hexane and ether as the eluants, and determination by GLC on a 10 ft × 4 mm i.d. glass column packed with 5 per cent SE-30 on Gas-Chrom Q. Results were calculated by the method of internal standardization in which dotriacontane served as the internal standard.

EXPERIMENTAL

APPARATUS AND REAGENTS

Adsorption column: An aluminum oxide chromatographic column was prepared as follows: aluminum oxide,* 80–100 mesh, neutral certified Brockmann activity I, was brought to Brockmann activity III by thoroughly mixing 1 ml of water with each 8 g of aluminum oxide and allowing this mixture to equilibrate overnight in a sealed container. Eight g of the equilibrated aluminum oxide was then slurried in hexane and poured into a 1.5 × 30 cm glass chromatographic tube containing a glass wool plug and 25 to 30 ml of hexane. Hexane was drained to the level of the adsorbent. The level of liquid in the tube was not permitted to fall below the top of the alumina before or during the analysis.

*Fisher Scientific Co., 711 Forbes Ave., Pittsburgh, PA 15219.

Gas chromatograph: An F and M* model 810 gas chromatograph equipped with a flame ionization detector was used with the following operating conditions: temperatures: detector 348°C, injection port 300°C, oven 285°C; carrier gas flow (helium) 66 ml/min; maximum range and attenuation settings, 10 × 32 or such that 8 to 10 μg of *d*-α-tocopheryl acetate gave 50 per cent or greater recorder response.

GLC Column: The GLC column was prepared as follows: 80–100 mesh Gas-Chrom Q† was coated with approximately 5 per cent SE-30‡ by the funnel coating method (6). The support was packed in a 10 ft × 4 mm i.d. glass column using line vacuum and gentle vibration. The packed column was conditioned overnight at 285°C with no carrier flow and then at 285°C for 2 days with a carrier flow of 10 to 20 ml/min. The flow was raised to 66 ml/min, oven temperature was lowered to 200°C, and 50 μl of Silyl-8‖ were injected onto the column.

Stock solutions: Individual stock solutions of *d*-α-tocopherol,# *d*-α-tocopheryl acetate,# and dotriacontane** were prepared weekly by accurately weighing approximately 50 mg of each into separate 10 ml volumetric flasks and diluting to volume with hexane. Because *d*-α-tocopherol is easily air oxidized and is light sensitive, its stock solution was stored under nitrogen. When not in use, the stock solutions were refrigerated. Exposure to light can be minimized by using amber volumetric flasks or by wrapping the flasks with aluminum foil.

Solvents: Solvents were American Chemical Society (ACS) reagent grade, or equivalent.

PREPARATION OF COSMETICS

Known amounts of *d*-α-tocopherol or *d*-α-tocopheryl acetate in hexane were added to samples of the following cosmetics: a commercial bath oil; a bath oil containing Tween 61,††† isopropyl myristate, talc, and perfume oils; a vanishing cream containing stearic acid, cetyl alcohol, water, glycerol, KOH, NaOH, and perfume oil; a vanishing cream containing stearic acid, lanolin, Carbopol 934,*** methylparaben, ethylparaben, propylene glycol, water, triethanolamine, and perfume oil; and two commercial shampoos. The final preparations contained 0.1, 1, or 7 per cent *d*-α-tocopherol or *d*-α-tocopheryl acetate.

Because *d*-α-tocopherol is light-sensitive, it was added to the sample just prior to analysis and exposure to light during the analysis was minimized.

*F and M Scientific Corp., Avondale, PA 19311.
†Applied Science Laboratories, Inc., P.O. Box 440, State College, PA 16801.
‡General Electric Co., Schenectady, NY.
‖Pierce Chemical Co., P.O. Box 117, Rockford, IL 61105.
#Eastman Kodak Co., 343 State St., Rochester NY 14650.
**Analabs, Inc., 80 Republic Dr., North Haven, CT 06473.
†††Atlas Chemical Industry, Wilmington, DE.
***B.F. Goodrich Chemical Co., 6100 Oak Tree Blvd., Cleveland, OH 44131.

PREPARATION OF SAMPLES

Bath oil: An accurately weighed sample of bath oil containing a minimum of 1 mg of the compound being determined was diluted to several milliliters with hexane. Several μl of the diluted sample were injected onto the GLC column to check for dilution and interfering peaks. If interfering peaks were present, the sample was chromatographed, using the Adsorption Column Procedure. If interfering peaks were absent, an aliquot of internal standard solution was added such that the peak heights of the internal standard and the compound being determined were approximately equivalent ($\pm$10 per cent). The amount of internal standard to be added was estimated from the previous injection. The solution was then analyzed according to the GLC Procedure.

Skin cream: An accurately weighed sample of skin cream containing a minimum of 1 mg of the compound being determined was quantitatively transferred to a separatory funnel with 50 ml of warm water. The mixture was acidified with a few drops of concentrated HCl and extracted with five 20 ml portions of hexane. The extracts were combined and concentrated on a steam bath under a gentle stream of nitrogen. Several μl of the concentrated extract were injected onto the GLC column to check for dilution and interfering peaks. In some cases, the presence of large amounts of other cosmetic ingredients in the extract prohibited concentrating the extract sufficiently to permit measuring the vitamin. In these instances and when interfering peaks were present in the chromatogram, the extract was chromatographed, using the Adsorption Column Procedure. If interfering peaks were absent, an aliquot of internal standard solution was added to the extract such that the peak heights of internal standard and the compound being determined were approximately equivalent ($\pm$10 per cent). The amount of internal standard to be added was estimated from the previous injection. The solution was then analyzed according to the GLC Procedure.

Shampoo: An accurately weighed sample of shampoo containing a minimum of 1 mg of the compound being determined was quantitatively transferred to a separatory funnel with 25 ml of methanol-water (1:1) and extracted with five 20 ml portions of hexane-diethyl ether (1:1). The extracts were combined and evaporated to dryness on a steam bath under a gentle stream of nitrogen. Several ml of hexane were then added to the extract. A few μl of the hexane solution were injected onto the GLC column to check for dilution and interfering peaks. If interfering peaks were present, the extract was chromatographed, using the Adsorption Column Procedure. If interfering peaks were absent, an aliquot of internal standard solution was added to the extract such that the peak heights of internal standard and the compound being determined were approximately equivalent ($\pm$10 per cent). The amount of internal standard to be added was estimated from the previous injection. The solution was then analyzed according to the GLC Procedure.

Adsorption column procedure: Samples or extracts to be chromatographed were quantitatively transferred in 15 ml of hexane to the alumina adsorption column. The column was eluted with several small portions of hexane. Care was taken to ensure that the solvent level did not fall below the top of the alumina. Thirty ml of hexane were collected. When *d*-α-tocopherol was present, a second eluate of 25 ml diethyl ether was collected. *d*-α-Tocopheryl acetate was contained in the hexane eluate and *d*-α-tocopherol in the ether eluate. The ether eluate was evaporated to dryness on a steam bath under a gentle stream of nitrogen and redissolved in a few milliliters of hexane. An ali-

quot of internal standard was then added to the fraction(s) containing the vitamin such that the peak heights of the vitamin and internal standard were approximately equivalent (±10 per cent). The amount of internal standard to be added was estimated from a previous injection. The solution was then analyzed according to the GLC Procedure.

DETERMINATION

GLC procedure: Each day, a standard solution containing known amounts of the compound being determined and internal standard was prepared in hexane such that peak heights of the two compounds were approximately equivalent (±10 per cent). The standard and sample solutions were injected alternately, with at least 2 injections of each. Injection volume was adjusted so that peaks were 50 to 100 per cent full scale and of approximately equal height for sample and standard solutions at the appropriate range and attenuation setting.

Calculation: The weight of the unknown in the sample was calculated as follows:

$$\text{Weight (mg) unknown} = (\text{Ru/Rs}) \times \text{Ks} \times (\text{ISu/ISs})$$

where Ru is the ratio of the peak height of the unknown in the sample to that of the internal standard added to the sample; Rs is the ratio of the peak height of the known standard in the standard solution to that of the internal standard in the standard solution; Ks is the weight (mg) of known standard in the standard solution; ISu is the weight (mg) of the internal standard in the sample; and ISs is the weight (mg) of internal standard added to the standard solution.

RESULTS AND DISCUSSION

Mahn *et al.* (4) stated that more than 10 μg of α-tocopherol should be injected on the GLC column for acceptable results. However, we found that peak heights varied linearly with the amount injected over the range tested (2 to 8 μg) for *d*-α-tocopherol, as well as for *d*-α-tocopheryl acetate and dotriacontane, although intercepts were not always zero (Fig. 1). We selected this range because the amount of vitamin E in cosmetics may be quite small and because we prefer to determine peak heights rather than peak areas.

Several investigators (3–5) found that, prior to analysis, it was necessary to saturate the column with several injections of the compound being determined in order to obtain reproducible results. We observed that this step could be eliminated by a single injection of Silyl-8. This initial treatment of the column also improved sensitivity in the 0 to 4 μg range, presumably by preventing significant loss of sample through interaction with the support. Interaction of the vitamin with the support may explain why Mahn *et al.* recommended chromatographing 10 to 15 μg of the tocopherol.

The peak given by *d*-α-tocopherol was completely resolved from that of dotriacontane (Fig. 2). The resolution of the peaks of *d*-α-tocopheryl acetate and dotriacontane was 1.4. The retentions of *d*-α-tocopherol and *d*-α-tocopheryl acetate relative to dotriacontane were 0.81 and 0.92, respectively. The time for completion of the chromatogram was approximately 20 min.

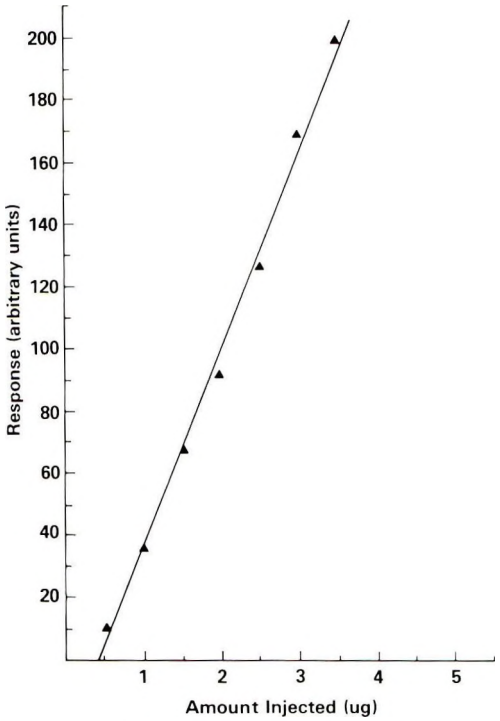

Figure 1. Relationship between weight of *d*-α-tocopherol and peak height response; 5 to 10 determinations for each point depicted

Table I shows the data obtained when 3 levels of *d*-α-tocopheryl acetate were determined in 3 cosmetics by this procedure. The average recovery was 98 per cent. An analysis of variance performed on these data supported the null hypothesis that there were no significant differences in recoveries with respect either to the level of vitamin or to the cosmetic class. Although the analysis showed that some of the sources of variation could be pooled to obtain a smaller estimate of variance, pooling was not done. The coefficient of variation was 5.1 per cent. This compares favorably with the 4.8 per cent given by Rudy *et al.* (5) for the precision of their collaborative study of α-tocopheryl acetate.

Values for the recoveries of *d*-α-tocopherol from cosmetics are given in Table II. The average recovery was 97 per cent. An analysis of variance demonstrated that there were no significant differences in recoveries between levels and cosmetic products. Sources of variation in these data could not be pooled to derive a better estimate of variance. The average recovery for the 0.1 per cent level was slightly lower than for the other levels, possibly due to oxidation during the course of the analysis. The coefficient of variation was 3.6 per cent. Rudy *et al.* calculated a coefficient of variation of 4.2 per cent when working with considerably larger amounts (approximately 0.2 to 1.0 g) than we did (1.0 to 30 mg). The apparent improvement observed may have resulted from treatment of the column with Silyl-8.

