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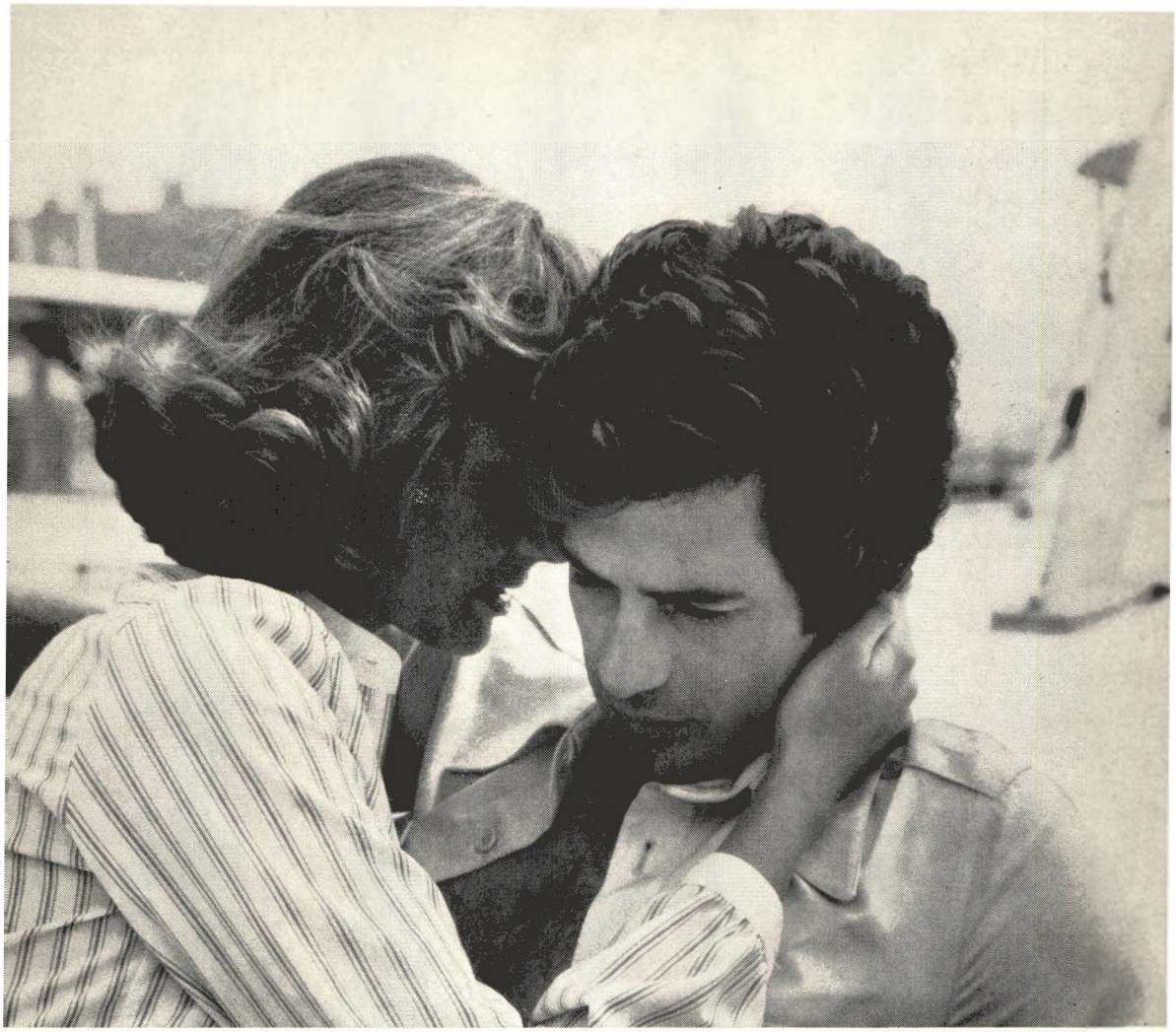

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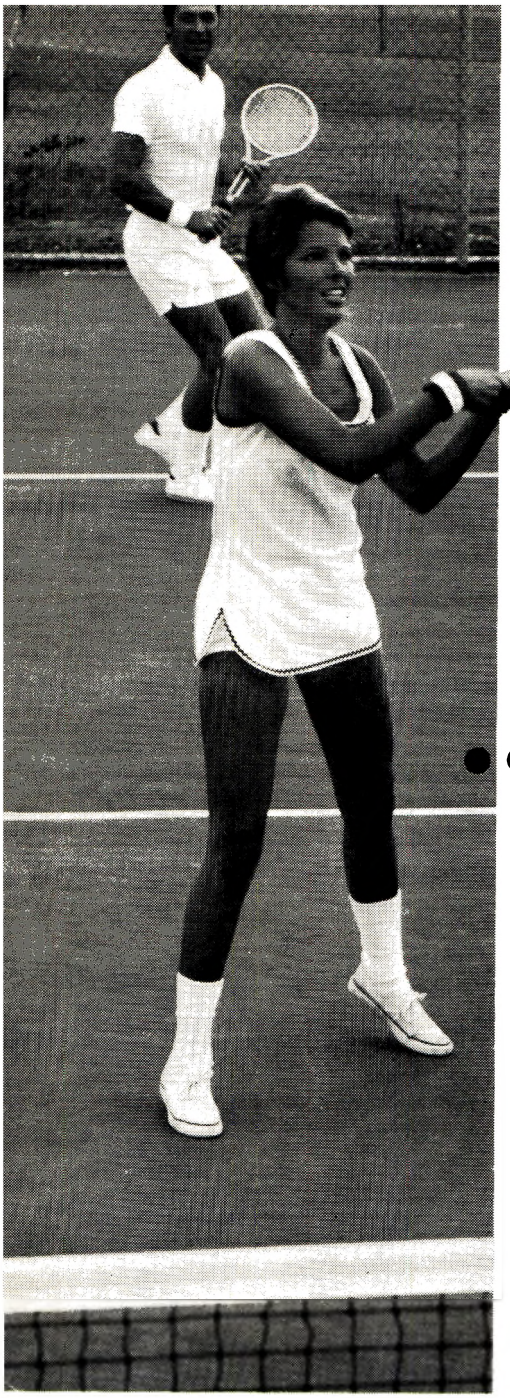

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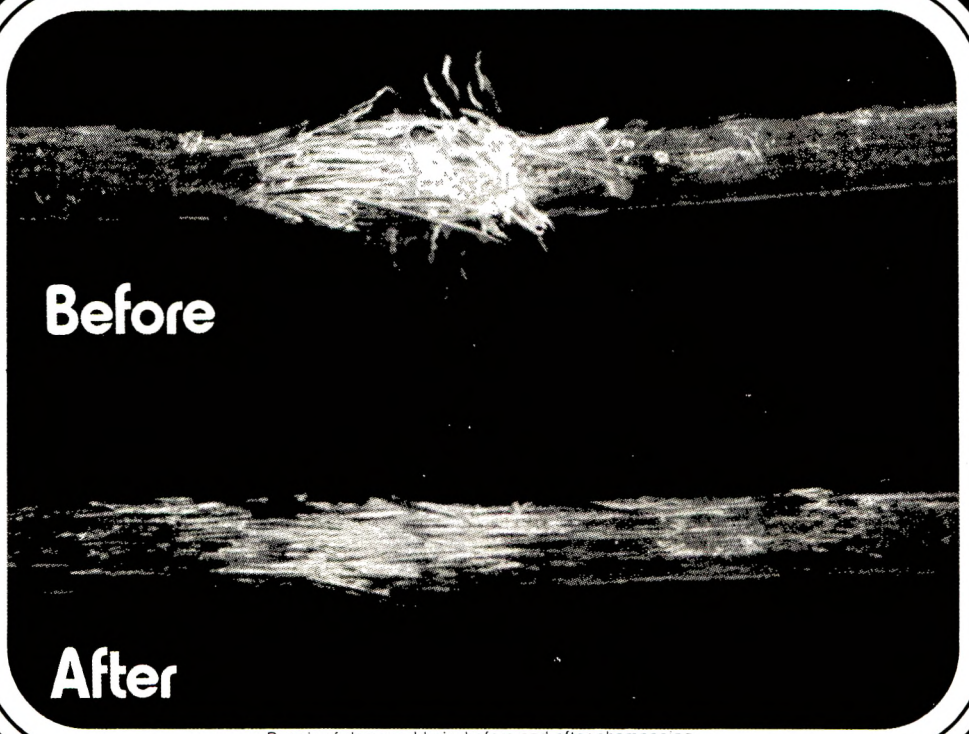

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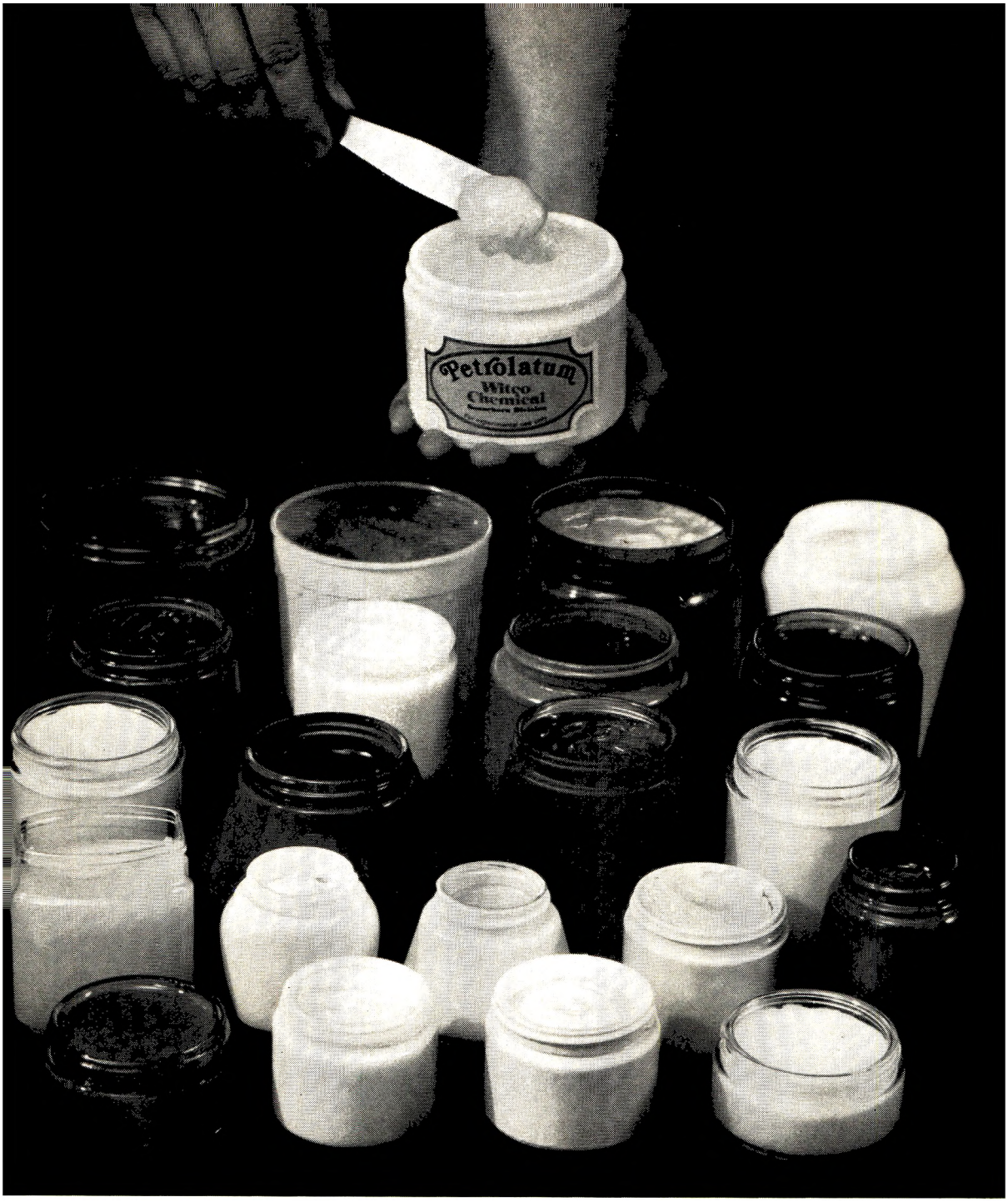

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SYNOPSES FOR CARD INDEXES

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

Characterizing cosmetic effects and skin morphology by scanning electron microscopy: Charles A. Garber and C. T. Nightingale. *Journal of the Society of Cosmetic Chemists* **27,** 509 (November 1976)

Synopsis—The scanning electron microscope has developed into an important tool for characterizing the effects of cosmetic products on human skin. Methods are described for "replicating" areas of stratum corneum as *in vivo* impressions, or "negative replicas." The "negatives" are replicated again to produce "positives," which are then studied in the scanning electron microscope. Through the use of selected control subjects, it has been possible to define the differences between dry and normal skin, the former generally exhibiting larger uplifting desquamating layers (flakes) of stratum corneum. Experimental findings note that beneficial clinical effects are generally accompanied by a reduction in the amount and/or size of the desquamating material. Examples will be given for (1) moisturizing products, (2) protein additives, (3) abradent cleansing products, and (4) moisturizing soaps. The effects, in some instances, are so subtle that unless the microscopy is done as BEFORE and AFTER pairs on the same identical areas, the effects will not be recognized. Once good micrographs are obtained, it is sometimes possible to quantitate the results through the use of Quantimet Image Analyzing Computer, a tool originally developed by metallurgists, but which has great potential for quantifying cosmetic effects.

Flouride ion from toothpaste: M. Hanocq, M. O. Schmitz-Masse, and M. Herpol-Borremans, *Journal of the Society of Cosmetic Chemists* **27,** 533 (November 1976)

Synopsis—The conditions for separating fluoride ion from toothpastes with the aid of microdiffusion were studied during the course of this investigation. Interference with this procedure by specific ions, such as aluminum or silicate, was noted.

Sorption of a cationic polymer by stratum corneum: Joseph A. Faucher and E. Desmond Goddard. *Journal of the Society of Cosmetic Chemists* **27,** 543 (November 1976)

Synopsis—A study was made of the sorption of a cationic cellulose polymer from aqueous solutions by several types of mammalian stratum corneum. The effects of surfactants and other additives were investigated, as well as were the influence of concentration and molecular weight of the polymer. Considerably more material is sorbed than can be accounted for by postulating monolayer coverage of the substrate. The data were found to be explained better by a mechanism of diffusion of the polymer into the outer layers of the stratum corneum than by multilayer absorption.

Diffusion theory analysis of transepidermal water loss through occlusive films: Eugene R. Cooper and Barry F. Van Duzee. *Journal of the Society of Cosmetic Chemists* **27,** 555 (November 1976)

Synopsis—Composite membrane diffusion theory is applied to transepidermal water loss measurements across skin treated with occlusive films. Since the permeability of stratum corneum increases with hydration, it is shown that certain films can be applied to skin to increase transepidermal water loss. Thus, even an increase in transepidermal water loss can indicate that the film is hydrating the skin quite well.