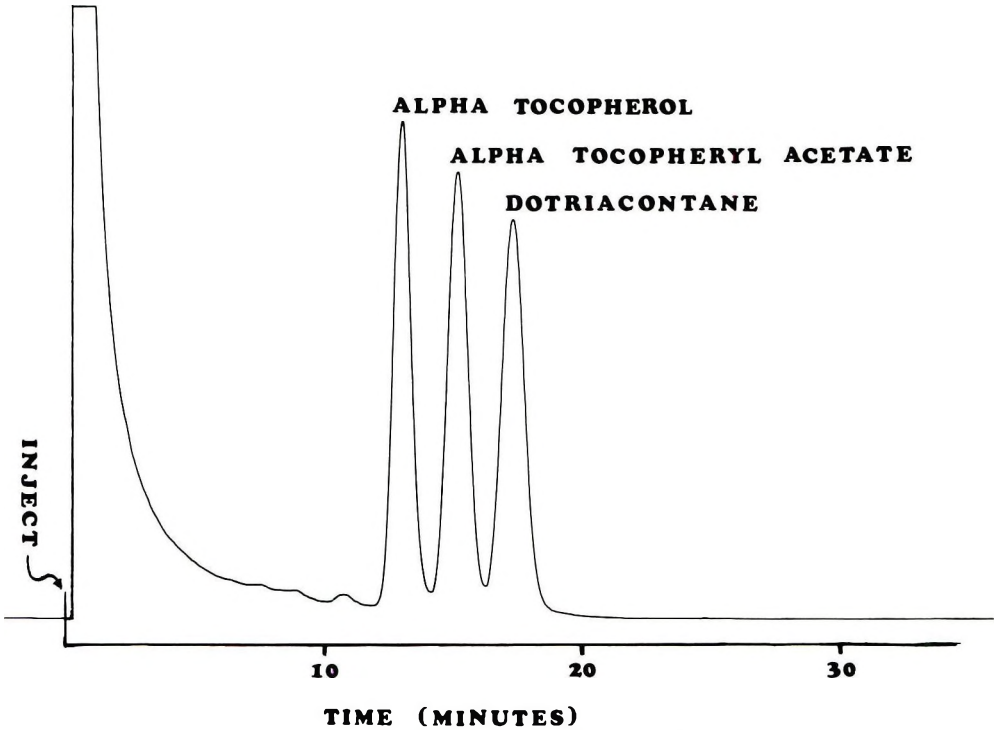

Figure 2. Chromatogram of α-tocopherol, α-tocopheryl acetate, and dotriacontane, obtained using conditions specified under GC and GLC Column

One source of variation in recoveries of the vitamin from shampoo resulted from the extraction procedure (see Tables I and II). Initially, this cosmetic was extracted with hexane from acidic aqueous solution. When the shampoo was extracted from 1:1 methanol-water with 1:1 hexane-diethyl ether, emulsification problems were eliminated and recoveries improved markedly.

Some commercial water-in-oil skin creams contained ingredients which had the same retentions as one form or the other of the vitamin and which were not removed by adsorption chromatography. More work on the separation procedure will be required before this type of sample can be analyzed by the method.

Because these ingredients could be mistaken for the vitamin, it is essential to identify the vitamin by means other than GLC retention. A qualitative thin-layer chromatographic method (7) is used in our laboratory. Samples on silica gel F-254 plates are developed with cyclohexane-diethyl ether (80:20) and the visualization is accomplished with shortwave uv light. α-Tocopherol and α-tocopheryl acetate can be identified as dark spots on a green fluorescing background with Rf values of 0.34 and 0.45, respectively. No interferences with this procedure have been noted.

The vitamin E content of several commercial cosmetics was determined by the GLC method. Recoveries of the vitamin from these products averaged 99 per cent of label claims.

Table I
Recoveries of α-Tocopheryl Acetate from Cosmetics

Vitamin Level (%)	Bath Oil		Cream		Shampoo	
	Added (mg)	Recovery (%)	Added (mg)	Recovery (%)	Added (mg)	Recovery (%)
7	140.0	93.0	66.1	108.9	58.6[a]	93.9
	140.0	95.1	66.1	99.5	58.6[a]	92.2
			66.1	101.7		
1	11.4	104.0	11.3	85.4	10.0[a]	89.3
	11.4	96.5	11.3	104	10.0[a]	85.4
			7.0	99	10.2[b]	98.0
			7.0	106	10.2[b]	96.0
			7.0	103	10.2[b]	97.0
0.1	2.3	100.0	1.0	96	3.9[a]	97
	2.3	100.9	1.0	96	3.9[a]	97
	2.3	103.8				
	1.0	100.0				
	1.0	100.0				
	1.0	100.0				

[a]Extracted with hexane from acidic aqueous solution.
[b]Extracted with hexane-ether (1:1) from methanol-water (1:1).

Table II
Recoveries of α-Tocopherol from Cosmetics

Vitamin Level (%)	Bath Oil		Cream		Shampoo	
	Added (mg)	Recovery (%)	Added (mg)	Recovery (%)	Added (mg)	Recovery (%)
7	16.5	90.3	29.8	99.0	21.0[a]	90.5
	16.5	97.0	29.8	96.0	21.0[a]	90.5
	8.5	100.0	29.8	92.0	21.0[a]	90.5
	8.5	100.0			12.8[b]	95.0
	8.5	100.0			12.8[b]	96.0
					12.8[b]	95.0
1	5.0	103.9	10.4	109.6	2.9[a]	100.0
	5.1	98.0	10.4	106.7	2.9[a]	103.4
	5.1	107.8	11.2	100.0		
			11.2	96.4		
			11.2	97.9		
0.1	2.5	92.0	1.0	87.0	1.0[a]	96.0
	2.5	92.0	1.0	91.0	1.0[a]	96.0
			1.2	93.2		
			1.2	93.2		
			1.2	93.2		

[a]Extracted with hexane from acidic aqueous solution.
[b]Extracted with hexane-ether (1:1) from methanol-water (1:1).

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Factors affecting the penetration of light through stratum corneum

JAMES L. SOLAN and KARL LADEN* *Gillette Research Institute. 1413 Research Boulevard. Rockville. MD 20850.*

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Synopsis

LIGHT TRANSMISSION values were obtained for isolated GUINEA PIG STRATUM CORNEUM exposed to WATER VAPOR, WATER, and ORGANIC LIQUIDS. Several of the variables involved, such as equilibration time, wavelength of light and REFRACTIVE INDEX of the liquids were examined. Increasing the RELATIVE HUMIDITY of the atmosphere surrounding the tissue resulted in a slight increase in light transmission, which was wavelength dependent. Immersion in water or other liquid produced a substantial increase in transmission. This effect increased with the refractive index of the liquid, reached maximum at the refractive index of stratum corneum, and then decreased.

INTRODUCTION

The skin of man and animals serves as a barrier to prevent the loss of moisture by the body and the entry of noxious chemicals and microorganisms. While there has been considerable interest by cosmetic scientists and dermatological researchers in how materials penetrate the skin and in means of altering the penetrability of the skin to applied chemicals, the penetrability of the skin to light and means of altering this penetrability is an area which has received less attention. This paper deals with treatments, which can enhance the penetration of light into skin and, thereby, affect the choice of topical treatments and ingredients for cosmetic products.

Transmission of ultraviolet (uv) light by epidermis was first studied by Hasselbalch (1) in 1911. Subsequently, studies on whole epidermis and various epidermal layers were reported. However, these studies utilized specimens of skin from living or dead animals and humans and the reported transmission values varied considerably (2–4). It was Lucas (5), who in 1931 recognized that skin is not optically homogeneous and that incident light, in addition to being diffusely reflected at the surface, is irregularly refracted as it passes through the various layers of cells. He clearly demonstrated this

*Present address: Carter Products Division, Half Acre Rd, Cranbury, N.J. 08512.

optical heterogeneity by use of glycerol and acetic acid as clarifying agents. The light transmission of epidermis increased significantly after immersion in these liquids. Especially noticeable was the increased transmission of shorter wavelength light. Blum (6) in 1946 speculated that light scattering by stratum corneum might be influenced by skin moisture, although, he could not show an appreciable effect on the radiation erythema threshold after application of water to skin. In contradiction, Cattano (7) concluded that the increased sensitivity of occluded skin to sunlight was due to increased hydration of the skin. More recently, Kahn (8) mentioned enhanced erythema after immersing 2 subjects' arms in tap water for 1 h prior to irradiation. These results have been further substantiated by Owens, Knox, Hudson, and Troll (9) who reported that uv injury to mouse skin after 10 minimal erythemal doses (MED) was substantially increased if the animals were maintained at 80 per cent relative humidity (RH) instead of at 10 per cent RH. Also, the uv damage was more severe when the mice were immersed in water for 6 h or if rabbit skin was hydrated with wetpacks prior to irradiation.

This paper describes spectrophotometric studies on isolated stratum corneum subjected to treatment in water vapor, water and other liquids.

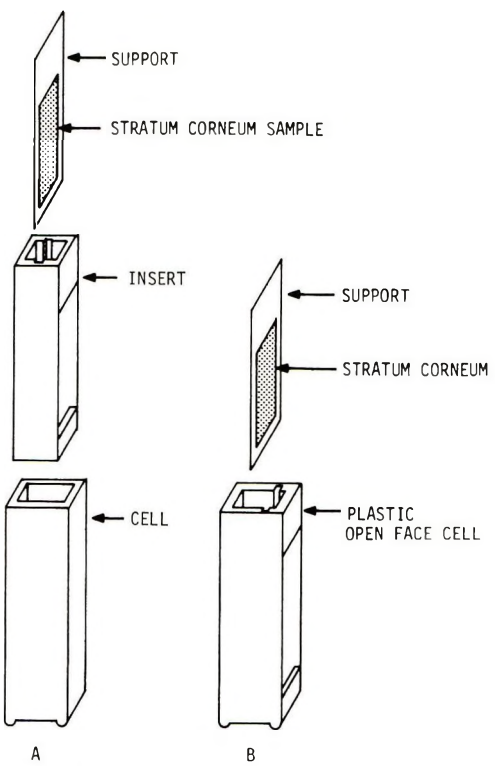

Figure 1. Device for measuring light transmission through stratum corneum: (A) sample support and cell insert; (B) plastic open-face cell

MATERIALS AND METHODS

LIGHT TRANSMISSION MEASUREMENTS

Isolated stratum corneum from the ventral and dorsal skin was obtained from wax depilated guinea pig skin by the method of Singer and Vinson (10). The stratum corneum was examined carefully to eliminate areas with excessive hair or tears. The light transmission measurements were made on 0.5 × 2.5 cm sections of tissue, which were mounted on brass frames and placed in a 1-cm spectrophotometer cell with the specially constructed holder shown in Fig. 1(A). Measurements of the spectral transmittance were made with a Beckman Du spectrophotometer* attached to a Gilford Instrument Company Model 220 Absorbance Indicator.† Absorbance data were converted to per cent transmittance for plotting and calculations. The cell compartment of the spectrophotometer was attached to a constant temperature water bath to maintain the samples at 25.0° ± 0.1°C.