New lanolin acid quaternary salts for use in hair treatment preparations: Justin P. McCarthy, Lee R. Mores, and Mitchell L. Schlossman. *Journal of the Society of Cosmetic Chemists* **27,** 559 (November 1976)

Synopsis—The action of quaternary ammonium surfactants on hair has been studied for many years. Several of the characteristics, which are important in formulating with these salts, are dependent upon their molecular configuration. In this paper, lonolin compounds which essentially comprise quaternary derivatives (quats) of lanolin acids are described. The preparation of a derivative of lanolin consisting essentially of the reaction product of a lanolin acid and a specific diamine followed by quaternization is outlined. The chemical and physical properties of quats are briefly reviewed and compared with emphasis on these new lanolin acid derivatives, and their chemistry and processing is highlighted. Each of these quaternary salts was incorporated into hair conditioning preparations and evaluated on human hair.

Hair body: Patricia S. Hough, J. Elaine Huey, and William S. Tolgyesi. *Journal of the Society of Cosmetic Chemists* **27,** 571 (November 1976)

Synopsis—Hair body can be defined as the structural strength and resiliency of a hair mass. The definition conforms to the qualities assessed subjectively by hair cosmetic users. Five groups of fundamental parameters govern the mass structural strength of hair: hair density on the scalp, material stiffness, diameter, configuration of the fibers, and fiber-fiber interactions. The potential influence of hair cosmetics on hair body can be systematically analyzed by deducing their effects on these separate fundamental parameters. It is proposed that current cosmetic products are effective in modifying hair body through only the last two factors: fiber configuration and fiber-fiber interactions.

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J. Soc. Cosmet. Chem., **27**, 509-531 (November 1976)

Characterizing Cosmetic Effects and Skin Morphology by Scanning Electron Microscopy

CHARLES A. GARBER, Ph.D. and C. T. NIGHTINGALE, B.S.*

Presented May 30, 1975, SCC Seminar, St. Louis, MO

Synopsis: The SCANNING ELECTRON MICROSCOPE has developed into an important tool for characterizing the effects of COSMETIC PRODUCTS on HUMAN SKIN. Methods are described for "replicating" areas of stratum corneum as *in vivo* impressions, or "negative replicas." The "negatives" are replicated again to produce "positives," which are then studied in the scanning electron microscope. Through the use of selected control subjects, it has been possible to define the differences between dry and normal skin, the former generally exhibiting larger uplifting desquamating layers (flakes) of stratum corneum. Experimental findings note that beneficial clinical effects are generally accompanied by a reduction in the amount and/or size of the desquamating material. Examples will be given for (1) moisturizing products, (2) protein additives, (3) abradent cleansing products, and (4) moisturizing soaps. The effects, in some instances, are so subtle that unless the microscopy is done as Before and After pairs on the same identical areas, the effects will not be recognized. Once good micrographs are obtained, it is sometimes possible to quantitate the results through the use of Quantimet Image Analyzing Computer,† a tool originally developed by metallurgists, but which has great potential for quantifying cosmetic effects.

Introduction

The characterization and definition of the effects of cosmetic products on human hair and skin has always been one of the most important responsibilities of the cosmetic chemist. Although the actual formulation of new products is generally based on fundamental principles of physical and surface chemistry, the measurement of the efficacy of such materials has generally been performed by subjective clinical evaluation. Only in recent years, in part

*Structure Probe, Inc., P.O. Box 342, West Chester, PA 19380.
†Imanco, Inc., Monsey, N.Y.

due to the rising demands for the scientific documentation of advertising claims, has interest been focused on the development of reliable quantitative measurements for product efficacy on human hair and skin.

We have found electron microscopy, and in particular, scanning electron microscopy (SEM) to be a powerful tool for scientifically documenting the effects of materials applied to human hair and skin. The transmission electron microscope (TEM) also has its place, but since SEM is basically a surface (topographical) tool, and since studies of products on hair and skin involve surfaces (protein deposits on the outside of a hair shaft; skin roughness is a surface phenomonen), the SEM is generally the instrument of choice. The SEM and TEM, rather than "competing" with each other, are actually complementary, and most important studies ultimately involve the use of both.

The present work is not the first application of SEM for cosmetic studies. In fact, as early as the 1940s (1, 2) various methods of replicating the outer cuticle structure of hair were devised through the use of platinum and carbon techniques. The SEM, which really started to develop as a scientific tool in the late 1960s, was quickly utilized to examine human hair, and Wolfram and Lindemann (3) published a study of the structure and morphology of hair. Further studies have demonstrated yet additional information on hair (4, 5) and, more recently, some very novel studies have been published on the elucidation of the actual structure of the cuticle (6). One of the most inventive approaches was for the study of porosity within human hair (7), which describes a method for the polymerization of methacrylate monomer *in situ* within the holes or pores that exist within the hair structure. The hair is then degraded away, leaving the now "plastic pores" (or "ghosts") available for collection and characterization by SEM. A method for demonstrating the repair of damaged hair and a classification scheme for identifying and quantitating different types of damage has now been reported by DiBianca (8). This latter method was used to substantiate the claim that a hair care product can repair damaged hair.

Although the amount that is now known and published about human hair is substantial, by comparison very little SEM and/or TEM work has been published about human skin. Virtually no SEM or TEM studies have been published that demonstrate the effects or efficacy of specific products on the stratum corneum. This absence of data is not for lack of interest, but because of the enormous experimental difficulties encountered with skin studies. These difficulties have, therefore, severely limited the application of SEM and/or TEM techniques to the skin area.

For TEM studies, a biopsy sample must be (1) "fixed" (hardened to keep it from degrading); (2) embedded (so it can be sectioned); (3) sectioned; (4) "stained" to bring out contrast; and (5) photographed within the high vacuum of the electron microscope. Put quite simply, the changes brought about by the fixing, embedding, and staining are enormous as compared to

the relatively subtle changes brought about by the application of a cosmetic product. In fact, even an oily material applied to the surface of a biopsy sample will tend to diffuse away into the embedding material and not remain on the sample.

Hence, for all of these reasons, SEM tends to be the tool of choice for most skin studies.

Our first SEM studies on human skin did involve biopsy samples, both animal as well as human. We learned quite quickly that the severe dehydration effects of the ultra high vacuum within the SEM left the sample so severely shrunken, distorted, and changed that any relationship between reality and what we were seeing would have certainly been fortuitous. Even some of the newer and more sophisticated methods of sample preparation, such as critical point drying or freeze drying, were not particularly better. Consequently, we have concentrated virtually all of our efforts toward procedures employing skin replicas, which have the advantage that we cannot only characterize by SEM the *in vivo* state of an area of stratum corneum, but we can also follow the same identical area in the micrographs as a function of time, in a sense, like a high magnification form of time lapse photography. In this way, we can follow the effects of a product as a function of time, and evaluate the efficacy of this product relative to a control.

Surely, we were not the first to make replicas of human skin. Facq (9, 10) and Berstein (11, 12) learned back in the late 1960s that normal silicone resin, either of the RTV-11 type* or even the impression materials used in dentistry, would make "acceptable" (relatively free of artifacts) replicas of the top surface of the skin (and, hence, also the top surface of the stratum corneum). Once having obtained the "impression" or "negative" as we prefer to call it, the negative is itself replicated, yielding a "positive" replica of the skin surface. There was also a problem with artifacts in the replicas, such as air bubbles, which tended to limit, in certain respects, the utility of these original efforts.

Unfortunately, artifacts were not the only drawbacks to the methods originally used. First, was the criticism that too small an area was being studied; how was it known that this small area was indeed representative of that area of stratum corneum as a whole? In addition, the enormous heterogeneities present from point to point on the stratum corneum were such that one could almost prove or disprove anything by a careful selection of the area.

Our approach was to develop a procedure that would enable us to do the following.

1. produce high resolution (virtually) artifact-free negative replicas;
2. convert the negative replicas to high resolution positive replicas;

*General Electric Company, Waterford, N.Y. 12188.

3. photograph the same identical areas, before and after treatment, as a function of time, and by following the same identical area, avoid some of the problems of heterogeneity from point to point;
4. make large montages, rather than randomly selected pictures so it would be obvious a large enough area was being photographed;
5. quantify the resulting images either manually or through the use of an image analyzing computer (such as a Quantimet);
6. correlate the results, quantitatively as well as qualitatively, with known clinical conditions.

The purpose of this paper, therefore, is to describe some of the methods we have developed for this purpose, to present the clinical basis for justifying this approach, and to show how the resulting data is presently being used to demonstrate efficacy and document advertising claims.

Experimental

A. *Preparation of Negative Replicas*

RTV-11 silicon resin is acceptable for making the negative replicas, although we find that better results are obtained with the high molecular weight fraction removed and when an absolute minimum of catalyst is used to setup the resin. Certain silicone-compatible surface active agents (such as "Aerosol OT,"[*]) seem to impart better release characteristics and may have their maximum benefit when replicating particularly rough skin (such as psoriatic subjects).

B. *Conversion of Negative Replicas to Positive Replicas*

Almost any thermoplastic resin can be used for this purpose, but we prefer fine spray-dried or as-polymerized polyolefin "bead" polymer. After the positive replica is completed, it is metallized to make the replica surface conductive to prevent sample charging in the electron beam.

C. *Preparation of Replica Cross-Sections*

For replica cross-section work, the positive replicas are diamond knife-trimmed, using a duPont/Sorvall MT2-B Diamond Knife Ultramicrotome.[†] The knife speed and angle must be adjusted for minimum chatter and thinnest sections (even though the sections are not important) as these are the conditions for obtaining the best undistorted and unsmeared cross-sections. Unfortunately, the softer resins yield the best detail in the positives; hence, we sometimes must do the sectioning in a cryostage at liquid nitrogen tem-

[*] American Cyanamid Co., Stamford, CT.
[†] E. I. duPont de Nemours and Co., Inc., Wilmington, DE 19898.

peratures as a means of minimizing smearing and preserving the cross-sectional edge. We have not been successful using glass knives for this purpose.

D.SEM

The work described in this paper was done on a JEOL Model #JSM-U3 SEM.* We have found this equipment to be particularly well-suited for this type of work for several reasons: (1) it can be modified without too much difficulty to provide a virtually distortion-free image in the 15 to 20 X range, an absolute necessity for putting together distortion free montages; (2) it has an extremely flexible goniometer stage, with all of the degrees of freedom necessary to relocate the same identical areas of a replica without exceptional difficulty; and (3) the electronic stability of the instrument is such that micrographs can be taken without discernable drift in brightness or contrast, an extremely important feature when montages are being made.

The most important aspect of our procedure is that every successive replica in a series is done on the very same identical area, same tilt, same magnification, in short, every aspect of the images are identical. We have eliminated any chance that a particular feature of the results might be due to the way the microscopy was done rather than due to real changes on the skin surface. This also means, therefore, that all microscopy, which is done generally in the form of large montages, is clearly from the same identical areas and this fact is so obvious, that even a nonmicroscopy-oriented observer would realize it.

E. *Quantitative Image Analysis*

All image analysis was done on a Quantimet 720B Image Analysing Computer equipped with the automatic detector, optical and epidiascope input modes, and classifier-collector modules with direct teletype output.

Results

An example of what one can typically obtain is shown on Fig. 1. This is an area from the back of the hand of a young female subject in her mid-twenties, and the microscopy was originally done as a montage at 100 X from the scanning electron microscope (but which was reduced for publication). The original individual fields that make up the montage can still be seen.

The "hill and valley" type of topography is "normal," particularly for younger subjects. The one major exception is what is sometimes called the "cobblestone" texture and an example of it is shown in Fig. 2. The term "cobblestone"

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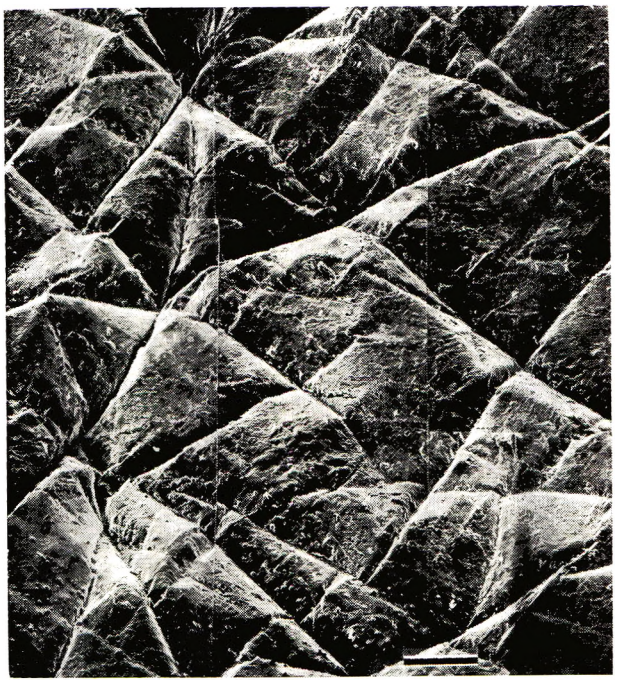


Figure 1. SEM montage taken from positive skin replica from back of hand of female subject in mid-20s. Example of "good" skin. Scale bar represents 300 μm.

texture was originally coined by D. R. Highley (13) who has found that this texture occurs in approximately 5 percent of the population. For studies on skin care products, we generally try to avoid using "cobblestone" subjects, because the effects of cosmetic products are more difficult to discern in the final montages and the quantitative analysis is more difficult.