INFLUENCE OF HYDRATION ON TRANSMISSION

To study the effect of the moisture content of the tissue on light transmission, a curve was first determined using a cell containing only the sample holder as a blank at ambient conditions (25.0°C and 40 per cent RH). The relative humidity within the sample cell was raised by placing about one-half ml of an appropriate saturated salt solution and a few crystals of the salt at the bottom of the cell. The prepared cells were placed in a chamber containing the same salt solution for equilibration. For transmission measurements, the cells were capped, placed in the instrument and readings were taken from 280 to 560 nm. The samples were then removed, rinsed with distilled water, and air dried overnight. The transmission curve was again determined at ambient conditions and then another saturated salt solution at a higher relative humidity was placed in the cell with the stratum corneum.

Kinetic studies were conducted similarly, except that the cell was capped and the transmission measurements started immediately after adding the salt solution. Dehydration was studied by mounting a sample in a specially constructed plastic cell, which had two open sides instead of optical faces (Fig. 1(B)). By permitting exposure of the tissue to the atmosphere, the sample could be more readily equilibrated in a controlled humidity chamber. After 24 h, at the desired high humidity, the sample was placed in the spectrophotometer and readings taken immediately and at intervals until no change was observed.

INFLUENCE OF IMMERSION ON TRANSMISSION

The effect upon light transmission of complete immersion of the stratum corneum was determined by comparing the spectral transmission curve obtained at ambient conditions to that obtained after filling the sample cell with liquid.

*Beckman Instruments Inc., Fullerton, CA 92634.
†Gilford Instrument Laboratories, Inc., Oberlin, OH 44074.

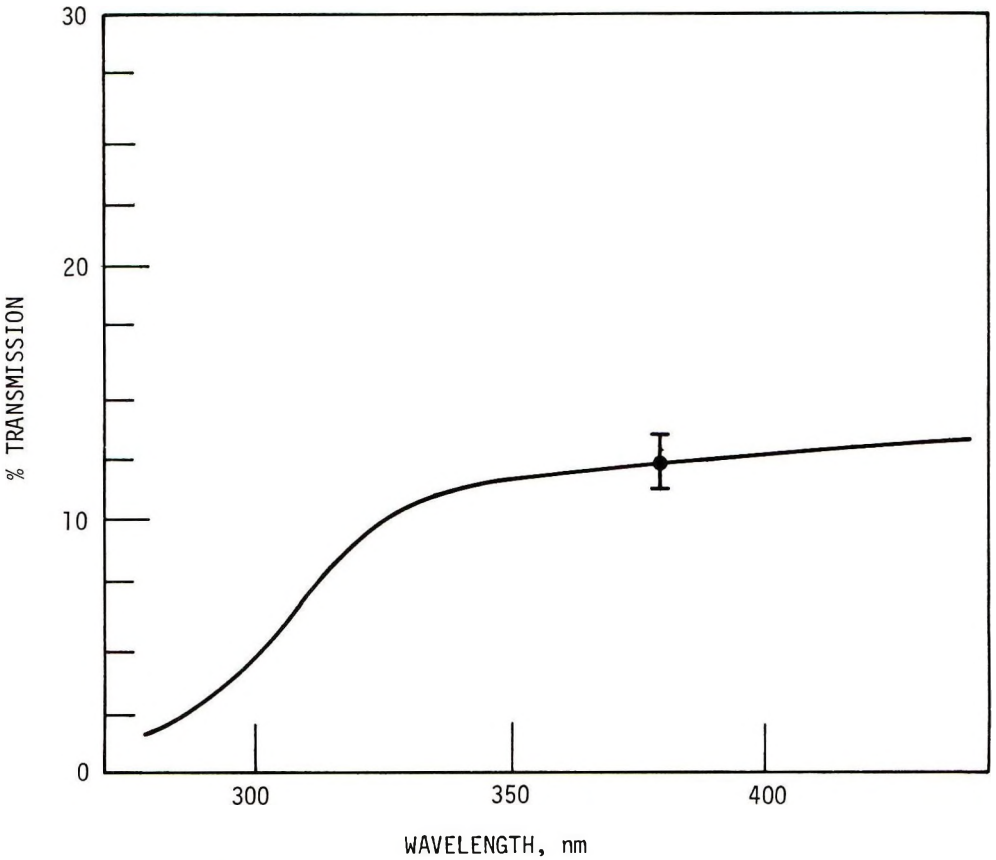

Figure 2. Spectral transmittance of guinea pig stratum corneum. Mean and standard deviation at 380 nm are shown by point and brackets, respectively

RESULTS

SAMPLE HANDLING AND OPERATING CONDITIONS

Although each stratum corneum sample served as its own control, it was subjected to removal and reinsertion into the cell in addition to water rinsing and drying. The effect of this sample handling on transmission measurements was determined as follows.

The transmission values of 3 samples were obtained at 360 nm, where the per cent transmission versus wavelength curve is relatively flat (Fig. 2). Then the devices were disassembled several times and the transmission remeasured after each assembly. The mean per cent transmission was 14.7 ± 1.0. Neither the average value, nor the deviation changed as a result of handling. A water rinse during the last disassembly followed by air drying overnight resulted in a slight but not significant decrease to 13.6 ± 0.6 per cent transmission.

The variation between animals and between sites was also determined. Initially, adjacent corneum sections were measured at the same time to minimize variation. Later

Table I
Animal and Site Variation in Transmission of Guinea Pig Stratum Corneum

Animal	Number of Specimens Evaluated	Per cent T @ 360 nm[a]
1	6	12.4 ± 1.6
	3 (matched)	11.1 ± 0.5
2	9	14.2 ± 3.7
	4 (matched)	17.8 ± 1.0
	3 (matched)	11.1 ± 1.1

[a]Mean and standard deviation

the sections were screened by measuring the spectral transmission and segregating them according to the type of curve obtained. The results in Table I indicate that the variation between stratum corneum sections from one animal is of the same magnitude as the variation between animals. When the samples were screened and matched, the variation was reduced. In all subsequent experiments, sets of 3 matched samples were treated simultaneously and the transmission values averaged.

The transmission curve obtained for guinea pig stratum corneum is shown in Fig. 2. The curve resembles those reported for other skin tissues including human stratum corneum. The light transmission is very low in the 280–290 nm range and increases sharply as the wavelength increases from 290 to 340 nm. Beyond 360 nm, the transmission is relatively flat out to 600 nm.

WATER VAPOR HYDRATION

The equilibration time for hydration of 3 matched corneum samples was obtained by adding a few drops of saturated potassium iodide (68 per cent RH) or barium chloride (90 per cent RH) to the cells containing the tissue. The cells were capped and immediately placed in the instrument for an initial transmission reading. Thereafter, the cells were stored in a constant humidity chamber containing the same saturated salt solution and removed at intervals for additional measurements. The data obtained at 68 and 90 per cent RH are plotted in Fig. 3. At 68 per cent RH, the light transmission at 360 nm increased only slightly during the first 2 h and remained constant thereafter. The samples at 90 per cent RH showed a larger change in light transmission and required about 8 h to reach equilibrium. The final light transmission values obtained at equilibrium hydration were used to evaluate the effect of water vapor in the wavelength range of 280–450 nm. The results are shown in Figure 4. At 90 per cent RH, the transmission curve is only slightly higher and nearly parallel to the curve obtained for the same sample at ambient (34 per cent RH) conditions. The curves at 68 and 80 per cent RH (not shown) were between those at 34 and 90 per cent RH. The curve obtained after flooding the cell with water is also shown in Fig. 4, but will be discussed below. The effect on the light transmission of increasing the hydration of the same set of samples by equilibration at 68, 80, and 90 per cent RH is summarized in Fig. 5. This shows the increase in per cent transmission (Δ %T) of hydrated tissue, compared to the same sample in dry state, plotted against relative humidity. It is apparent that at a given wavelength of light, the change in transmission increases with the relative humidity of the atmosphere surrounding the stratum corneum. Figure 6 shows the change in trans-

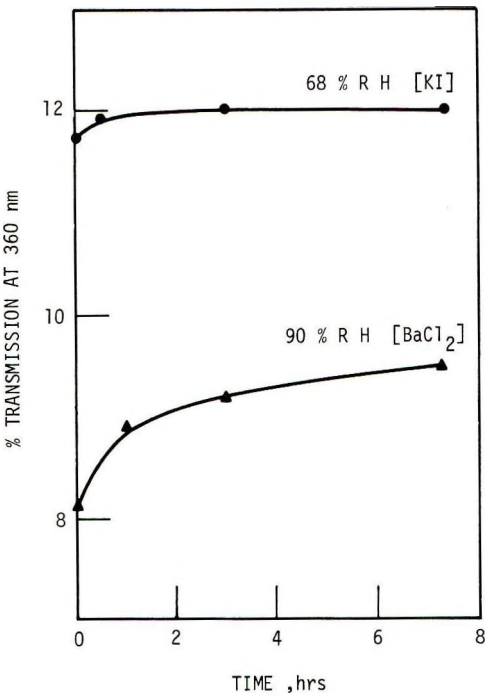

Figure 3. Equilibration of light transmission during hydration

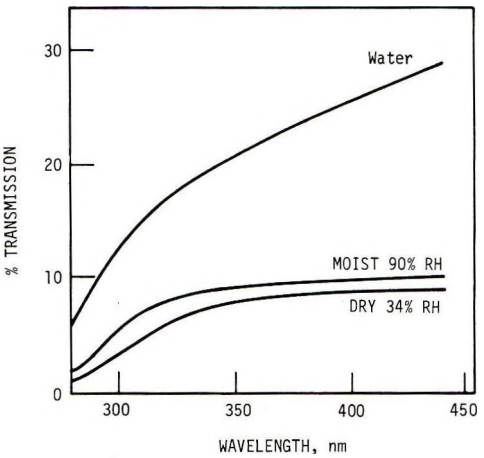

Figure 4. Effect of water and water vapor on light transmission by guinea pig stratum corneum

mission as a function of wavelength at a constant relative humidity of 90 per cent (lower curve). It can be seen that the greatest change in transmission occurs in the region of 290–310 nm, which is the most critical with respect to solar damage to the skin. The reversibility of the hydration effect is shown in Fig. 7 for stratum corneum hydrated at 90 per cent RH and then returned to 40 per cent at ambient conditions. The point at the left side of the graph indicates the light transmission of dry tissue. The transmission at 300 nm increases to about 4 per cent during hydration, and then slowly decreases back to the original ambient light transmission value as the moisture is lost to the air. The data indicate that, in the absence of other factors, raising the moisture content of guinea pig stratum corneum will reversibly increase the amount of erythema-producing light penetrating to the living layers of the epidermis.

LIQUID WATER HYDRATION

A simple extension of the water vapor hydration study at 90% RH involved filling the cell with water and immediately remeasuring the light transmission. The large increase shown in Fig. 4 occurred over the whole wavelength range. In contrast to the water vapor effect, the transmission increased immediately, and the curve exhibits an increasing difference at higher wavelengths. This effect is shown more dramatically in Fig. 6, which shows the change in transmission plotted against wavelength. It can be speculated that water increases the light transmission of skin by reducing reflection and refraction of light rays due to abrupt changes in refractive index at the air-skin surface

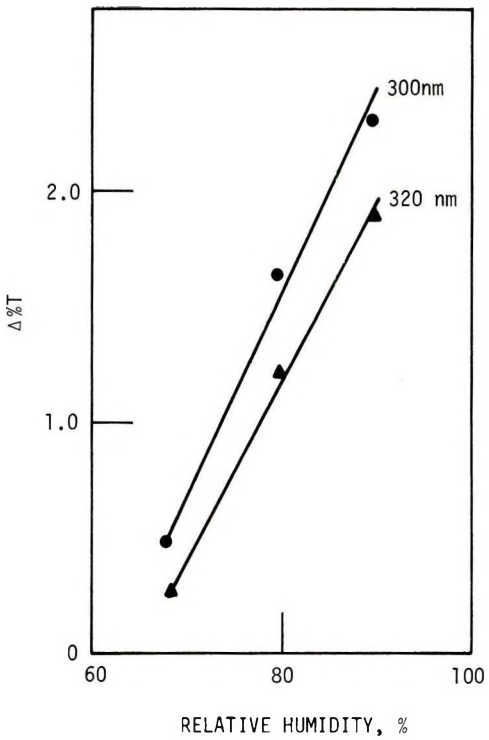

Figure 5. Effect of relative humidity on the change in per cent light transmission

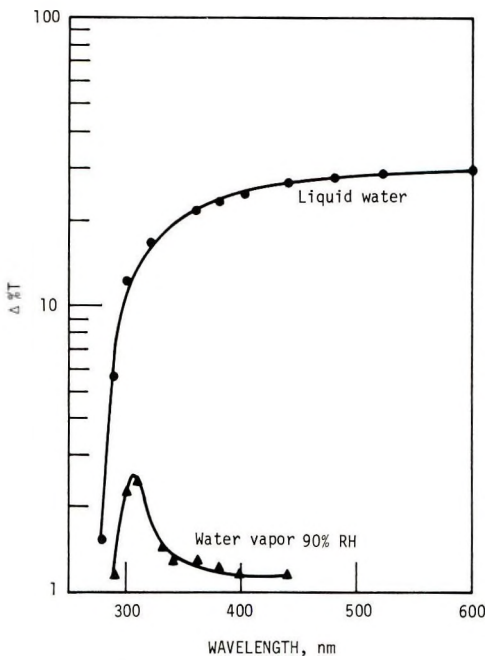

Figure 6. Change in per cent light transmission of guinea pig stratum corneum exposed to water and water vapor

and between cell layers within the stratum corneum. If this is the mode of action, then it should be possible to increase the light transmission even further by bathing the tissue in liquids with refractive indices close to that of skin. Human skin is reported to have an index of refraction number of 1.55 (11), and the transmission should increase as the refractive index of the liquid surrounding the tissue approaches 1.55.

REFRACTIVE INDEX OF LIQUID SURROUNDING STRATUM CORNEUM

Several different liquids with refractive indices greater than water were evaluated for their effect on light transmission. In this study, 3 matched stratum corneum samples were utilized for each test liquid. The results are shown in Fig. 8, where the untreated corneum transmission curve was obtained by averaging all the readings taken at ambient conditions. The data indicate that liquids with $N_D > 1.33$ have an even greater effect on light transmission than does water. The refractive index of each medium is shown on the right in Fig. 8 and indicates that, as the index approaches that of skin, the transmission increases. This effect was explored further by evaluating several other liquids with indices both above and below that of stratum corneum. The results (Fig. 9) show the change in per cent light transmission at wavelengths of 320 and 400 nm as a function of the refractive index of the liquid surrounding the tissue. The transmission increases with refractive index to a maximum at about 1.54, at which point a four-fold

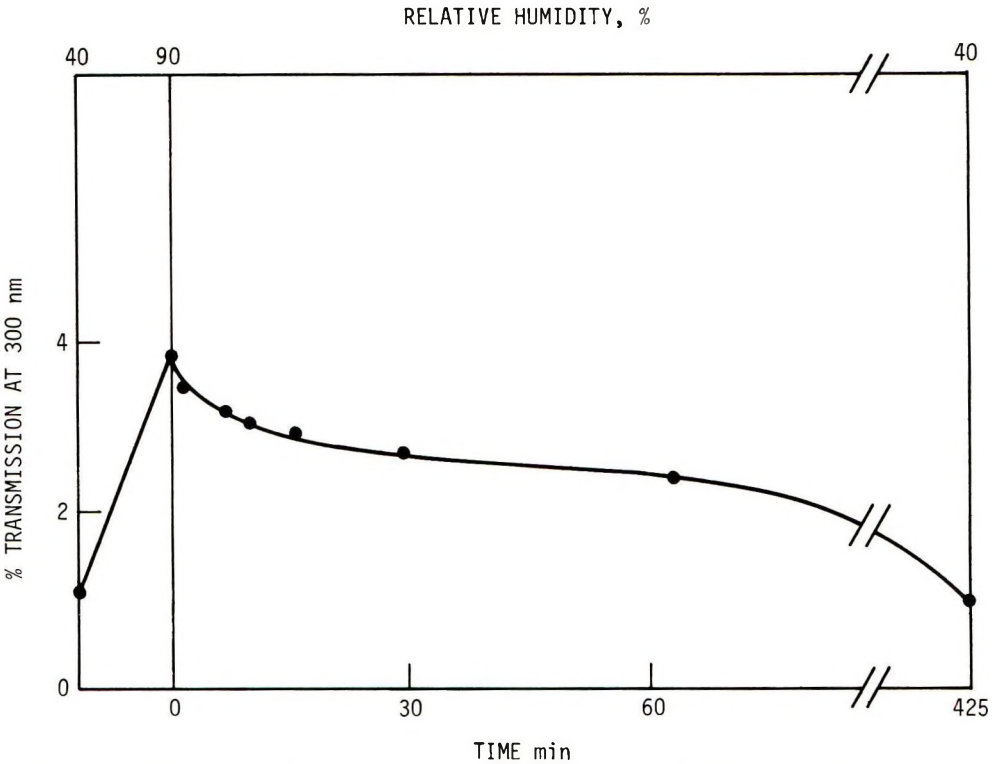

Figure 7. Effect of reversal of hydration of stratum corneum on light transmission. Light transmission is plotted against time as the relative humidity is changed from 90 per cent at zero time to 40 per cent

increase in transmission occurs. The peak at 1.54 is very close to the index of refraction of human stratum corneum.

DISCUSSION

Stratum corneum is a heterogeneous material, which causes an incident beam of light to scatter from the plane of the skin. The stratified nature of the corneum enhances total reflection as a result of abrupt changes in refractive index between the various cell layers. The result is that when a simple spectrophotometer is used to measure transmitted light, a portion of the light falls outside the collection slit of the phototube. This condition leads to an underestimate of the total transmission and the resulting value is referred to as directly transmitted light. The total transmission can be obtained by interposing a diffuse reflectance sphere between the sample and the photodetector. Everett, Yeargers *et al.* (12) used this device to measure both the light fraction transmitted directly through a stratum corneum sample (excluding forward scattered light) and the total light transmitted including both direct and scattered (0-90° from light path) light. Our data showing the spectral transmission of guinea pig corneum before and after immersion in ethyl benzoate ($N_D = 1.5028$) are shown in Fig. 10.

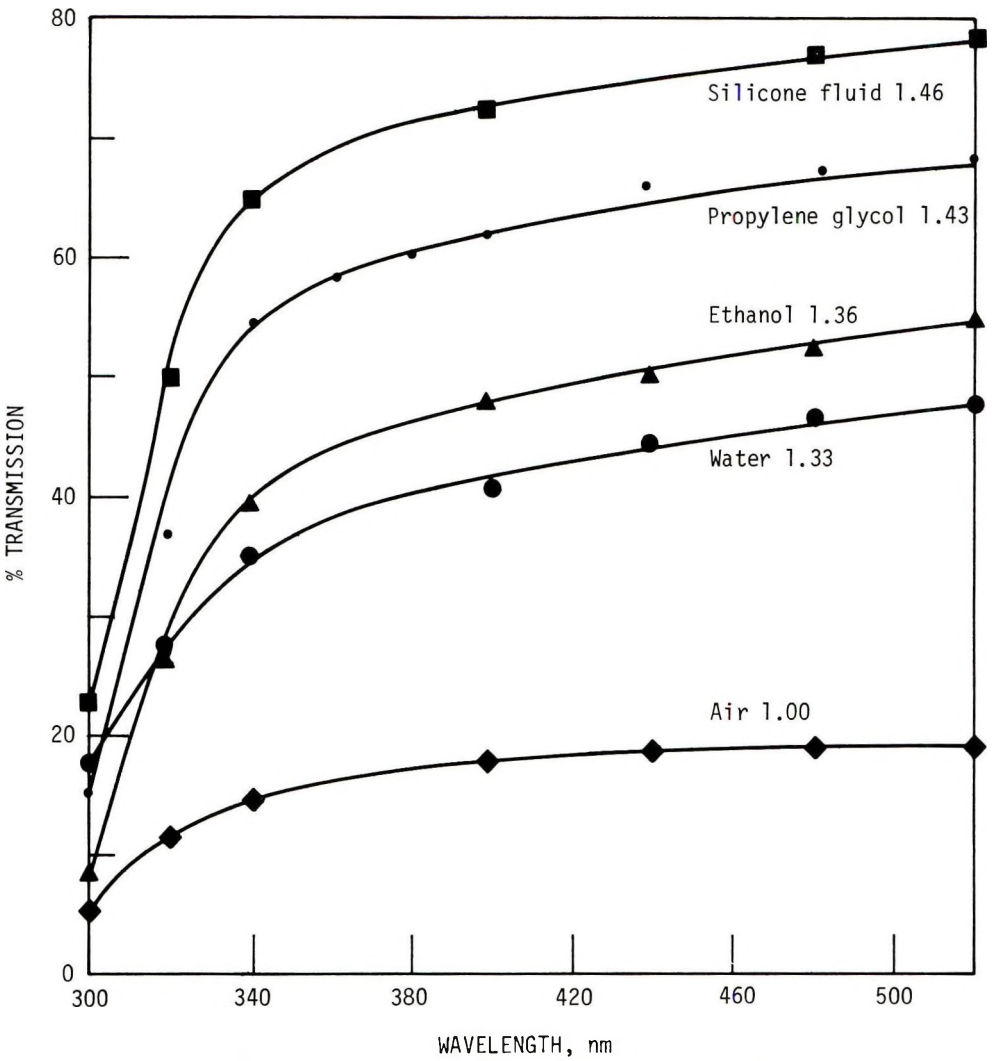

Figure 8. The effect of liquids with different refractive indices on light transmission through stratum corneum

For comparison, the curves of Everett et al. (12) of the total transmission of human stratum corneum are included and show a general resemblance to the curve for dry guinea pig corneum. The amount of light transmitted over the spectral range for the human stratum corneum is about 3–4 times greater, depending on the method of isolation. This is probably due to the light collection mechanics utilized by Everett *et al.* (12), which catch more of the forward scattered light. The ethyl benzoate treated guinea pig tissue (upper curve) transmits substantially more light than the highest of the human corneum specimens. Therefore, the data indicate that, despite less than ideal conditions for light collection, the changes in light transmission observed from the various treatments are valid.