One must be extremely careful when making both the negative as well as the positive replicas, so as not to produce artifacts. Figure 2 was actually made in mid-1972, and was one of our earliest attempts. It also contains the 3 most commonly found artifacts: (1) air bubbles in the negative replica; (2) air bubbles in the positive replica; and (3) a glazed area of improperly mixed replicating material (in the negative). Even our most experienced replica makers still occasionally produce these artifacts, but the goal is always to minimize their frequency of occurrence. In this way, even though some areas of a replica might be bad, we can generally find at least some areas which have replicated well in all the replicas of a sequence. Type A artifacts can be minimized by using only the freshest resin and catalyst, which are then mixed smoothly without whipping any unnecessarily large amount of air into the

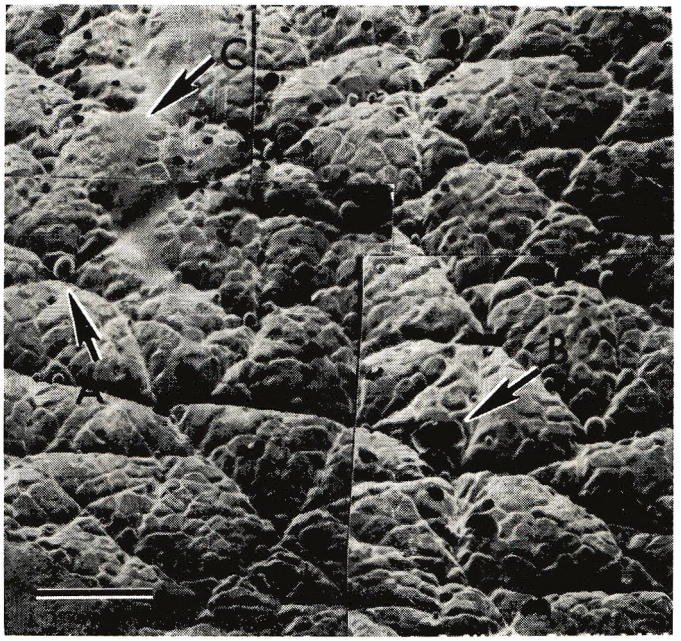
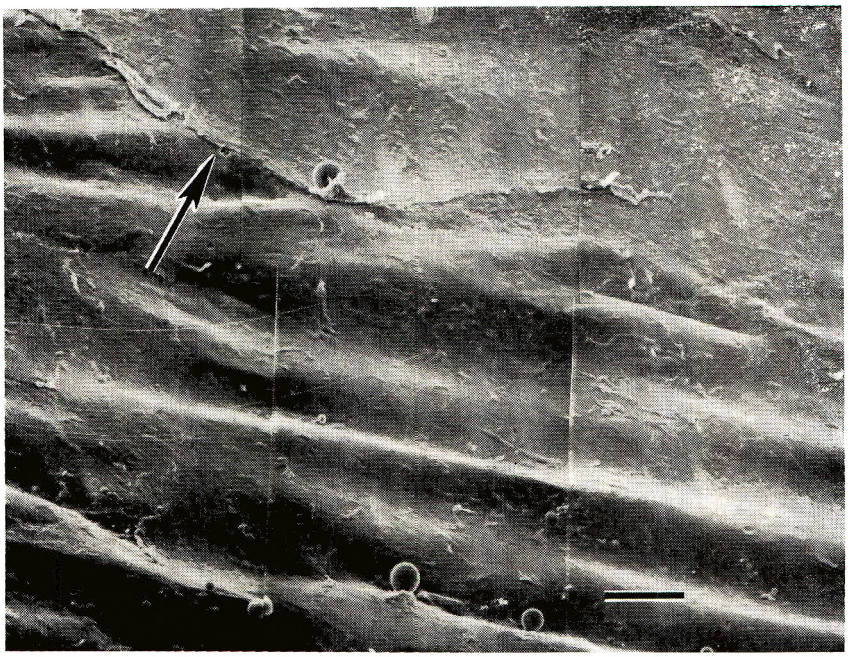


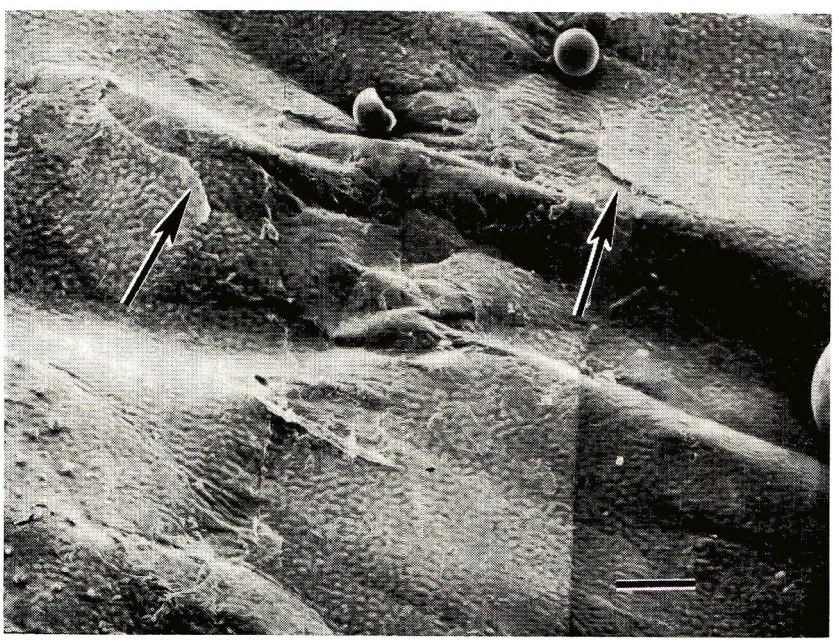
Figure 2. SEM montage of "cobblestone" skin, positive replica, male subject about 30 years old. Typical artifacts: (A) air bubbles in negative; (B) air bubbles in positive and (C) glazed area of improperly mixed replicating material.
Scale bar represents 1000 μm.

resin. Type B artifacts are caused by either unstable positive replicating material, the use of too high a temperature when the positives are made, or not sufficient contact pressure of the positive replica material with the negative. Type B artifacts are not as devastating as type A, as the option always exists for trying to make a better positive from the same negative. Type C artifacts are the most frustrating, since they can be so easily confused with real cosmetic effects. An emollient, for example, which forms a coating can look surprisingly similar to type C artifacts. This type of artifact is almost always the result of either improper mixing of the resin with the catalyst, less than active catalyst, or a resin temperature below room temperature (resin should be stored under refrigeration to minimize autopolymerization of resin). Since many of the micrographs used in this paper were prepared as long as 4 years ago, not all will be of the same high quality as Fig. 1, and special mention will not, in general, be made of these artifacts.

The ultimate objective of this work, from the very beginning, was to use this replica approach to demonstrate improvement in the condition of the stratum corneum as a result of the application of a cosmetic product. Hence,



(a)



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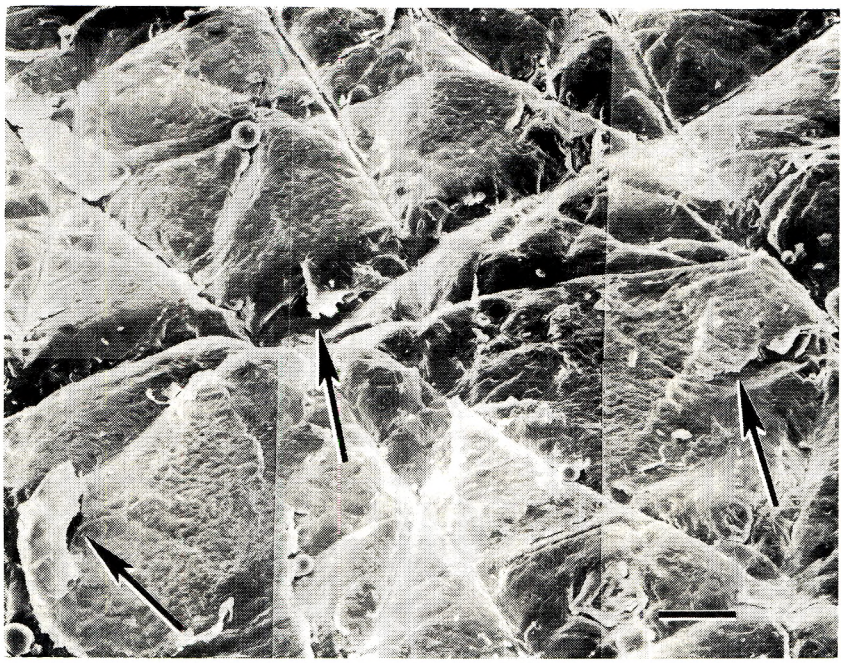

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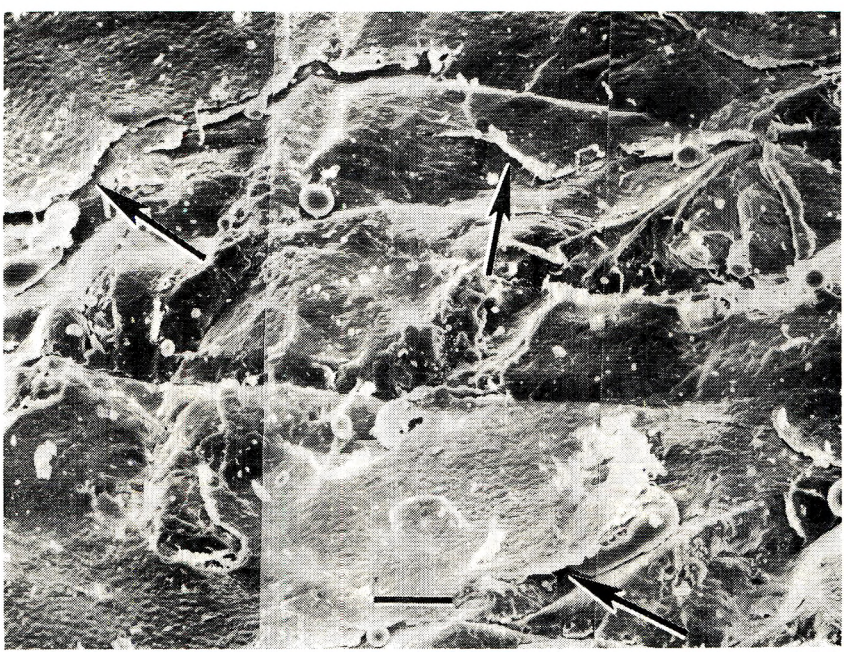


(d)

Figure 3. SEM montages of clinically graded stratum corneum: (a) normal; (b) "mildly flaky," (c) moderately flaky, and (d) severely flaky. As condition becomes worse, size and number of the unlifting layers increases. Scale bar reperesents 200 μm

the primary interest has been in dry skin, and we developed a criterion for evaluating the quality of the stratum corneum. Figure 3 shows a sequence of 4 montages taken from the calf area of elderly females. This work was done in collaboration with Dr. Albert Kligman, of the University of Pennsylvania, who actually made the clinical evaluations from these subjects. All four montages are at the same magnification and viewing conditions, and the only variable here is the clinical variation from subject to subject. "Normal" skin (Fig. 3(a)) basically shows a relatively smooth surface and the individual cells are desquamating away as extremely small clusters (or perhaps individually) and not as large layers. Note the absence of what we will later refer to as uplifting layers. Mildly Flaky (Fig. 3(b)) shows slightly more evidence of layers (arrows) but that does seem to be the primary difference. Moderately Flaky (Fig. 3(c)) shows not only a substantial increase in the number of layers, but they seem to be lifting away or uplifting from the surface of the stratum corneum. Severely Flaky (Fig. 3(d)) differs only in terms of the numbers of uplifting layers, and, of course, the size of the layers has increased as well. In fact, after being involved with a large number of different projects involving many different subjects and different dermatologists, we have come to the following general conclusions.

1. Dry skin, flaky skin, chapped skin, or some of the other terms used to describe "bad" skin, from a dermatological standpoint, when viewed by replication in this fashion, all look similar.

We would not go so far as to say these conditions have similar causes, but, certainly, the end result is similar; the stratum corneum begins to desquamate more as entire layers of dry material rather than small groups of individual cells, and these layers are the cause of undesirable clinical manifestations. These layers are responsible for the rough feel as well as the appearance.

2. Whatever one does to "improve" these types of skin conditions, and when there is in fact a discernable clinical effect, the change has always been accompanied by a reduction in the size and number of the uplifting layers. In almost three years of regularly directing projects of this type, we have observed no exceptions. When obvious differences in the replicas have not been observed, we have later learned that the differences observed clinically (in a clinical testing environment) were considered marginal and were not substantial.

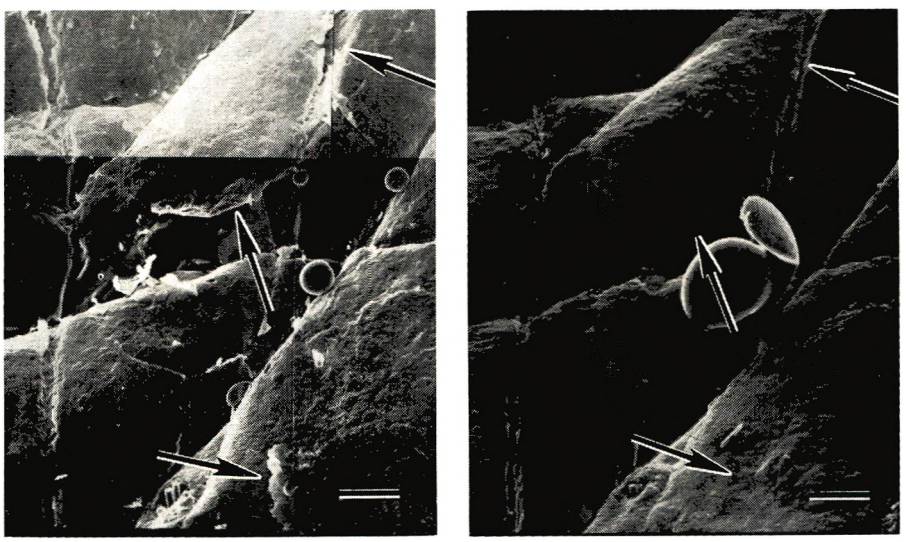
These conclusions certainly must be considered somewhat "radical" in that not once did the word "moisture" enter into the discussion. Everything has been explained away solely on the basis of uplifting layers, and if moisture is important, then its efficacy must be due to its effect in changing the mechanism of desquamation from large layers back to individual cells. In recent years, the amount of "moisture" in the stratum corneum has generally been considered the primary parameter for evaluating skin quality. If the impli-

cations of the SEM results are correct, the efforts expended to quantify the presence, absence or subtle changes in water content in the stratum corneum may be lessons in experimental eloquence, but from a scientific standpoint, they may not be measuring the really important variable. We believe we have found strong evidence that the effect of water alone, if it does do something, is miniscule compared to the overall covering and lubricating effects of the oils and other materials present in the typical product. A BEFORE and AFTER 1-h warm water bathtub soak set of replicas show almost no change in the replicas, although, clinically there is a huge change. The inescapable conclusion is that this type of moisturization produces demonstrable clinical effects, but the changes are not within (or on) the stratum corneum but are, in fact, underneath it!

To better communicate the basis for our conclusions, a few additional examples are in order.

A. *Moisturizing Soap*

Figure 4 shows the same identical area of clinically chapped skin from a female (mid-thirties) subject, before and after washing with a "moisturizing"



(a) (b)

Figure 4. SEM montages of chapped skin (back of hand): (a) before, and (b) after treatment with "moisturizing" soap. Note dramatic reduction in prevalence of uplifting layers of stratum corneum. Location of air bubbles artifact in after was most unfortunate. Scale bar represents 300 μm

soap. We do not know what exactly would have been considered the "active" ingredient.

Our protocol was to do the following; (1) make BEFORE replica; (2) wash with experimental soap; (3) rinse off soapy water; (4) wait 30 min. (for maximum chapping effects to occur); and (5) make AFTER replica.

In the BEFORE, we can see all of the manifestations of "bad" skin namely the uplifting layers, (see arrows) which are general and cover the area. After one washing, the subject felt better, the original chapped appearance was nowhere near as prevalent, but most important, there was a dramatic reduction in the number of uplifting layers. Whenever we run this particular protocol, we generally run Ivory soap* as a control on the other hand, and we have never seen an improvement of this type with Ivory soap. Hence, we can be confident the effect is due to the soap used and is not caused by some other parameter. Furthermore, the Ivory soap control acts as proof that any smoothing effects cannot be explained in terms of a cleansing effect of the replicating material.