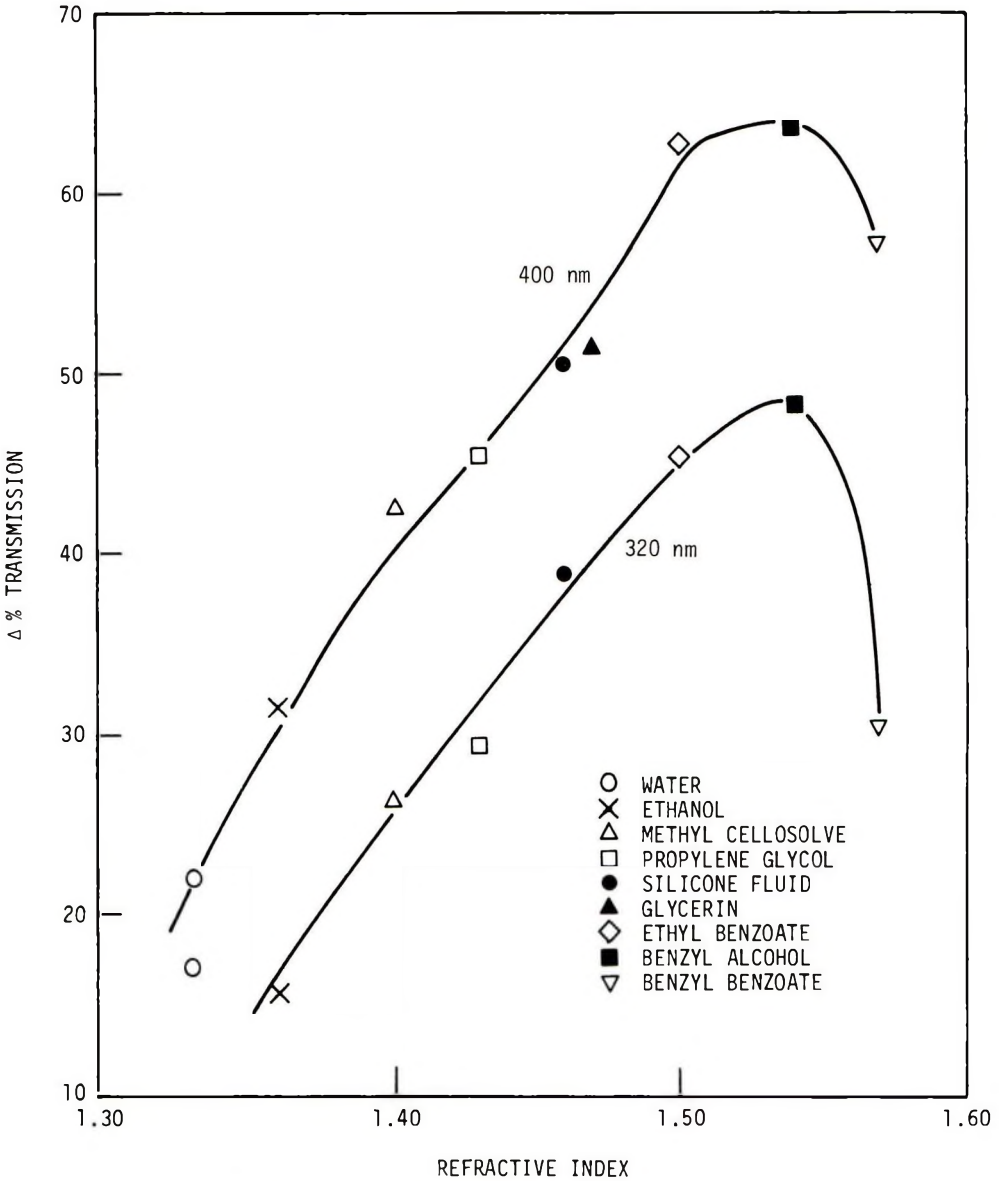

Figure 9. The effect of refractive index on light transmission

The hydration studies indicate that water acts on stratum corneum in at least two ways to increase light transmission. The first is a result of liquid water which acts on the surface to reduce light reflection and scattering. The second occurs as a result of hydration during which water is taken up by the cells and intercellular material causing a reduction in internal scattering due to multiple changes in refractive index at the inter-

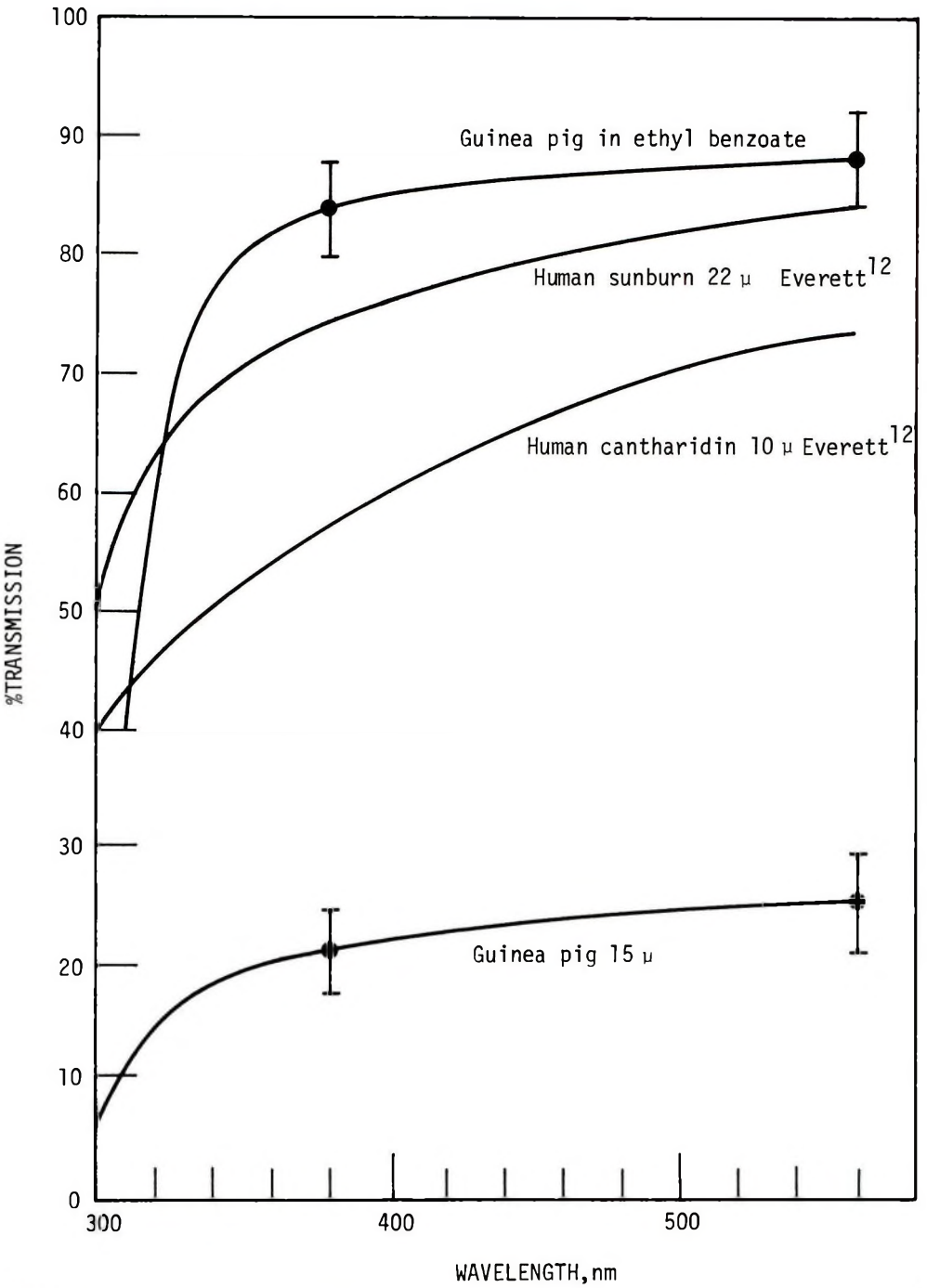

Figure 10. Light transmission through human and guinea pig stratum corneum. Typical means and standard deviations are shown by the points and brackets, respectively

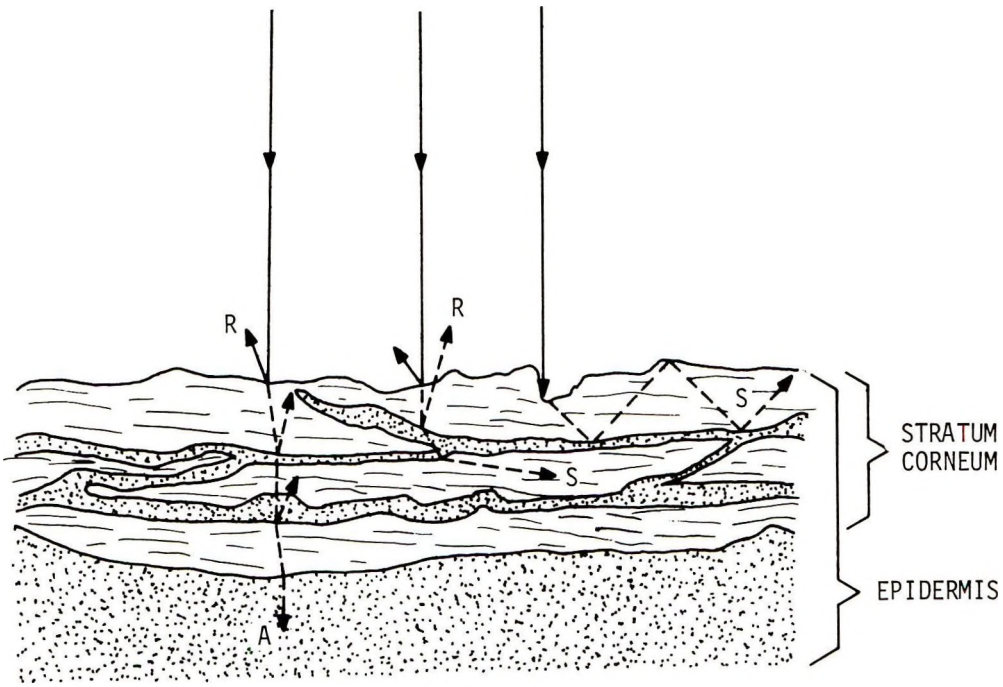

Figure 11. Human skin illustrating the reflection (R), scattering (S) and absorption (A) of light

faces of the cells. A related effect of water involves formation in a gel due to solvation of the stratum corneum proteins. The result is dilution of intracellular and tissue protein, which has been shown to cause a decrease in refractive index (13). The result is that the refractive index of the hydrated corneum becomes closer to that of the surrounding medium, e.g., water = 1.333; sebum = 1.464. The effect of refractive index on the reflection of light at the boundary of two media can be computed for light incident upon a plane surface by use of the Fresnel formula. For an incident ray perpendicular to the boundary, the amount of light reflected, r, is given by the formula (11):

$$r = \left(N_2 - N_1 / N_2 + N_1\right)^2$$

where N_1 is the index of refraction of one medium and N_2 is the index of refraction of the other. For the air-tissue interface ($N_1 = 1$, $N_2 = 1.5$) r is 4 per cent. It is apparent, that the reflection decreases with decreasing difference in refractive index. However, the surface of stratum corneum is highly discontinuous, causing an impinging beam of light to interact at shallow angles of incidence, thus increasing the reflection. The stratified nature of the corneum (see Fig. 11) enhances the total reflection as a result of abrupt changes in refractive index between the various layers. Other factors to be considered are internal scattering and forward scattering at the emerging surface. The forward scattering would probably be reduced, but is difficult to determine. The internal scattering could only be altered if the liquid in contact with the stratum corneum is capable of penetrating into the tissue. Water vapor is known to penetrate the stratum corneum rapidly and the maximum increase in transmission of hydrated tissue

at 300 nm (Fig. 6) can probably be explained by considering the ultrastructure of stratum corneum. This layer of the skin is composed of flattened dehydrated cells 0.6 to 0.8 μm thick and separated by optically less dense interphases. Two components of the stratum corneum, the tonofibril (200–400 Å in diameter) and the desmosome (~200 Å thick) both are most effective in scattering shorter wavelengths (11). Therefore, if water is taken up by the medium surrounding these scattering centers and/or these components themselves, the result would be a change in refractive index and a consequent increase in transmitted light.

Our results, coupled with the recent findings of others (8, 9), clearly demonstrate that water can alter the penetrability of the skin to uv light. These findings suggest the need for extra caution against uv radiation by bathers as well as those exposed to sunlight coupled with high humidity. Additionally, just as water can alter the skin barrier to light, so can other liquids. Many of the liquids used for cosmetic and toiletry formulating are of suitable refractive index for enhancing light penetration into the living layers of the skin. Cosmetic researchers and formulators should consider the alteration of optical properties of the skin along with the effect upon the barrier properties of skin when evaluating ingredients and formulations.