B. *Abradent Cleanser*

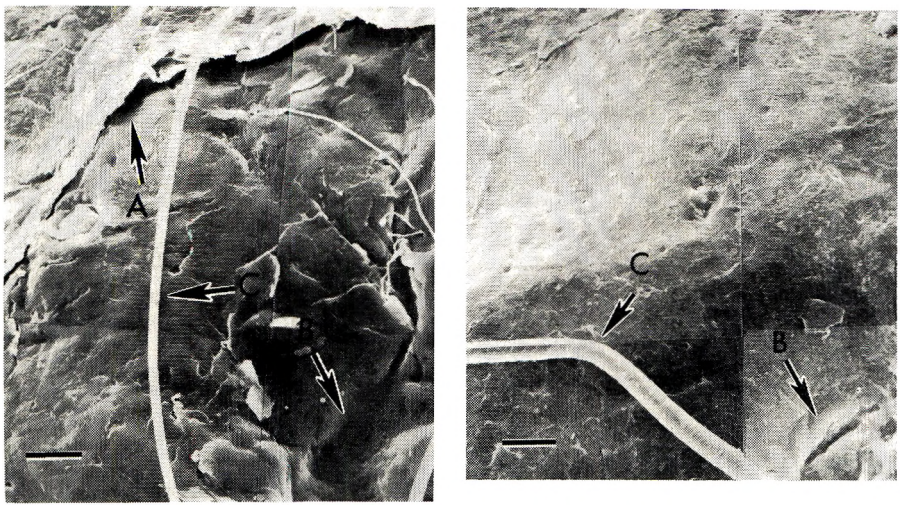
It is well accepted that the skin clinically feels smoother after the application of an abradent facial cleanser. Figure 5 shows the uplifting layers present in the BEFORE, but, which are removed in the AFTER. Hence, again we see a process which results in a beneficial clinical effect once the uplifting layers are removed. Surely no one would call this "Moisturization," but we have "improved" the skin by removing the uplifting material.

For a control, on the opposite side, we apply soap and water only. Soap and water does have an effect, but certainly nowhere even approaching the effect of the abradent cleanser. Hence, in this instance, not only can we demonstrate the efficacy of an abradent product, but we can demonstrate superiority.

C. *Moisturizing Hand Lotion*

Certainly, it is recognized that the application of many of the common lotions and creams presently available will improve and bring relief to sufferers of dry or chapped skin. Are these "moisturizing" products really adding moisture to the stratum corneum? Or are their beneficial effects obtained by some other mechanism? Figure 6 gives an excellent insight into the mechanism of what really happens. Initially, there is a complete coverage and, even though the product is rubbed in, at these magnifications, we very clearly see the covering. Water alone will not cause this effect and as previously pointed out, water alone shows virtually no change whatsoever. Is this moisturization?

*Procter & Gamble, Cincinnati, OH.



(a) (b)

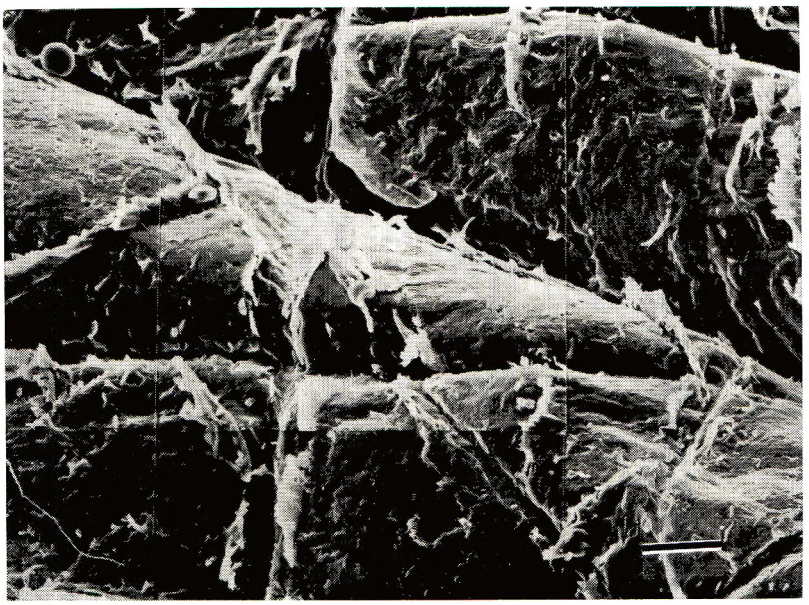
Figure 5. SEM montages of dry facial (female subject, upper 40's): (a) before and (b) after cleansing with abradent facial cleanser. Uplifting layers present originally (arrow A) are removed during treatment. To lower right is small comedon that has been partially cleaned during process (arrow B). Fiber appearing material is facial hair (arrow C). Scale bars represent 50 μm

Maybe it is and maybe it is not depending on how one defines moisturization, but clearly the total effect is far beyond what water alone will do. In any case, we can define a definite improvement as measured by the reduction of the uplifting layers of stratum corneum, even if their absence is due to their being covered up. During the time of the experiment, the subject certainly experienced a beneficial clinical effect, the skin felt softer, and in general, the subject would have perceived the skin was moisturized.

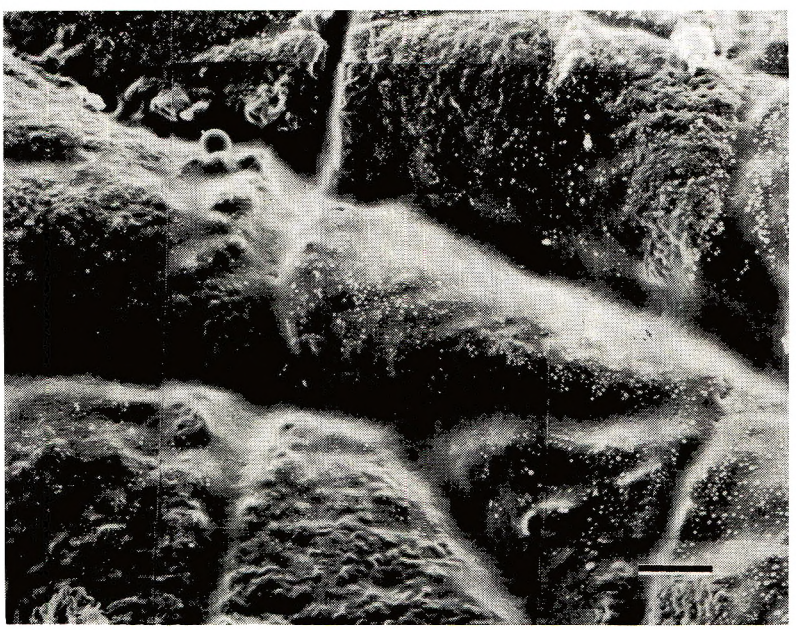
D. *Active Ingredients*: (*soluble collagen, proteins and special cellulosic-type polymers*)

In the last several years, much attention has been focused on the efficacy of certain active raw ingredients when incorporated into skin care products. We have examined many of them, and some do seem to have an effect, and we can follow the changes brought about by these materials through replica studies. One such study was performed in collaboration with Kurt Neulinger (14) utilizing the following protocol on a chapped skin subject.

1. The back of the hand was soaked for 10 min. in 5 per cent sodium lauryl sulfate solution to further roughen the skin. After waiting 20 min, the BEFORE replica was made (Figure 7(a)).



(a)



(b)

(c)

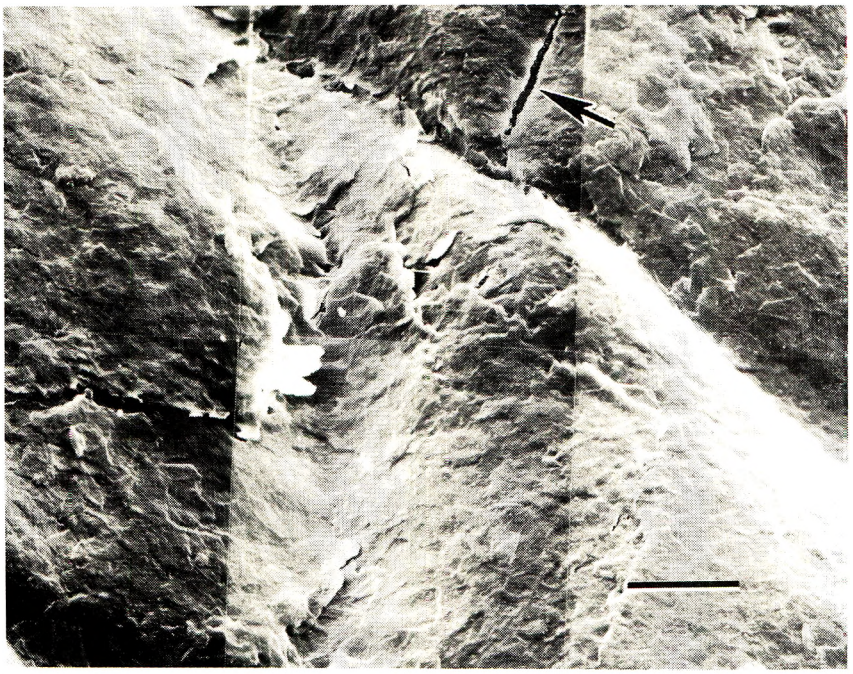
Figure 6. SEM montages of chapped skin: (a) before, (b) after 1 h, and (c) after 5 h applying "moisturizing" lotion. Note covering of uplifting layers after 1 h and onset of their reemergence after 5 h. Scale bars represent 300 μm

2. Water was then patted onto the back of the hand, and after waiting 20 min, the AFTER WATER replica was made (Figure 7(b)).

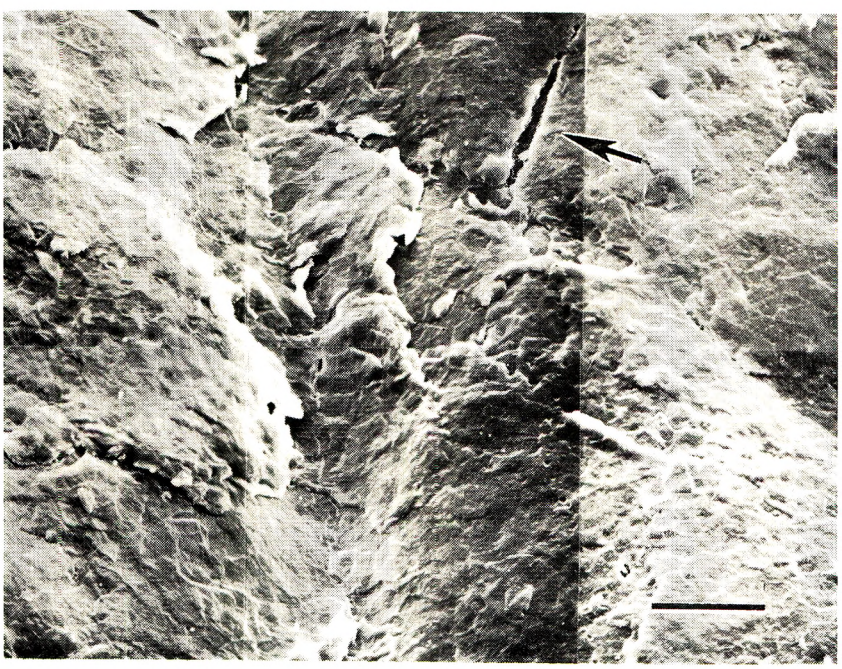
3. Collasol* was patted onto the back of the hand exactly as was done for the water control followed by a gentle rinse. After 20 min, the AFTER COLLASOL PLUS WATER replica was made (Figure 7(c)).

4. "Collasol" was again applied, but not rinsed off, and after 20 min, an AFTER COLLASOL replica was made (Figure 7(d)). The first point that is most readily apparent (Fig. 7) is the difference in overall appearance between the two replicas with (Fig. 7 (c, d)) and the two without (Fig. 7 (a, b)) "Collasol." The BEFORE and WATER ONLY replicas show the manifestations of dry skin by virtue of the presence of some uplifting layers, but both AFTER COLLASOL PLUS WATER RINSE, and AFTER COLLASOL show improvement over WATER ONLY. Such observations certainly provide

*Croda, Inc., New York, N.Y.



(a)



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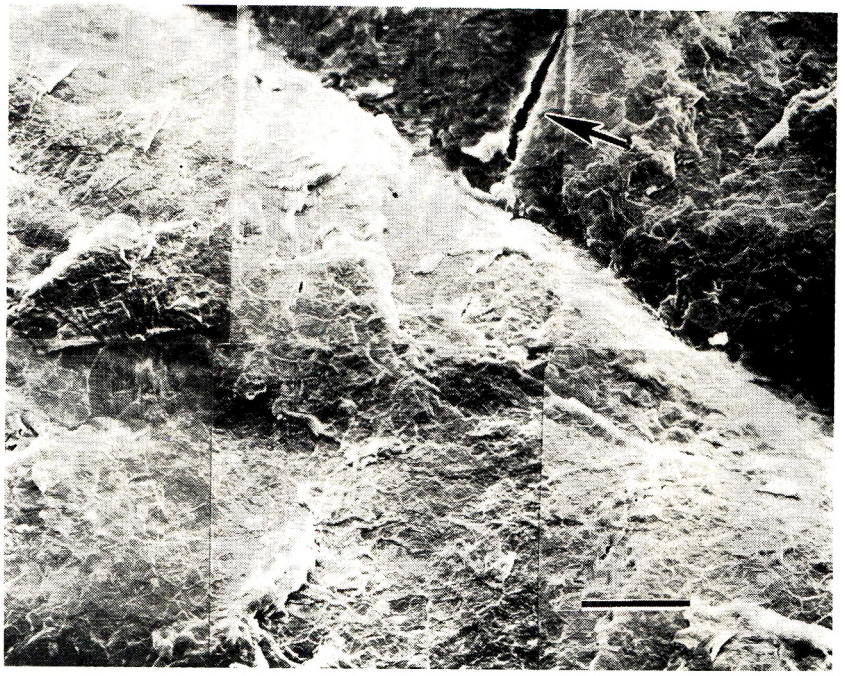

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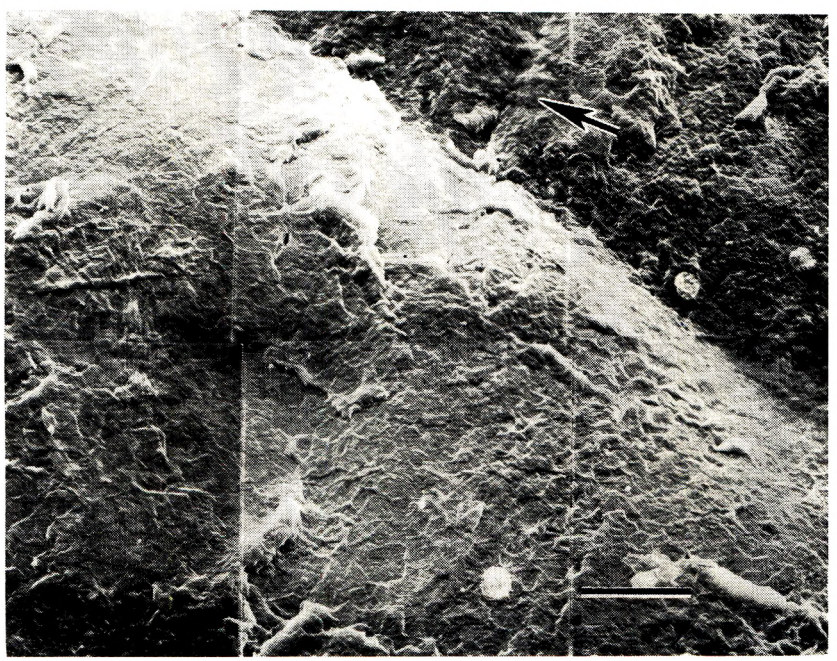

(d)

Figure 7. SEM montages showing effects of Croda "Collasol" when applied to mildly dry skin: (a) before, (b) after water only, (c) after collasol plus water rinse, and (d) after collasol (no rinse). Note indications of smoothed skin texture, and that water alone does virtually nothing. Scale bars represent 100 μm

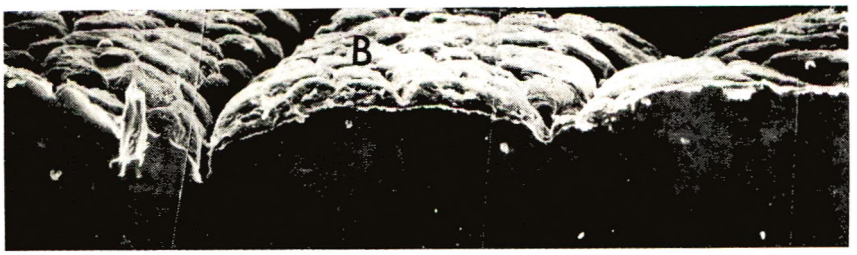

Figure 8. SEM cross-sectional montages showing "profile" of human skin

evidence that this material is substantive to human skin. When Collasol is applied and not rinsed off, there has been an even more obvious smoothing effect.

Are these moisturizing effects? Clearly, water alone did virtually nothing to the stratum corneum that we can see. There are those who believe materials such as Collasol attract moisture, thereby "holding" moisture to the skin. In any case, one does apparently perceive a clinical effect with Collasol (11) and the replicas tend to support that clinical fact.

To summarize, these results indicate that any cosmetic treatment that reduces the number or size of uplifting layers on the stratum corneum will result in a beneficial clinical effect and the quantitative measurement of efficacy of a product can be obtained by measuring the number of uplifting layers present.

We have used this approach quite successfully, not only for the protocols already described, but also for demonstrating the following: (1) product persistence and its resistance to challenge such as from soapy water or sea water; (2) long term therapeutic effects by following subjects for weeks instead of only hours (or a few days); from the montages, a reduction in the size and number of uplifting layers suggests a definite quantitative improvement.

Another commonly mentioned result of the application of a moisturizer is the "plumping" of the stratum corneum. We cannot ourselves properly define "plumping." However, we do know that if a subject (1) sits in hot bath water for an hour, the stratum corneum is thought of as being plumped, or (2) wears an occlusive patch for 48 h, the skin is similarly thought of as being "moisturized" and "plumped."

Yet, by replication, as we previously indicated, we see virtually no change on the surface of the stratum corneum! Since both soaking in hot water as well as a 48 h occlusive covering produce substantial clinical changes, but yet by replication we see little or no change, we are forced to conclude that the real changes, in these instances, are not in the stratum corneum but are, in fact, underneath this top horny layer.

To gain a better insight into the changes that do occur, if any, we have developed a method for cross-sectioning (see Experimental section) positive skin replicas to reveal in cross-section the profile of the topography of the skin surface (Fig. 8).

We have seen "effects", namely a dramatic (apparent) smoothing, when an occlusive layer, such as a typical lotion, is applied (such as Figure 6(b)). In other words, when the "valleys" of the topography are filled in (or a covering layer has been applied), we can demonstrate a definite effect on cross-section replicas. However, for the more subtle case, where the effect is due primarily to a reduction in the number of uplifting layers (such as Figs. 4 and 7), the cross-sectional veiws have not been particularly useful.

Discussion

It is clear that the scanning electron microscope, when used to photograph replicas of human skin, can be a powerful tool for evaluating the efficacy of skin care products. By associating the concentration and size of the uplifting layers with skin quality, we can assess the long (or short) term benefit of a particular cosmetic formulation.

An example of the type of quantitation that is possible is demonstrated in Figs. 9, 10, and 11, where we have the same replica sequence used in Fig. 6 (BEFORE, AFTER 1 h, AFTER 5 h,), except at slightly lower magnification. Figure 9 shows the original montages; Fig. 10, the montages with what we call "marked overlays" and the "marked overlays" are shown alone in Fig. 11. What we are really doing is marking on the overlay all bad areas as defined by uplifting layers. The larger the blackened areas, the worse the skin condition.

In this fashion, it then becomes possible to quantitate the degree of improvement and follow how long the effect persists.

The ultimate question is still with regard to "moisturizing." From our data, it would appear that the action of most typical moisturizers is to penetrate into (but not necessarily through) the stratum corneum, plasticizing the otherwise dry horny layer. Whether we are speaking specifically of humectants, occlusive lipids, or something as mundane as mineral oil, the mechanism seems to be the same, namely a covering, which is then followed by a diffusion of the topically applied materials into the layers of the stratum corneum.

Once so swollen, a combination of surface tension effects (which keep the uplifting layers flattened down on the plane of the horny layer) and lubrication effects lead to the perceived clinical effects. Some materials, such as Collasol, certain proteins, and cellulosic-derived polymers may work primarily by binding water to the top surface, after which the surface tension effects dominate. Clearly, without the presence of an oily layer, such materials could accomplish the desired clinical effects without being greasy at the same time. In general, however, for the typical moisturizing product presently on the

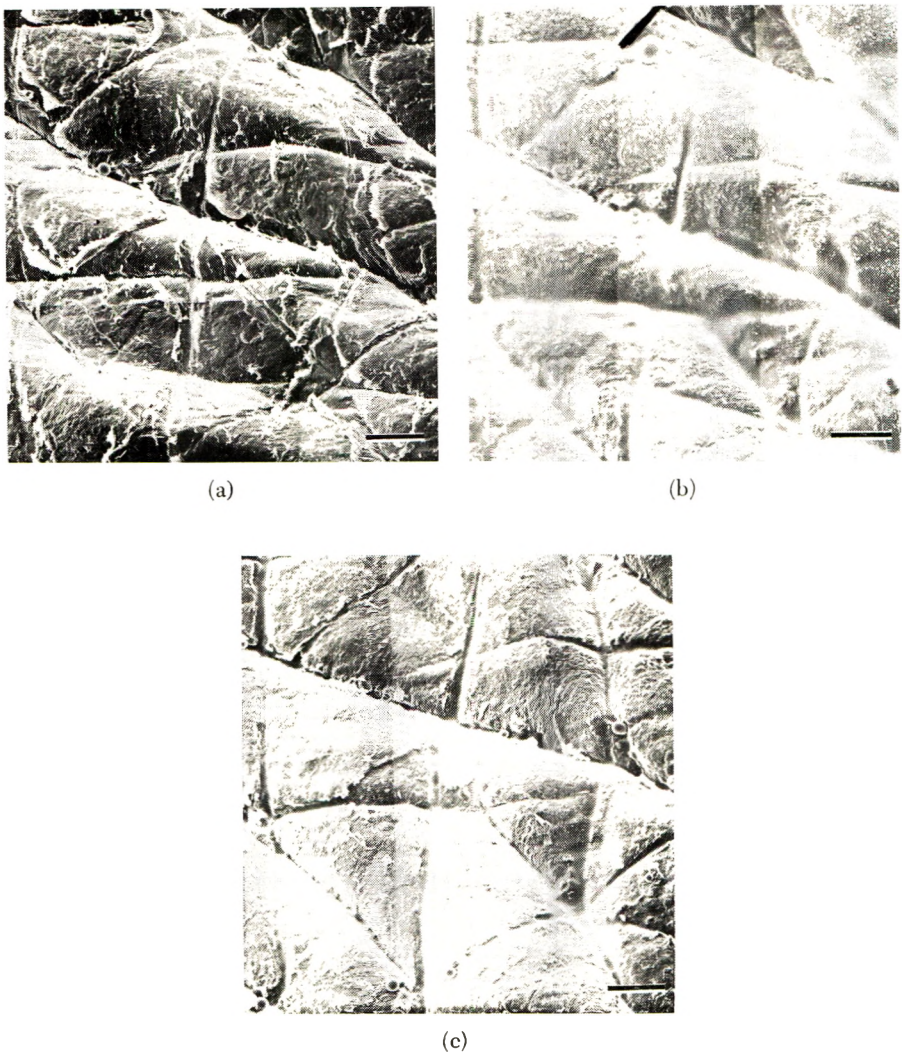

Figure 9. SEM montages showing: (a) before, (b) after 1 h, and (c) after 5 h applying typical commercial hand lotion. Scale bars represent 330 μm

market, although water may be involved, the primary effect is due to the oils and additives other than water.

Conclusion

SEM on *in vivo* skin replicas made as BEFORE and AFTER pairs from the same identical area of stratum corneum demonstrate that beneficial clinical

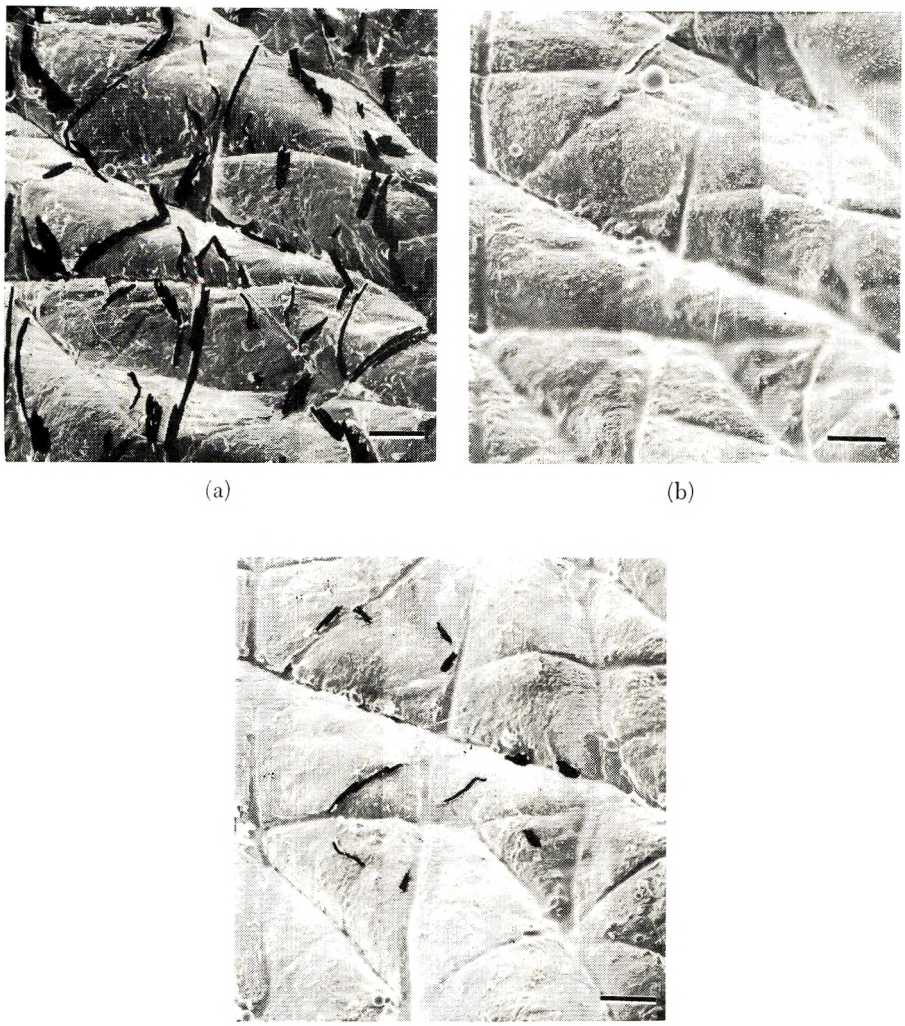

Figure 10. Same as Fig. 9, but all uplifting layers have been blackened on transparent overlay

effects seen with the application of a cosmetic product correlate with a reduction in the size and numbers of uplifting layers of skin. Water alone seems to have little effect on the stratum corneum and the primary mechanism of action of most typical commercial moisturizers seems to be one of plasticizing, lubricating, and even covering the brittle uplifting layers that are responsible for the undesirable clinical effects. In any case, the term "moisturi-

Figure 11. Transparent overlay from Fig. 10 showing uplifting layers present (a) initially (12 per cent area black), (b) after 1 h (0.3 per cent area black), and (c) after 5 h (1 per cent area black)

zation" probably does not properly describe the mechanism of action of the typical moisturizer products presently being sold.

Acknowledgments

The authors are grateful to the microscopists who actually took the SEM pictures (Carol Kazimir, Patricia Kaiser, John Ware); to Richard W. Swayne

for help in the development of the replicating procedures, and to Dean Lawthers for his suggestions involving the quantitative image analysis. We are also grateful for the stimulating discussions on skin texture and quality with many individuals active in the cosmetics industry including Sal DiBianca (American Can Company); Dr. John Hiller (Yardley); R. R. Riso (Stepan Chemical); Dr. George Cohen (Bristol-Meyers); Dr. Martin Rieger (Warner-Lambert); Albert Kligman, M.D. (University of Pennsylvania); Dr. Myra Barker (Pantene) and D. G. Muccia (Leeming/Pacquins).

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J. Soc. Cosmet. Chem., 27, 533-541 (November 1976)

Methoden zur Bestimmung von Fluoridionen in Zahnpasten

I. Studie zur Trennung der zu bestimmenden Ionen durch Mikrodiffusion

M. HANOCQ*, M. O. SCHMITZ-MASSE** und M. HERPOL-BORREMANS**

Synopsis—The conditions for separating fluoride ion from toothpastes with the aid of microdiffusion were studied during the course of this investigation. Interference with this procedure by specific ions, such as aluminum or silicate, was noted.