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The effect of fiber diameter on the cosmetic aspects of hair

NALING E. YIN, ROY H. KISSINGER, WILLIAM S. TOLGYESI, and ELLYN M. COTTINGTON, *Gillette Research Institute, 1413 Research Boulevard, Rockville, MD 20850.*

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Synopsis

Most COSMETIC ASPECTS of a head of HAIR depend on the physical characteristics of the HAIR MASS. In turn, the hair mass characteristics are determined (directly or indirectly) by the properties of its individual FIBER COMPONENTS. Among fiber properties, diameter is of great significance. It influences hair body, tangling, combing, and resistance to damage. Both human hair and a model system using synthetic fibers were used to study the fiber diameter contribution. When these systems were assessed using combing, body, and abrasion test methods, it was found that the fiber diameter was directly related to hair body, combing ease, and abrasion resistance when all other hair or synthetic fiber properties were equal.

INTRODUCTION

Many of the important, consumer appreciated hair characteristics are based on the mechanical behavior of the fiber mass. The mechanical behavior, in turn, is determined by fiber properties and fiber–fiber interactions. Some of the most important fiber properties which influence the mass behavior are moduli, frictional characteristics, cross-sectional shape, longitudinal configuration and, last but not least, diameter. The present paper is concerned with the influence of fiber diameter on some cosmetic attributes of hair.

Cross-sectional size of terminal scalp hair is subject to significant variations among different population groups (1). For individuals, the mean diameter ranges from under 50 to about 90 μm, even in a relatively small sample of Caucasian adult population (2, 3).

In addition to differences between individuals in mean fiber size, the diameter shows a certain level of polydispersity on single heads, even among neighboring fibers. The polydispersity—when defined by the ratio of thickest to thinnest diameter—ranges from less than 1.4 to above 2.0 on adult Caucasian women (3).

The diameter significantly influences the deformability of the fiber, which in turn, is an important factor in determining the mechanical response of the hair mass. The resistance to longitudinal deformation varies only with the square of the diameter; that is, with the fiber mass. The bending and torsional stiffness of cylindrical beams, on the other hand, increases with the fourth power of the diameter. By combining the latter correlation with the fact that bending and torsion are the only important deformations of fibers under normal on-head conditions, it was expected that even relatively small differences in diameter—in the range of 10 per cent—would cause observable changes in some aspects of hair mass behavior. The above statement assumes that no other parameters important in specific types of mass behavior change systematically with fiber diameter.

Although the cuticle–cortex volume ratio varies with the diameter in human hair (4), the elastic modulus in the dry state was found to be independent in both intact and bleached fibers (5). Some increase in friction with increasing fiber diameter has been reported (6, 7) for keratin fibers. No information is available concerning any systematic dependence of longitudinal and cross-sectional shapes on diameter, beyond the known anthropological influence on both characteristics.

In light of the above, we chose to study combing, set holding, body, and abrasion resistance characteristics of human hair, as functions of fiber size, using objective methods. For some measurements, we used synthetic wig fibers to clarify and/or confirm the human hair data. Known effects of fiber diameter, as, for instance, on tensile strength, were not evaluated. Some obvious attributes, such as fuller look due to larger fiber size, were noted, but not studied. Similarly, the effects of fiber size modification by swelling, with or without internal polymer deposition, or by external coatings were not investigated.

EXPERIMENTAL

MATERIALS

Human hair: Medium brown hair of European origin was obtained* in the form of homogeneous bundles.

Synthetic fiber: Elura®† wig fiber was obtained in 30 and 40 denier sizes, corresponding to 56 and 65 μm in idealized diameter. These were designated as group 1 and group 2 synthetic fiber groups, respectively.

*De Meo Brothers, New York, N.Y.
†The Monsanto Company, Decatur, AL.

Chemicals: All materials were either laboratory grade chemicals or commercial cosmetic products.

PROCESSES

Synthetic fiber: Samples of the Elura were desized by soaking in methanol for 15 h, followed by soaking at 40°C with aqueous Woolite®* for 30 min, and finally shampooing with White Rain shampoo.† All determinations were carried out on the desized fibers in the form of 16 cm long, 6500 fiber tresses.

Human hair: (Separation by size) Small, 0.5 to 1.0 g bundles of hair were taken from the large master bundle. The root ends of these small bundles were pushed against a standard number 230 laboratory sieve with 63 μm nominal hole size. Fibers, which penetrated the sieve, were pulled through and designated as group I, representing the lowest mean diameter. When no more fibers could be passed through the fine sieve, the process was repeated with the remaining strands on a standard number 170 sieve of 82 μm nominal hole size. Fibers passing through this sieve constituted group II and were of midrange mean diameter. The residual fibers of the original strands, which did not pass through either of the sieves, were designated group III and represented the highest mean fiber diameter bundle. Hair from each size group was formed into 1000 fiber tresses by gluing the root end of the fibers to a plastic tab. On each tab, the fibers were distributed over a 7 mm wide area. Two such tresses of each size group were used for each different laboratory test.

Fiber modification: Visual inspection of the tresses indicated that the size groups differed from each other not only in fiber diameter but in at least one other physical characteristic. The waviness of the tresses increased with increasing fiber diameter. The extent of this inherent fiber configurational difference had to be eliminated or, at least, reduced in order to retain the fiber size as the only significant variable. For this reason, the tresses were first bleached and then straight waved using commercial processes. In the final step, the fibers were water set in a straight configuration at 45°C. Subsequently, the tresses were trimmed to 16 cm length. All studies were carried out on these chemically modified fiber tresses.

METHODS OF EVALUATION

Fiber diameter: A small strand, about 30 fibers, was taken from each hair group. After equilibration at 70°F and 65 per cent RH, a 50 mm long segment, accurate to better than 1 per cent, was cut from the middle of each fiber, using a specially constructed tool, while the fiber was extended with a 5 g load to ensure straight configuration. Each segment was weighed in the conditioned form on a microbalance with an accuracy of 0.1 per cent. The diameter of each fiber was calculated from its weight and length assuming uniform cylindrical shape for the whole segment and using 1.3 g/cm^3 for density.

*Boyle-Midway, Inc., New York, N.Y.
†Gillette Co., Boston, MA.

Combing: The test was carried out at 70°F and 65 per cent RH on an Instron Tensile Tester®* with the hair tress attached to the strain gage and the comb to the crosshead. The amount of hair to be combed was evenly distributed in seven cavities of a cosmetic comb (Ace®)† and the comb was pulled through at a speed of 50 cm/min. The force-displacement curves and their integrated values were recorded for 10 consecutive strokes on each tress.

Since in normal combing, the mass of hair engaged by the comb is determined primarily by the cross-sectional area of the cavity and not by the available amount of hair, the number of fibers combed in our tresses was varied according to the mean fiber diameter. Equality of the combed mass was maintained by combing the total tresses, 1000 fibers, of group I, 78 per cent of the fibers in group II tresses, and 54 per cent of the fibers of group III tresses.

Hair body: Body was determined by employing our omega loop test method (8). In this test, the energy characteristics were determined when a hair tress, held in the shape of the Greek letter Ω was repeatedly compressed to a given strain and allowed to recover. The average force and work of 10 successive deformations were used for comparison. In this test, the total 1000 fiber tresses were used for all fiber size groups.

Water set: The set holding ability was determined by measuring the uncurling of hair set on a pin curler. Wetted-out tresses were rolled on 1.7cm diameter curlers, rewetted, and allowed to dry at 70°F and 65 per cent RH for 19 hr. The tresses were removed from the curlers with minimal disturbance of the structure and their hanging length was recorded as a function of time at 70°F and 65 per cent RH. In a second set of experiments, the tresses were combed out after removal from the curlers but before relaxation. The set retention was calculated according to the following equation:

$$SR_t = [(L_l - L_t)/L_l] \times 100$$

where SR_t equals per cent set retention at time t, L_l equals absolute length of the tress before setting, and L_t equals hanging length of the set tress at relaxation time t.

Heat set: Set holding of the synthetic fiber tresses was measured similarly, but setting was achieved by a 100°C dry heat treatment for 1 h on 1.7 cm diameter tubes.

Abrasion test: The abrasion resistance of the tresses was determined according to the ASTM-D1175 test method used for textiles. In it, a 2.54 cm long segment of the tensioned tress is drawn across a 1 mm wide blade in a reciprocating fashion. The number of cycles needed to break through the tress is taken as the measure of its resistance to abrasion.

RESULTS AND DISCUSSION

FIBER SIZE

Fiber diameter needs to be classified as idealized and averaged due to the indirect method of its determination. For this reason, the basic assumptions and their validity

*Instron Corporation, Canton, MA.
†Amerace Esna Corporation, Butler, N.J.

for the specific measurements need to be discussed. The method used two quantities, length and weight, and two assumptions, material density and constant circular cross-section of the fiber segment. The accuracy of the cutting distance was better than 1 per cent in our tool. In order to ensure that the axial length of the fiber was equivalent to the cutting distance, the fibers had to be straightened by preloading. According to another study (9), the bends and curves are removed even from very kinky Afro hair fibers at a few grams force. On the other hand, the 5 g loading represents only about 20 per cent of the yield force even for thin hair fibers in the dry state; therefore, the decrease in cross-sectional area is not above 0.5 per cent, due to material stretching. The error in weighing the fibers was even less; therefore, it can be concluded that the method was reliable to 1 per cent in determining the average mass per unit fiber length.

From the point of view of determining an absolute fiber diameter, the use of 1.3 g/cm^3 for material density is debatable. This figure was somewhat arbitrarily chosen from available data (10). Density is, of course, a function of the medium in which it is measured. While absolute validity is not claimed for this value, small variations would not significantly alter our calculated diameters, since it enters the equation as a square root term. Furthermore, the present study was concerned with relative differences among size selected fiber groups and the numerical quantities were largely immaterial as long as they were kept constant.

The second assumption, uniform circular geometry, is obviously invalid for the description of even Oriental hair (11). The cross-section is neither circular nor constant along a single fiber. For these reasons, the calculated diameters should be considered as idealized and averaged. Nonetheless, we have no reason to assume that the sized fiber groups separated from a homogeneous hair mass had widely different cross-sectional shapes. Therefore, the calculated diameter can be accepted as a descriptive term and can be safely used for the present comparative study of fiber size influences on mass behavior.

The distribution of fiber diameters within each size group and the mean diameters of the three groups are shown in Fig. 1. Figure 1 shows that each size group contains fibers in a range of diameters. In this respect, the fiber groups represent actual on-head compositions (3) in polydispersity. While the distribution curves of all three groups overlap, their means are more than 15 per cent different from each other, which is more than sufficient to cause observable differences in on-head behavior. Based on another study (3), in which fiber diameters were determined by the same technique, groups I, II, and III can be considered below average, above average, and coarse, respectively, for adult American women of Caucasian origin.

GENERAL CHARACTERISTICS

Very significant differences were observed among tresses made from the 3 hair groups. As the fiber thickness increased, the bulk of the assembly increased very sharply for identical tress weight. The increased bulk, derived from the more pronounced waviness of the thicker fibers, is one aspect of hair body.

One possible explanation for the relationship between fiber thickness and waviness is that the thinner fibers originated from individuals with inherently straighter hair; that is, the thinner hair was synthesized in straight configuration.