Einleitung

Von allen krankhaften Zuständen scheint die Zahnkaries am weitesten verbreitet zu sein. Zu den bei den Zahnärzten gebräuchlichen Mitteln, sie zu bekämpfen, gehört die Suche nach einer Zahncreme, die außer einer kosmetischen auch eine funktionelle Wirkung besitzt. Eines der hauptsächlichen Mittel, dieses Ergebnis zu erzielen, ist, die Widerstandskraft des Zahnschmelzes zu verbessern. Dabei werden Fluoridionen als wirksam angesehen. Diese Anionen haben jedoch eine wohlbekannte pharmakologische Eigenschaft: ein enger Spielraum trennt die therapeutische Dosis von der nur wenig erhöhten, bei welcher die ersten toxischen Symptome auftreten. Deshalb verbietet die Königliche Verordnung vom 24. 5. 73 das Verkaufsangebot, den Verkauf, die an Bedingungen gebundene oder unentgeltliche Überlassung kosmetischer Produkte, welche verschiedene Fluorderivate in Mengen enthalten, die die zulässigen Grenzen überschreiten (0,125 % oder 0,2 %, je nach Substanz).

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Diese Verfügungen erfordern demnach eine sehr strenge Kontrolle besonders für den Analytiker. Dieser aber stößt häufig auf größere Schwierigkeiten vor allem wegen der Zusammensetzung der Mischungen, und das um so mehr, als wegen o.e. Kgl. Verordnung die Hersteller nicht gezwungen sind, den Gehalt an Fluoridionen und die Art der verwendeten Stoffe anzugeben; es ist deshalb schwierig, theoretisch die gegenseitige Beeinflussung der verschiedenen Substanzen vorauszusehen. Um dieses Problem zu lösen, schien es uns unerläßlich, bei der Durchführung der verschiedenen Bestimmungsmethoden eine vorherige Trennung der zu bestimmenden Anionen vorzunehmen, da die Anwesenheit störender Ionen oder die Bildung von Fluoridkomplexen mit anderen Verbindungen nicht auszuschließen ist.

Unter den Methoden zur Trennung des Fluors ist diejenige, die auf der Diffusion als Fluorwasserstoff basiert, auf jeden Fall die eleganteste und einfachste (1–3). In früheren Untersuchungen hat der eine von uns (4, 5) den Gebrauch einfacher Petrischalen aus Polystyrol als Diffusionszellen empfohlen: der Fluorwasserstoff wird aus der komplexen Mischung durch Perchlorsäure freigesetzt und an Natriumhydroxid gebunden, das sich auf der Innenseite des Deckels einer Petrischale befindet. Diese einfache Technik, die wir hier regelmäßig angewendet haben, hat sich zu unserer völligen Zufriedenheit bewährt, außer – wie wir im Verlauf dieser Arbeit zeigen werden – bei der Bestimmung von Aluminiumfluorid, die nach der Abtrennung des Anions mit dieser Methode nicht quantitativ ist.

Experimenteller Teil

Apparaturen und Reagenzien

Apparaturen

Beckman Spektrophotometer acta V mit 1 cm-Quarzküvette. Polystyrol-Petrischalen mit 50 mm Durchmesser und 12 mm Höhe, mit Deckel (Mikrodiffusionszellen).

Reagenzien

Pufferlösung pH 3,5

15 g Natriumacetat-trihydrat (Merck p.a.) in etwa 250 ml doppelt destilliertem Wasser lösen; dann 117 g kristallisierbare Essigsäure 99–100 % (Merck p.a.) hinzufügen und auf 500 ml mit doppelt destilliertem Wasser auffüllen.

Alizarincomplexon-Lösung 10^{-3} M.

Zu 5 ml einer ungefähr 0,5 N-Natronlauge 385,2 mg Alizarincomplexon (B.D.H.*) geben und bis zur vollständigen Lösung rühren. Nach Verdünnung auf ca. 900 ml mit doppelt destilliertem Wasser 400 mg Natriumacetat-trihydrat (Merck p.a.) zugeben und den pH-Wert durch Zugabe einer ungefähr normalen Salzsäurelösung auf 5,0 bis 5,5 einstellen (die Farbe springt von violett auf rot um). Mit doppelt destilliertem Wasser auf 1 l auffüllen und nach Filtration durch Whatman-Nr. 1-Papier die Lösung in einer braunen Glasflasche aufbewahren.

Lösung von Cer(III)-nitrat 10^{-3} M.

Man stellt eine ca. 0,02 M-Cer(III)-nitratlösung her: $Ce(NO_3)_3 \cdot 6\ H_2O$ (Merck puriss.), indem man 2,167 g dieses Reagens in 250 ml doppelt destilliertem Wasser löst. Der genaue Titer dieser Lösung wird mit Hilfe einer Lösung von 0,05 M-Dinatriumäthylendiamin-tetraacetat in Gegenwart von Xylolorange als Indikator auf pH 6 eingestellt. Einem genau berechneten Volumen der Lösung (ca. 50 ml) fügt man 0,1 ml konz. Salpetersäure (Merck p.a.) (mindestens 65 % und Dichte etwa 1.40) und 50 mg Hydroxylaminhydrochlorid (Merck p.a.) hinzu und ergänzt dann auf 1 l mit doppelt destilliertem Wasser.

Wässrige Lösung von 50 % Dimethylsulfoxid (V/V),

hergestellt aus einer Verdünnung von Dimethylsulfoxid Merck für Synthese.

Äthanolische Natronlauge 0,5 N:

Man löst 10 g Natriumhydroxid (Merck p.a.) in 200 ml doppelt destilliertem Wasser. Nach dem Abkühlen füllt man mit Äthanol 94 % auf.

Perchlorsäure 70 % (Merck p. a.):

Stammlösung: man löse genau 1,1050 g Natriumfluorid (Merck p.a.), das vorher bei 105° getrocknet wurde, in 100 ml doppelt destilliertem Wasser. Danach bereitet man die Lösungen, von denen 1 ml = 1 µg F^- (1 ppm), 1 ml = 10 µg F^- (10 ppm) und 1 ml = 100 µg (100 ppm) enthalten, mit doppelt destilliertem Wasser. Alle Lösungen werden in Gefäßen aus Polyäthylen aufbewahrt.

* British Drug House

Verfahrensweise

Trennung der Fluoridionen durch Mikrodiffusion

Die Innenseite des Deckels der Petrischale wird zunächst mit einer bekannten Menge von festem Natriumhydroxid überzogen. Zu diesem Zweck wird 0,1 ml der 0,5 N äthanolischen Natriumhydroxid-Lösung gleichmäßig über die ganze innere Oberfläche des Deckels durch leichte Drehbewegung verteilt. Die alkoholische Lösung wird im Vakuum eines mit getrocknetem Calciumchlorid beschickten Exsikkators verdampft und hinterläßt ein gleichmäßiges, völlig fest haftendes Depot.

Andererseits wird eine genau gewogene Probe der Zahncreme, etwa 2 g, in 250 ml doppelt destilliertem Wasser dispergiert. Gleich nach dem Rühren gibt man in den Unterteil der Petrischale 1 ml dieser Suspension, 1 ml doppelt destilliertes Wasser, 4 ml 70%ige Perchlorsäure und 20 ml Silbersulfat. Das Ganze wird dann schnell mit dem Deckel bedeckt, der mit seinem Natriumhydroxid-Depot ausgerüstet ist. Die verschlossene Schale wird für 10 Stunden (4, 5) in einen Brutschrank von 60° gestellt. Man kann erwarten, daß unter diesen Bedingungen der von der starken Säure in Freiheit gesetzte Fluorwasserstoff vom Natriumhydroxid-Depot gebunden wird.

Nach Beendigung der Diffusion werden die Schalen aus dem Brutschrank genommen und sofort geöffnet. Das Deckelinnere wird dann fünfmal nacheinander mit je 1 ml doppelt destilliertem Wasser aufgenommen, jede Portion quantitativ in einen geeichten 50-ml-Glaskolben überführt. Dann bestimmt man die Menge spektrophotometrisch nach folgendem Verfahren.

Spektrophotometrische Bestimmung

In einen geeichten 50-ml-Kolben füllt man eine bestimmte Menge der Lösung, die 5 bis 25 µg Fluoridionen enthält. Man fügt dann nacheinander, indem man nach der Zugabe jedes Reagens' umrührt, 2 ml der Eichlösung vom pH 3,5 hinzu, sowie 5 ml der 10^{-3} M-Cer(III)-nitratlösung, 25 ml der 50 % (V/V) wäßrigen Dimethylsulfoxid-Lösung, 5 ml der 10^{-3} M-Alizarincomplexon-Lösung und füllt schließlich mit doppelt destilliertem Wasser auf. Nach 10 Minuten mißt man die Absorption bei 625 nm in einer 1-cm-Küvette im Vergleich gegen eine Lösung mit den gleichen Reagenzien, jedoch ohne Fluorid.

Experimentelle Ergebnisse

Im Verlauf einer früheren Arbeit (4, 5) wurde folgende Abhängigkeit der Diffusionszeit von verschiedenen Faktoren gefunden, welche die Geschwindigkeit des Vorgangs beherrschen:

$$K = 2{,}3 \frac{l}{t} \; a \log \frac{a}{a - x} \quad \frac{v}{\sqrt{sa \cdot se}},$$

wobei a die ursprünglich vorhandene Fluoridmenge bedeutet, x die Substanzmenge, die in der Zeit t diffundiert, und K die Küvettenkonstante. v, sa und se bedeuten das jeweilige Flüssigkeitsvolumen in der Zelle, die Absorptions- und die Emissionsfläche.

Von dieser Gleichung ausgehend, war es uns möglich, unter Berücksichtigung der nach der Kgl. Verordnung vom 24. 5. 73 maximal zulässigen Dosis und der Größe des Versuchsmusters, die notwendige Zeit vorauszusagen, in welcher die Diffusion bei 60° beendet ist: sie wurde mit 18 Stunden veranschlagt.

Wenn auch diese Methode erlaubt, die Fluoridionen leicht und quantitativ aus der Mehrzahl komplexer Zubereitungen abzutrennen, so muß doch darauf hingewiesen werden, daß man auf die eventuelle Anwesenheit solcher Ionen oder Substanzen achten muß, die den normalen Verlauf der Analyse stören könnten. Von Perchlorsäure freigesetzte Chloridionen gefährden, wenn ihre Konzentration hoch genug ist, die endgültige Bestimmung, die durch die spektrophotometrische Methode erfolgt; man hindert sie daran zu diffundieren, wenn man in die Zelle eine kleine Menge Silberperchlorat oder -sulfat gibt, welche sowohl Bromide wie Jodide binden. Die Anwesenheit von Tricalciumphosphat (Merck p.a.) und Siliciumdioxid (Merck p.a.) stören die Trennung der Fluoridionen nach dieser Methode nicht im geringsten. Die in Tabelle I gesammelten Resultate zeigen das ausreichend. Das gilt nicht im gleichen Maße, wenn die zu analysierende Lösung oder Mischung Natriumsilikat (Merck p.a.) enthält. Es war uns in der Tat unmöglich, nach den laut unseren Berechnungen ermittelten Zeiten mehr als 67 % aus den Versuchsproben wiederzufinden; nach 48 Stunden findet man nur 82 % von den 20 µg vorgegebenen Fluoridionen. Diese Abweichung kann erklärt werden durch eine rasche Bildung von Hexafluorkieselsäure, die überzutreiben eine Temperatur um 140° erfordert. Weil letztere bei der beschriebenen Methode nur 60° erreicht, ist es nicht verwunderlich, daß die Trennung des Fluors unvollständig ist.

Wir haben auch versucht, Aluminium(III)- und Zinn(II)-fluorid nach Trennung des Anions durch Mikrodiffusion zu bestimmen. Tabelle II gibt die verschiedenen Ergebnisse wieder.

Die quantitative Bestimmung von Zinn(II)-fluorid nach dieser Methode ist kein Problem; dagegen ist die des Aluminiumfluorids höchst unbefriedigend. Nach 24 Stunden beträgt der wiedergefundene Prozentsatz nur etwa 10 %.

µg F theoret. x	Fremd-substanz 20 mg	Diffusions-zeit in Stunden	µg F gefunden $\bar{x}$	$\bar{x} - x$ µg F	% F wieder-gefunden
5	—	18	4.98	— 0.02	99.6
10			9.99	— 0.01	99.6
15			14.73	— 0.27	98.2
20			20.09	+ 0,09	100.5
8	$(PO_4)Ca_3$	18	7.94	— 0.06	99.25
12			12.08	+ 0.08	100.63
15			15.10	+ 0.10	100.56
20			19.97	— 0.03	99.85
5	SiO_2	18	4.98	— 0.02	99.6
10			10.04	+ 0.04	100.4
15			15.00	—	100.00
20			19.98	— 0.02	99.90
5	SiO_3Na_2	18	3.37	— 1.63	67.40
		24	3.87	— 1.13	77.40
		48	4.36	— 0.64	87.20
10		18	6.38	— 3.62	63.80
		24	7.42	— 2.58	74.20
		48	8.49	— 1.51	84.90
20		18	12.21	— 7.79	61.05
		24	14.76	— 5.24	73.80
		48	16.40	— 3.60	82.00

Tabelle I

Mikrodiffusion des Fluoridions in Anwesenheit fremder Substanzen. Spektrophotometrische Bestimmung.

Man kann dieser Schwierigkeit leicht begegnen, indem man zunächst in einem Platintiegel eine Schmelze mit Natrium-Kalium-Carbonat vornimmt. Die unter diesen Bedingungen erhaltenen Werte, die in Tabelle II aufgezeichnet sind, sind ebenfalls in Ordnung.

Die Trennung durch Mikrodiffusion kann demnach sowohl bei allen Fluorverbindungen als auch bei kosmetischen Präparaten jeglicher Zusammensetzung angewendet werden. Daß dem so ist, haben wir an einem Spezialprodukt nachgewiesen, dessen Rezeptur hier angegeben ist. Es besteht aus einem Gemisch von Zinn(II)-fluorid und Natriumfluorid mit theoretisch 100 mg F^--Ionen auf 100 g.

Zusammensetzung:

Zinnfluorid	272 mg
Natriumfluorid	75 mg
Natriumbenzoat	4 mg
Eugenol	25 mg
Methyl-p-hydroxybenzoat	100 mg
Excip. ad	100 g

Verbindung	Theorie µg F	Gefunden µg F	Unterschied µg F	wiedergefunden % F
AlF_3	7.72	0.78	— 6.94	10.10
	5.64	0.57	— 5.07	10.10
	3.42	0.29	— 3.13	8.48
	6.50	0.59	— 5.91	9.07
AlF_3*	4.56	4.48	— 0.08	98.24
	5.12	5.21	+ 0.09	101.75
	6.42	6.48	+ 0.06	100.93
SnF_2	10.42	10.34	— 0.08	99.23
	9.58	9.60	+ 0.02	100.20
	12.04	12.00	— 0.04	99.66
	14.06	13.92	— 0.14	98.86

Tabelle II

Bestimmung der Aluminium- und Zinnfluoride durch Spektrophotometrie nach Trennung der Anionen durch Mikrodiffusion

Die verschiedenen Ergebnisse sind in Tabelle III zusammengefaßt; sie zeigen, daß nach der berechneten Zeit die Diffusion beendet ist und daß sie nicht von den anderen Wirk- und Füllstoffen des analysierten Präparates beeinflußt wird. Das gleiche gilt für die spektrophotometrische Messung. Um das zu beweisen, haben wir eine Überdosierung bei zwei Versuchsmustern vorgenommen (mit Sternchen bezeichnet). Die in diesem Falle erhaltenen Resultate zeigen ebenso wie die Analysen aller anderen deutlich, daß die Trennungsmethode und die vorgeschlagene spektrophotometrische Meßtechnik völlig dem gewünschten Ziel entsprechen.