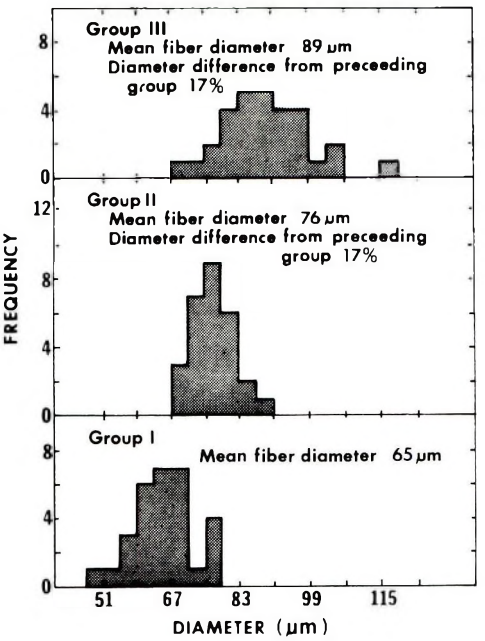

Figure 1. Fiber diameter distribution

While this possibility cannot be discounted, we have observed (3) that thinner fibers on a single head were straighter than the thicker ones. This observation presents the alternate possibility that the thin hair is straighter as a consequence of postsynthesis straightening effects through plastic deformation of the fibers. These are derived from the low, but continuously acting lateral pressure of the constraining neighboring fibers, longitudinal extension due to fiber weight, and the intermittent, but high force levels of combing. Since all these straightening effects involve bending and torsional deformations, which have fourth power dependence on diameter, the thinner fibers are less able to resist straightening.

Irrespective of the reasons for the differential curl level, the present study was aimed at the effects of fiber diameter on a number of aspects of hair behavior; therefore, attempts were made to normalize fiber geometry. Since water relaxation at 40°C was not adequate, all the tresses were bleached then waved in a straight configuration and finally water set. All further hair studies were carried out on this type of hair, which—even if not intact—is a cosmetically acceptable hair condition. This sequence of treatments eliminated the curvatures of large arc segments. However, it did not produce geometrically straight fiber lines on the wavy coarse hair. The straightened fibers had small amplitude, small radius bends indicating nonhomogeneous response to the relaxing treatment. We refer to these bends as "microcrimp." The thicker hair—with more initial curl—had more microcrimp than the thinner fibers. The increasing bulk with the increasing fiber diameter of these chemically modified tresses is shown in Fig. 2.

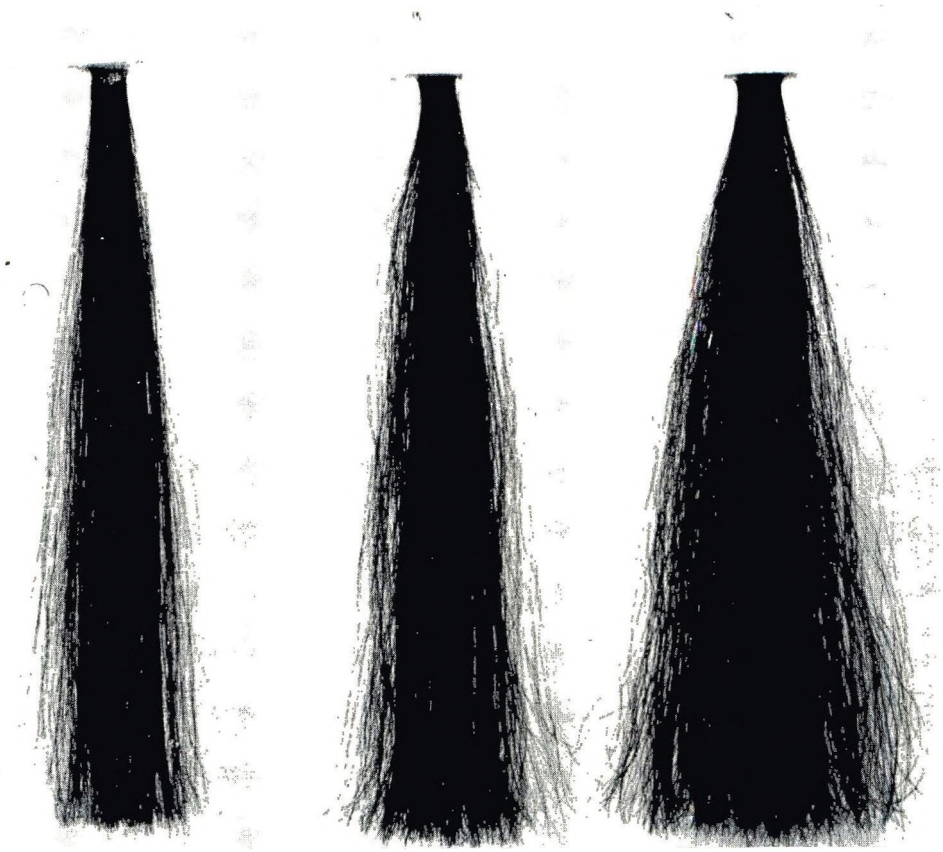

Figure 2. Tress bulk with increasing fiber diameter

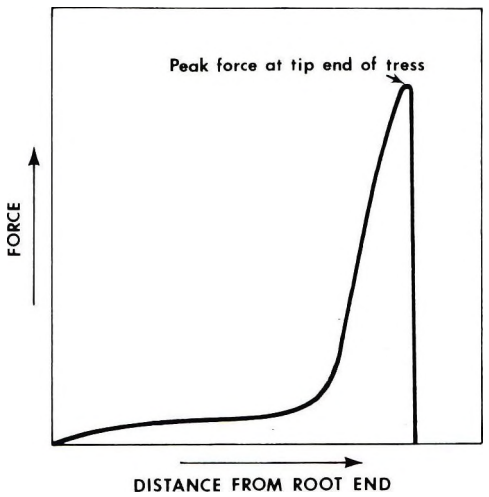

Figure 3. Schematic combing force curve

Table I
Instron Combing of Hair Tresses

Fiber Group	Peak Force, g	Combing Work, cm-g
I	25.8	82.5
II	28.8	109.7
III	33.2	150.4

COMBING

The combability of the size separated hair bundles was studied with our standard technique, where the force exerted on the hair tress is recorded as a comb is pulled from root to tip at a constant speed. For this test, the tresses were mass equalized based on the thesis that the hair engaged by a comb in a single stroke is determined by the free cross-sectional area of the cavities and not by the total mass of hair present.

A schematic example of a force displacement curve in hair tress combing is shown in Fig. 3. The "End Peak Force" and the total "Combing Work" are used for characterizing the combing. The results for the three groups of hair are given in Table I.

The results showed an increase in combing effort with increasing fiber diameter. The differences can be considered moderate. When surface characteristics of hair are changed, the variation in combing effort can be up to an order of magnitude. Nonetheless, the rank order was reproducible in the present case, even after repeated setting of the tresses. The trend was unexpected on mechanistic grounds established in our earlier work (12). According to that, a tress combs easily if fibers belonging to a common cavity can separate from neighboring groups far in advance, more than 4–5 diam ahead, of the approaching comb. This early separation of fibers through inplane sliding from a frictional hold is achieved via their bending stress, which is created by the presence of the comb teeth between neighboring fiber groups. Since the bending stiffness of beams increases with the fourth power of their diameter, the combing force was expected to decrease with increasing fiber diameter, provided everything else was equal. As stated previously, this was not the case with the hair tresses. Because our overall mechanistic view of combing has been confirmed by numerous tests, we tend to view the present results as being influenced by characteristics other than fiber diameter. The most plausible factor is the longitudinal configuration. The small radius microcrimps—even with amplitudes not larger than the fiber diameter—can be expected to considerably retard and arrest lateral sliding of other fibers, thereby preventing the early disengagement of overlapping fibers in front of the comb.

This hypothesis was tested on tresses of synthetic wig fibers of different denier. Since the fibers originated from the same manufacturer using the same process for the different sizes, it could be assumed that they differed in diameter only. The results given in Table II show the expected correlation; thicker fibers combed more easily.

While within the scope of the experimental set-up we could not directly prove easier combing for human hair with increasing fiber diameter, a plausible explanation, the longitudinal configuration of the different hair samples, was found for the cause of the anomaly. On substrates where fiber size was the only variable, the expected trend was found; therefore, it may be proposed that for human hair, too, the combing ease

Table II
Instron Combing of Synthetic Fiber Tresses

Fiber Group	Peak Force, g
1.	1150
2.	624

improves with fiber diameter. The critical factor is to ensure that all other parameters are constant.

SET HOLDING

The ability of a hair mass to hold a specific configuration is very important cosmetically for styleability, manageability, and for body. It is obvious that curl relaxation involves bending deformations with possible torsional components. Both of these are inverse functions of the fourth power of the diameter, while the weight, which represents the driving force, increases only with the square of the diameter. On this basis, the set holding of the tresses was expected to increase with fiber diameter. The results, shown in Figs. 4 and 5, confirm the expectations. Without offering a quantitative interpretation of the results, it is obvious that increasing fiber diameter significantly improves the set holding of human hair. Any possible effects of the microcrimping with increasing fiber diameter is, of course, unknown. The fact that fiber diameter is important in

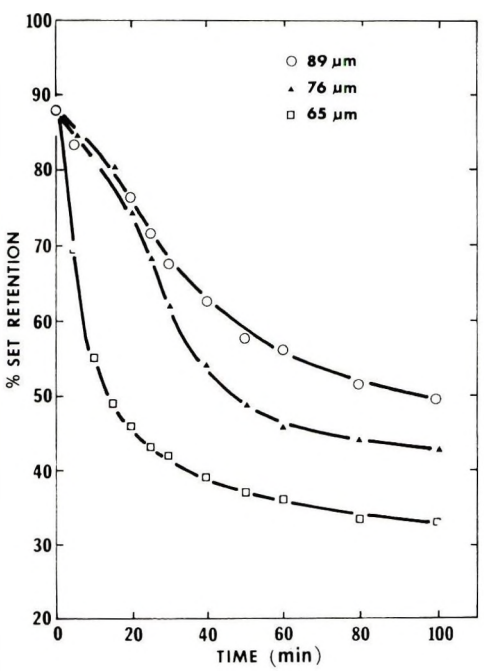

Figure 4. Curl holding of hair tresses without comb-out

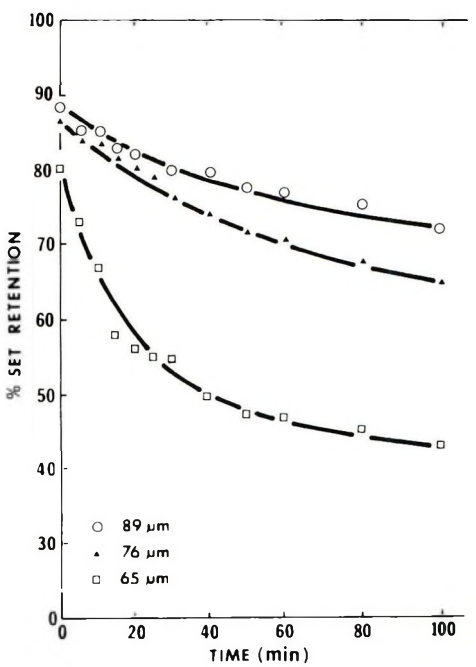

Figure 5. Curl holding of hair tresses with comb-o

resisting the uncurling under its own weight was confirmed with synthetic fibers. Tresses made of Elura fibers were heat set under mild conditions and their "fallout" pattern was observed as a function of time in a manner similar to the hair experiment. The set retention for the 56 and 65 μm fiber assemblies was found to be 41 and 58 per cent, respectively.

HAIR BODY

Hair body, according to our definition, is a measure of resistance of a hair mass to external forces regardless of the method of evaluation, i.e., visual, tactile, or instrumental (13). Accordingly, our method determines the compressive strength of a loop formed from a tress of hair. The primary indicators we use are the force and work to obtain a certain level of deformation. Other values such as self-collapse, stress decay, and recovery can also be used. While the conditions of the measurement are somewhat arbitrary, the method seems to correspond with subjective ratings.

The results of the measurements are given in Table III, showing both the absolute values and their ratios relative to the thinnest hair, group I.