* Ergebnisse erhalten nach Schmelze mit $NaKCO_3$

Versuchs-menge g	F^- enthalten mg	F^- gefunden mg	F^- gefunden mg/100 g	Differenz mg/100 g	F^- gefunden mg/100 g
2.0032*	150	2.96	147.82	— 2.18	
		3.08	153.75	+ 3.75	149.27
		2.93	146.26	— 3.74	
2.0046*	125	2.57	128.20	+ 3.20	
		2.53	126.29	+ 1.29	128.39
		2.61	130.69	+ 5.69	
2.0037	100	2.10	104.85	+ 4.85	
		2.05	102.36	+ 2.36	103.30
		2.06	102.70	+ 2.70	
2.0075	100	2.06	101.14	+ 1.14	
		2,07	102.96	+ 2.96	102.52
		2,07	102.96	+ 2.96	
2.0040	100	2.06	102.64	+ 2.64	
		2,07	103.14	+ 3.14	102.69
		2.05	102.29	+ 2.29	

Mittel der Ergebnisse: 102,78 mg F/100 g
s = 0,96
s % = 0,93 %

Tabelle III

Bestimmung des Fluoridions in einer Zahncreme

Schlußfolgerung

Wir glauben gezeigt zu haben, daß die Trennung der Fluoridionen in Zahnpasten durch Mikrodiffusion einfach und rasch durchführbar ist. Diese Technik läßt sich jedoch nicht bei Proben anwenden, die Aluminiumfluorid und Silikationen enthalten; deshalb wird eine zusätzliche Untersuchung dem Studium der Trennung dieser Ionen aus kosmetischen Präparaten mit Hilfe eines speziell für diesen Zweck konstruierten Wasserverdampfungsapparates gewidmet sein.

Zusammenfassung

Im Verlauf dieser Arbeit werden die Bedingungen zur Trennung von Fluoridionen in Zahnpasten durch Mikrodiffusion untersucht. Diese Technik wird gestört durch die Anwesenheit bestimmter Ionen wie Aluminium und Silikat.

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Sorption of A Cationic Polymer by Stratum Corneum

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Synopsis: A study was made of the SORPTION of a CATIONIC CELLULOSE POLYMER from aqueous solutions by several types of MAMMALIAN STRATUM CORNEUM. The effects of surfactants and other additives were investigated, as well as were the influence of concentration and molecular weight of the polymer. Considerably more material is sorbed than can be accounted for by postulating monolayer coverage of the substrate. The data were found to be explained better by a mechanism of diffusion of the polymer into the outer layers of the stratum corneum than by multilayer absorption.

Introduction

It has been known for some time that cationic surfactants and polymers are quickly bound to the skin and tenaciously held. However, data previously available in the literature (1-3) are only qualitative, and give little insight into the mechanism of adsorption. Some preliminary kinetic observations from this laboratory have been reported earlier (4); they dealt with the sorption by

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mammalian stratum corneum of Polymer JR,* a cationic cellulose ether derivative. The present work is a more detailed investigation of the sorption of this polymer, including the influence of other additives.

Experimental

Samples of stratum corneum were obtained by careful removal of the outer layer of several types of mammalian skin as follows.

1. *Fetal Pigskin*† was obtained frozen. Upon warming of the whole skin, the stratum corneum layer could be readily peeled off in large pieces by hand. Sixteen mm disks were punched out with a cork-borer. A typical desk was 18 μm thick and weighed 2.8 mg, corresponding to a density of 0.8.

2. *Human stratum corneum* was obtained in the form of small irregular pieces stripped from the legs and arms of a subject who had been sunburned in the summer time. A typical piece, weighing 1.7 mg, had the form of a rectangle 6 by 9 mm. The thickness was about 25 μm, corresponding to a density of 1.24.

3. *Neonatal rat stratum corneum:* live young rats were obtained.‡ They were not more than 1 to 2 days old. The animals were sacrificed by being placed in an atmosphere of CO_2 for several hours; after death the whole skin was removed by a surgical scalpel. The skin was placed in a desiccator jar and exposed to ammonia vapor for about 1 to 3 h. Following this, the skins were put in water and the epidermal layer was gently separated from the dermis. The epidermis so obtained was floated on the surface of a pan of water. After an hour, the membrane was removed by bringing up a metal screen under it. The membrane was placed top down on a wet paper towel and the screen removed. At this point the "Malpighian layer" could be gently scraped off, leaving the desired stratum corneum on the towel. The paper and stratum corneum were placed again in water until separation occurred. The stratum corneum layer was recovered by a small Teflon®** screen and air dried. A typical piece of stratum corneum was about 25 μm thick and 5 x 6 cm in area. It weighed about 20 mg, corresponding to a density of 0.7.

The surfactants used in this study were as follows: *Tergitol®* 15-S-9* the 9 mol ethoxylate of a secondary C_{11} to C_{15} alcohol *sodium lauryl sulfate*,§ *Barquat MB-50*-// Myristyldimethylbenzylammonium chloride.

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†Pel-Freez Biologicals, Inc., Rogers, Arkansas.
‡Marland Breeding Farms, West Milford, N.J.
**E. I. du Pont de Nemours & Co., Wilmington, Del.
§BDH Chemicals Ltd., Poole, England.
//Lonza, Inc., 22-10 Route 208, Fair Lawn, N.J. 07410.

Polymer JR is a quaternary nitrogen containing cellulose ether (5). It is available in three grades: JR-125, JR-400, and JR-30 *M*. Approximate molecular weights for these grades have been estimated from their solution viscosity behavior as compared to that for hydroxyethylcellulose (HEC), a closely related but uncharged polymer (6).

The estimates are as follows: JR-125, mol wt 250,000; JR-400, mol wt 400,000; JR-30 *M*, mol wt 600,000. Radio-tagged samples of these various grades were prepared by carrying out the polymer synthesis with ethylene oxide tagged with C-14. A tagged sample of HEC equivalent to JR-125 was also prepared.

The uptake of Polymer JR was determined by experiments with these tagged polymers. Samples of stratum corneum of about 2 mg weight were weighed to the nearest tenth of a milligram and placed individually in 1-oz glass vials. Ten ml of a water solution of tagged polymer were pipetted into each vial and left to contact the skin for a given time at room temperature after which the solution was poured off. The skin was rinsed with 20 ml of distilled water three times. It was then removed from the original vial and placed in a new vial. (This eliminated the necessity of correcting for any radioactivity due to polymer adsorbed on the glass walls of the original vial.) The new vial was placed in a 50°C oven for several hours to drive off moisture. The stratum corneum was dissolved by treatment with tissue solubilizer, followed by addition of methanol and a scintillation liquid. The vials were counted by the normal liquid scintillation method. Triplicate samples were run for each contact time. Because of the small sample size and the relatively large amount of polymer in solution, there was no appreciable change of polymer concentration during a given experiment.

In view of the sizable sorption values which were found in the course of this work, some further discussion of the experimental technique seems appropriate here. In addition to true sorption, there are two possible mechanisms by which polymer molecules can be "trapped" by the stratum corneum samples and hence, counted in our procedure. First, is simple associaton of viscous polymer solution with stratum corneum. If this occurred to any extent, it would be expected that at equal concentrations, the polymer of highest molecular weight, and hence, most viscous, would be trapped in the greatest amount. Exactly the inverse is the case; JR-125 shows much higher sorption than does JR-30 *M*. Also, convincing evidence against this objection is the fact that Polymer JR-125 shows nearly 50 times as much sorption as does a hydroxyethylcellulose of equal solution viscosity (see Figure 3 later on in this paper).

A further study of the possibility of viscous entrapment was made by investigating a much more vigorous rinsing procedure, *viz.* 4 successive rinses

of 20 ml each, with each rinse conducted for 15 min on a mechanical shaker. No significant lowering of sorption was noted compared to that observed with the rinsing procedure described above.

The second possible mechanism is that some of the polymer is dissolved in the normal water of swelling associated with stratum corneum. This water permeates the entire structure; hence, any polymer it contains will probably not be easily removed by a single quick rinse. The amount of this associated water is about three to five times the dry sample weight, estimated from the increase in weight of samples of stratum corneum immersed in water. However, either very little polymer can penetrate with this water of hydration or it is readily rinsed out, as can be inferred from the sorption data for uncharged hydroxyethylcellulose (see Figure 3 later on in this paper). The measured uptake, after rinsing, for this material is less than 0.5 μg/mg after 24 h contact. This is insignificant compared to the large amounts of Polymer JR sorbed in this period of time.

Results and Discussion

Figure 1 shows data obtained for the various types of stratum corneum exposed to 0.1 per cent Polymer JR-125. Typical sorption curves are observed

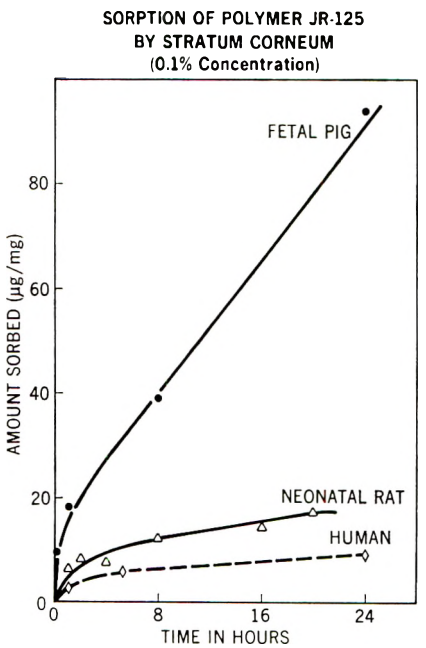

Figure 1. Sorption of Polymer JR-125 by different types of stratum corneum

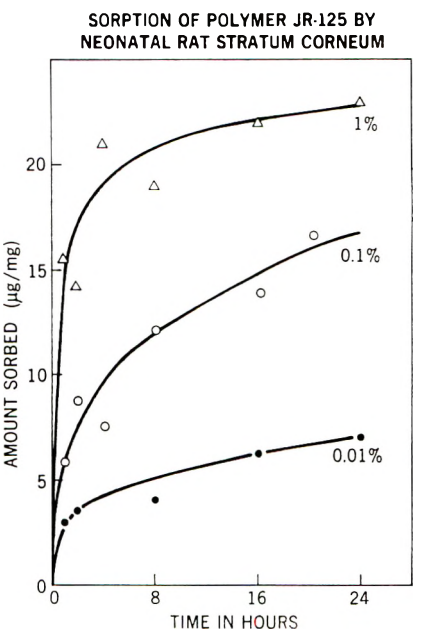

Figure 2. Sorption of varying concentrations of Polymer JR-125

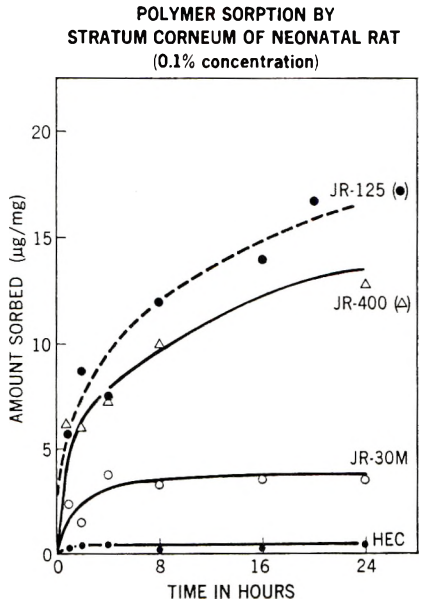

Figure 3. Sorption of hydroxyethylcellulose and various grades of Polymer JR

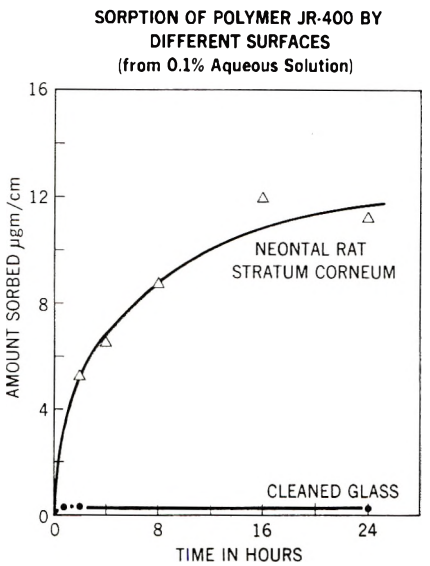

Figure 4. Sorption of Polymer JR-400 by different surfaces

with fairly rapid pickup at short times and a leveling off at longer times. Fetal pig is noteworthy for its high values of sorption. This may be related to the fact that in such a young animal the normal barrier properties of stratum corneum are not fully developed. Determination of moisture vapor transmission confirmed this; values of 8 to 9 mg/cm^2/h were obtained. On the other hand, neonatal rat stratum corneum does have a highly developed barrier function as was demonstrated by Singer and coworkers (7). Our measurements confirmed this; values of 0.2 to 0.4 mg/cm^2/h were found for this material. The pieces of human stratum corneum were too small and too irregular to permit measurement of moisture vapor transmission.

Neonatal rat stratum corneum is recognized to be a good model for human stratum corneum. Figure 1 demonstrates that the uptake of polymer on these two substrates is much closer than that on the fetal pig membrane. Conceivably, the lower uptake on the human stratum corneum reflects the age and higher density of the latter material.

Neonatal rat stratum corneum was used for the subsequent experiments on polymer sorption. In Fig. 2 is shown the effect of varying concentrations of JR-125. Substantial pickup is noted even at the lowest level. In Fig. 3 are plotted data for the various molecular weights of Polymer JR and for the sample of hydroxyethylcellulose. As mentioned in the Experimental section of

this paper, sorption is inversely related to molecular weight. The uncharged hydroxyethylcellulose shows very little sorption, representing essentially only a monolayer coverage of the substrate.