The only important resistance to the collapse of a hair mass structure under its own weight, or any other force, derives from the bending and torsional stiffness of the fibers. The other primary factors for body, such as number of fibers per structural volume, sliding characteristics and fiber configuration, contribute numerically to the value or to the pattern of load distribution within the structure, but do not represent new types of load bearing elements. Therefore, in its most basic form, when all other factors are equal, the measured body should be a linear function of the fourth power of the diameter of the component members according to the following equations:

$$S = 4fl^3/\pi Md^4$$

$$\theta = 32Cl/\pi Md^4$$

where:

S = bending flexure
θ = twist
C = force couple
f = force
l = length of beam
M = Young's Modulus
d = diameter of beam.

Correspondingly, the force values should be 1.9 and 3.5 times higher for groups II and III hair samples, respectively, than for group I. The measured values, according to the data in Table III, were somewhat higher, 2.2 and 4.9. The extraneous increase beyond the fourth power correlation with fiber diameter is attributed primarily to one or more of the other factors already mentioned. The increasing level of microcrimp with increasing hair diameter is expected to stabilize the stress structure against individual, stepwise fiber collapse. Additionally, fiber friction has been shown to increase with diameter in keratin fibers (6, 7), though it was not measured in the present work. The validity of the body measurements was checked out on synthetic fibers. Due to their

Table III
Hair Body of Hair Tresses

Fiber Group	Compressive Force, g	Force Ratio	Compressive Work, cm-g	Work Ratio
I	5.2	1.0	3.1	1.0
II	11.2	2.2	5.8	1.9
III	24.4	4.9	12.2	3.9

Table IV
Body of Synthetic Fiber Tresses

Fiber Group	Compressive Force, g	Force Ratio	Compressive Work, cm-g	Work Ratio
1.	85.5	1.0	32.8	1.0
2.	173.9	2.0	93.3	2.8

Table V
Abrasion Resistance of Hair Tresses

Fiber Group	Cycles to Break	Ratio of Cycles
I	6695	1.0
II	8891	1.3
III	12523	1.9

fiber size difference the expected force ratio was 1.7. The results are shown in Table IV.

Similar to human hair, the synthetic fibers increased in measured body with increasing diameter beyond the expected fourth power function. At the present, the reasons for this behavior are unknown.

ABRASION RESISTANCE

The abrasive degradation of hair, due mostly to brushing and combing during its life on a head, has been discussed mechanistically and descriptively (14, 15). The method used for this study was a slightly modified ASTM test for textiles. In it the tresses are simultaneously flexed and abraded while under an axial load. This provided an accelerated simulation of the combing and brushing treatments. The results are shown in Table V.

The data indicate an increase in abrasion resistance with increasing fiber diameter. The tresses in this test were equal in fiber number, that is, the hair mass increased with the square of the fiber diameter. It is interesting to note that the mass ratios of the tresses, 1, 1.4 and 1.9, completely correspond to the relative abrasion values. If the specific surface area played any significant role in the abrasion, which in some erosion processes is rate determining, the relative abrasion resistance values should have increased at a rate higher than the second power of the diameter. The possible quantitative effects of the microcrimp should accelerate the rate of abrasion because of higher

resistance to sliding; therefore, the thicker fibers would have been less favored. Whether this factor was responsible for balancing the specific surface area effects, or that these opposing factors played no part in governing the rate of abrasion, cannot be determined from the present data. Nonetheless, it can be concluded that higher fiber diameter will result in significantly lower rate of abrasive hair degradation when the number of fibers and all other characteristics are equal.

CONCLUSIONS

The cosmetic benefits of thicker hair were objectively demonstrated in a number of problem areas with specialized testing techniques. In the case of combing, synthetic fibers had to be used, because it proved impossible to bring the different sized hair fibers to identical geometric configurations. The thicker fibers were curlier originally, though not necessarily for genetic reasons, and retained some frizz characteristics after straightening treatments. For this reason, lower combing efforts with increasing fiber diameter were demonstrated only on synthetic fibers. Set holding measurements showed the expected improvement with increasing fiber size. The improvement in hair body and abrasion resistance could even be treated in a semiquantitative form, showing very significant increases in these characteristics with increasing fiber size. The improvements in all cases, especially in hair body, could be well noticed subjectively and, therefore, would apply for on-head conditions as well.

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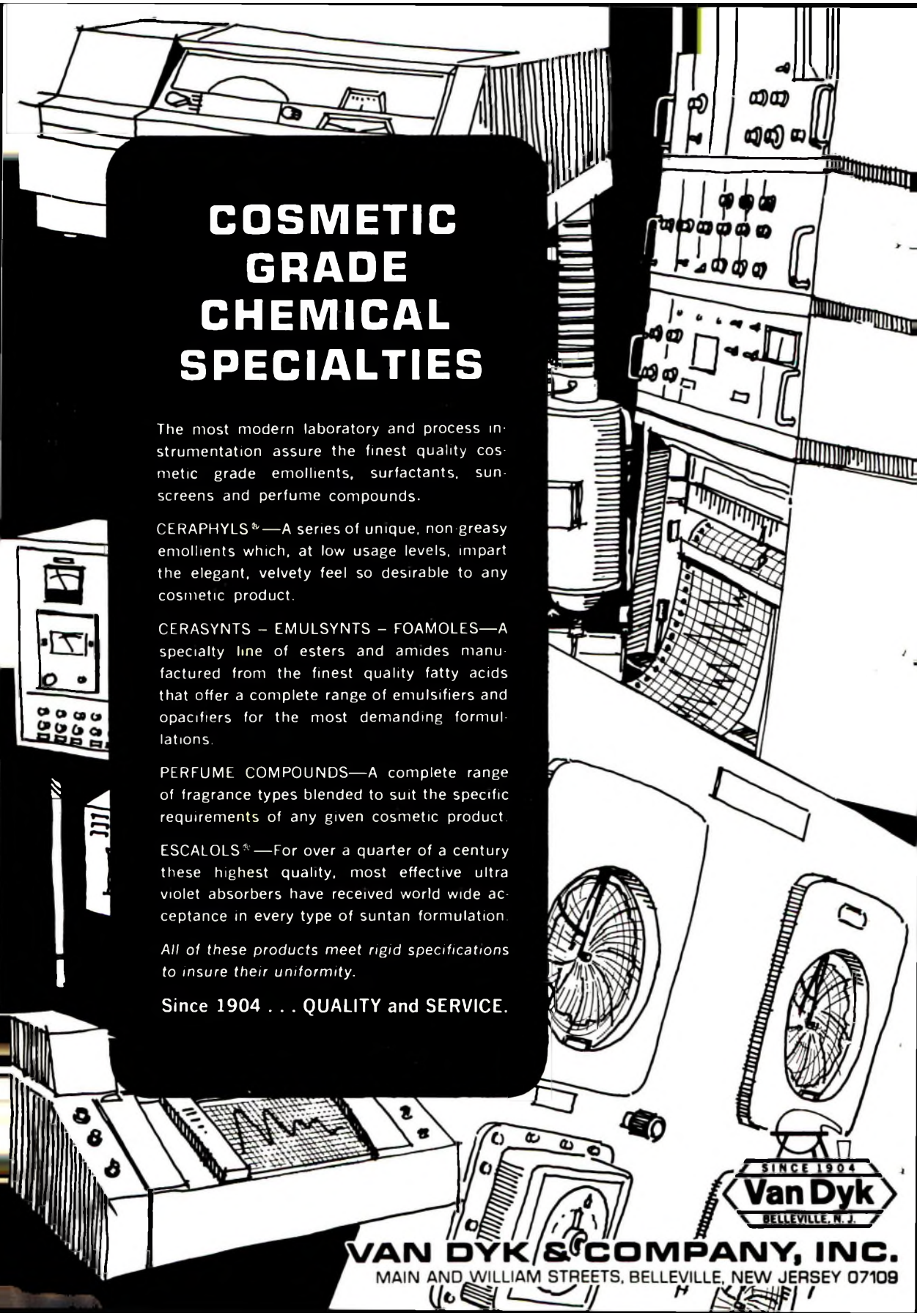

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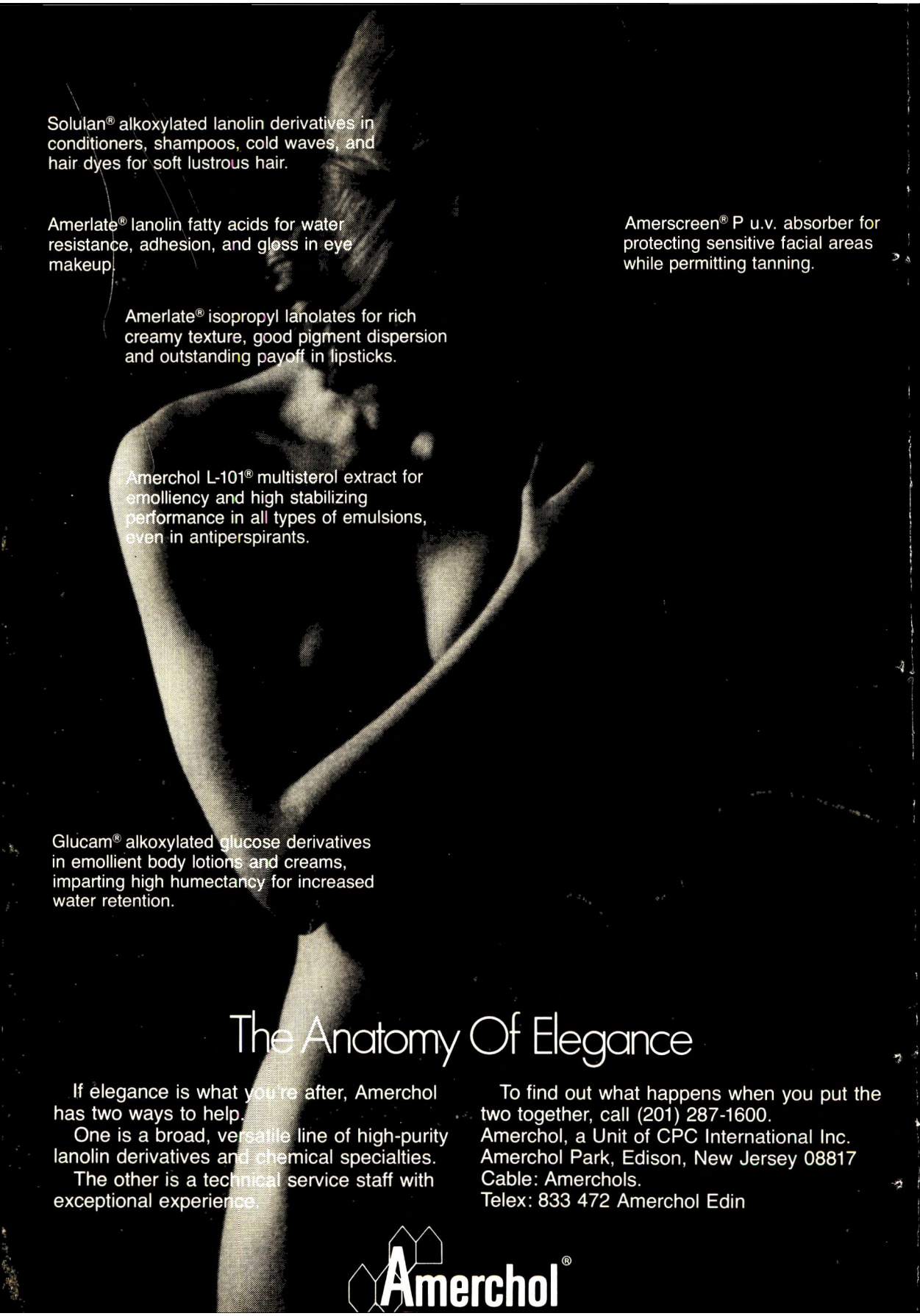

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