Sorption of Polymer JR as a Diffusion Process

The relatively high amount of polymer uptake by stratum corneum shown in Fig. 1 to 3 invites speculation about the mechanism involved. In this connection, it is relevant to examine first the behavior of Polymer JR on impenetrable inorganic substrates. Adsorption of this polymer (JR-125) from 0.1 per cent aqueous solution onto cleaned glass was measured and yielded values of about 0.25 $\mu g/cm^2$. This level of deposition is reached in less than 5 min and does not change with time. Such adsorption corresponds to a covering of one monolayer, if the reasonable assumption is made that each anhydroglucose unit has an effective area of 25 $Å^2$, and the adsorbed polymer has a flat orientation on the surface. In order to make a comparison with skin, the BET surface area of neonatal rat stratum corneum was determined and found to be 0.47 m^2/g, compared to a geometric surface area of 0.113 m^2/g. Monolayer coverage of this substrate would require only about 0.9 μg polymer/mg. It is clear from the data of Fig. 1 to 3 that the actual uptakes greatly exceed this amount. Figure 4 gives a comparison of the adsorption on glass and stratum corneum on an area basis. The qualitative difference between the two substrate types is striking. The absence of multilayers on glass is presumptive evidence that they do not occur on other substrates. Instead the shape of the sorption curve for neonatal rat stratum corneum suggests that the polymer is slowly being absorbed. In the dry state, neonatal rat stratum corneum has a density of about 0.7. This indicates considerable void space, since the basic keratin of this substrate has a density of 1.4. Additionally, upon immersion in water, the stratum corneum quickly takes up about three to five times its own weight of water, thus providing more aqueous free space for penetration of dissolved species. The data indicate that molecules as large as those of Polymer JR are able to enter the substrate in this way, but probably no further than a few microns in distance.

The picture of sorption which emerges corresponds to a semiinfinite solid in contact with a bath containing a constant concentration C_o of the diffusing polymer. This is described (8) by the partial differential equation:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

with conditions

$$C = C_o \text{ at } x = 0 \text{ for } t > 0$$
$$C = O \text{ at } t = 0 \text{ for } x > 0$$

The solution is

$$C = C_o \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)$$

where erfc (x) is the "error function complement:"

$$\text{erfc}\,(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2} du$$

The data obtained here do not correspond to concentrations at differing distances in the substrate, but to total material absorbed at varying times. We thus need the integral of the above solution over unit surface of the membrane:

$$Q = \int_0^\infty C(x, t)dx = C_0 \int_0^\infty \text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) dx$$

By virtue of

$$\int_0^\infty \text{erfc}\,(u)\, du = \frac{1}{\sqrt{\pi}}$$

this becomes

$$Q = 2C_0 \sqrt{\frac{Dt}{\pi}}$$

This well-known formula was quoted without derivation in a classical paper (9) on the diffusion of small molecules in animal tissues.

A test of the validity of this approach is that sorption should follow a square-root of time dependence. This was indeed generally found to be the case for the experiments reported here, at least for the first several hours. At longer times, particularly over 1 day, deviations from $\sqrt{t}$ do occur. By using Hill's formula above, diffusion constants can be calculated from the slope of the initial, linear part of the Q versus $\sqrt{t}$ curves. An area of 0.47 m^2/g was assumed in all cases corresponding to the observed BET area rather than the calculated geometric areas. Calculations were made for some of the more interesting cases. For example, the data of Fig. 1 gave the following table.

Type of Stratum Corneum	Diffusion Constant (cm^2/sec)
Fetal Pig	9.6×10^{-9}
Neonatal rat	1.07×10^{-10}
Human	7.8×10^{-11}

The different grades of Polymer JR in neonatal rat stratum corneum at 0.1 per cent concentration (Fig. 2) led to the following table.

Grade	Diffusion Constant (cm^2/sec)
JR-125	1.07×10^{-10}
JR-400	9.7×10^{-11}
JR-30 *M*	1.2×10^{-12}

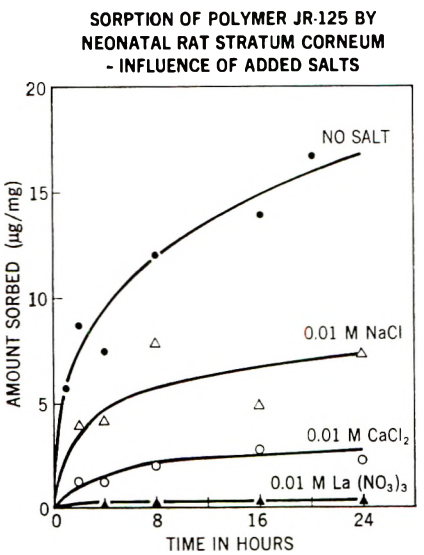

Figure 5. Effect of salts on the sorption of Polymer JR-125

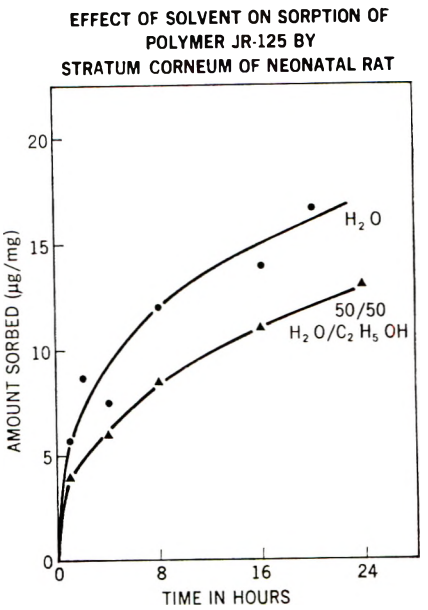

Figure 6. Effect of solvent on the sorption of Polymer JR-125

These values are for the diffusion of polymer in the membrane medium, and are only valid for the first few hours of the sorption process. It is of interest to compare these numbers with the aqueous diffusion of the polymer. No specific value has yet been determined for that process, but an estimate can be made by considering the diffusion constant of the chemically related polymer HEC. A sample of HEC of mol wt 330,000 (about the size of Polymer JR-125) has a diffusion constant of 1.1×10^{-7} cm^2/sec (6). This can be regarded as a lower limit for the aqueous diffusion of JR-125, which as a polyelectrolyte, should diffuse even faster than if it were uncharged (10). It is evident that the membrane diffusion is orders of magnitude slower than aqueous diffusion; a similar observation was made long ago by Hill (9).

For long times, the diffusion in the membrane slows considerably, evidenced by a decreasing slope of the Q versus $\sqrt{t}$ plot. This was also demontrated by experiments with a permeability cell modeled after that of Loveday (11). A 1 per cent solution of radio-tagged Polymer JR-125 was placed above an intact piece of neonatal rat stratum corneum and stirred distilled water was placed below. Samples were taken from the bottom of the cell at periodic intervals for counting analysis. No measurable passage of polymer occurred through the membrane in 2 weeks. From the familiar time lag for-

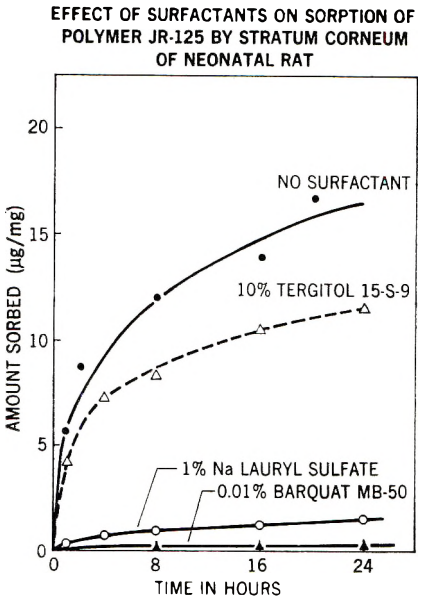

Figure 7. Effect of surfactants on the sorption of Polymer JR-125

mula (12), it can be estimated from this experiment that the diffusion constant of the polymer *through* the membrane must be of the order of 10^{-14} cm^2/sec or less. The picture which emerges, therefore, is one of hindered diffusion due, largely, to sorption of the charged macromolecule along the diffusion routes.

The driving force for this sorption must involve coulombic attraction between the cationic polymer and the negatively charged stratum corneum. It has been shown already in Fig. 3 that an uncharged polymer, of essentially the same basic structure as Polymer JR, shows little more than monolayer adsorption. If the above deduction is correct, the uptake of Polymer JR should be sensitive to the addition of ionic substances. This is, in fact, the case, as is demonstrated in Fig. 5 for addition of simple salts. There is a strong valence effect in the inhibition of sorption: $La^{+++} > Ca^{++} > Na^{+}$. This can be explained as a charge density effect. The higher valence ions compete more effectively for available sorption sites since they are more tightly held by the substrate. It is, of course, true that the polymer solution properties are changed by the presence of salt. However, significant depression of sorption can be observed at salt levels of 0.001 *M*, which is too low to have much effect on the polymer solubility or configuration in solution.

Another consequence of the coulombic attraction theory is that the addition of organic solvents should cause a decrease in sorption, due to lowering of the dielectric constant of the solution with attendant decrease in dissociation of the cationic polymer and hence lessened attraction to the substrate. Figure 6 shows this effect for ethanol-water. There is a limit to how far one can go in this direction, since Polymer JR is insoluble in pure liquids of low dielectric constant.

Polymer JR finds commercial use in lotions and shampoos. In these vehicles it is mixed with many additives, some of which are surface active. Therefore, it was of interest to determine the effect of typical materials of this type on polymer uptake. Figure 7 shows some of the different possibilities. From the above discussion, it is not surprising to see that a nonionic surfactant, such as Tergitol® 15-S-9, has only a slight inhibitory effect even at a high level of concentration relative to the polymer. However, the anionic sodium lauryl sulfate causes a large decrease in polymer sorption. This is probably due to a combination of two effects. One is the competition for sites by the sodium ions, and the other is the known interaction of surfactant and polymer (13). Somewhat surprising is the great effect of the cationic surfactant, Barquat MB-50. The explanation for this may be that the free spaces in the outer layers of substrate become blocked by sorption of the rather large surfactant cations, or that the latter ions merely preempt the adsorption sites.

Conclusion

The data shown here support the hypothesis that a cationic polymer is capable of slowly diffusing into the outer layers of stratum corneum, rather than forming multilayers on it. Although the conditions of sorption used in these studies are extreme and unlikely to be even approached in any practical application, the uptake observed emphasizes the highly substantive nature of the polymer. The driving force for this diffusion is charge attraction between the cationic polymer and the negative sites within the stratum corneum. Added electrolytes and low dielectric constant solvents tend greatly to decrease the sorption by competition for sites or by decreasing the effective charge of the polymer. Ionic surfactants also reduce the sorption.

Acknowledgment

The procedure utilized for separating the neonatal rat stratum corneum was outlined for us by Dr. E. J. Singer and Mr. E. K. Boisits of Lever Brothers Company.

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MEMBERSHIP DIRECTORY

1977

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J. Soc. Cosmet. Chem., **27**, 555-558 (November 1976)

Diffusion Theory Analysis of Transepidermal Water Loss Through Occlusive Films

EUGENE R. COOPER, Ph.D. and BARRY F. VAN DUZEE, Ph.D.*

Synopsis: Composite membrane DIFFUSION THEORY is applied to TRANSEPIDERMAL WATER LOSS measurements across skin treated with OCCLUSIVE FILMS. Since the permeability of stratum corneum increases with hydration, it is shown that certain films can be applied to skin to increase transepidermal water loss. Thus, even increase in transepidermal water loss can indicate that the film is hydrating the skin quite well.

Introduction

Cosmetic chemists have long been concerned with enhancing the barrier properties of the skin. The benefits derived from an intact resistive barrier range from enhanced skin condition to prevention of environmental insult from gases, fumes, dirt, and microbes.

One of the main advantages which results from the application of an occlusive cosmetic barrier is enhanced skin condition (1-3). As a result, there has been an effort to find materials which reduce the transepidermal water loss (TWL) of skin and which might be incorporated into cosmetic formulations (4). This search has been conducted by measuring the water loss through skin *in vivo* before and after application of a potential occlusive agent. However, this method of screening occlusive agents may eliminate some compounds which are actually good hydrating agents.

Application of 3 mg/cm^2 of petrolatum to the surface of skin results in an immediate decrease in the rate of insensible water loss followed by an increase in the rate to a value higher than the original one after about 3 h.

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Osborne and Gerraughty (4) appear to have observed a similar phenomena with polyoxyethylene glycols and esters. These types of compounds are certainly occlusive, but the result of their application to skin is an increase in TWL. This increase in water loss can be explained by use of a simple diffusion theory of composite membranes if the diffusion coefficient of skin increases as the stratum corneum becomes more hydrated. In the Theoretical section of this paper, we will demonstrate how this increase in TWL is evidence of increased skin hydration in the stratum corneum.

Theoretical

Let us view the TWL experiment (with an occlusive film) as the diffusion of water across the stratum corneum and film into the atmosphere. We assume that both the stratum corneum and occlusive film can be assigned a diffusion coefficient (D), an activity coefficient (γ), and a thickness (l). We thus consider diffusion across a composite membrane as depicted in Fig. 1. Here, a_i is the constant water activity beneath the stratum corneum and a_o the constant activity outside the thin coating. The subscript 1 corresponds to the stratum corneum and the subscript 2 corresponds to the thin coating.

We assume that the diffusion equation (5)

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{1}$$

holds within each membrane, and that the flux and activity are equated at the boundaries. (We have considered D to be constant for each membrane, even though this may not be the case for nonuniformly hydrated stratum corneum.) In the steady state $\left(\frac{\partial c}{\partial t} = 0\right)$, we have the flux ($J_s$) given by

$$J_s = \frac{a_i - a_o}{\alpha_1 + \alpha_2} \tag{2}$$

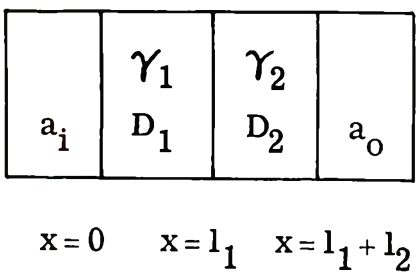

Figure 1.

where $\alpha_j = l_j\gamma_j$. A measure of the hydration (water content) per unit area of stratum corneum during steady-state diffusion can be obtained by integrating the concentration across the stratum corneum. This amount (Q) of water per unit area of stratum corneum is given by

$$Q = \int_0^{l_1} dx\, c_s^{(1)}(x) = \frac{l_1(a_i - a_o)}{\gamma_1}\left[\frac{a_i}{a_i - a_o} - \frac{1}{2(1 + \alpha_2/\alpha_1)}\right] \tag{3}$$

where $c_s^{(1)}(x)$ is the steady-state concentration in the stratum corneum and is given by

$$\gamma_1 c_s^{(1)}(x) = J_s[\alpha_2 + \alpha_1(1 - x/l_1)] + a_o \tag{4}$$

Let us suppose that the diffusion coefficient for stratum corneum is dependent upon hydration. According to Scheuplein and Ross (6), this variation can be greater than an order of magnitude for zero and 100 per cent relative humidity outside the skin. Grice *et al.* (7) also give evidence (TWL measurements) that diffusion is dependent on hydration. We can now use equations (2) and (3) to predict the effect of a film on the hydration of the stratum corneum and flux (TWL). We assume that a_o is near zero, and thus, have "dry" diffusion when the film is absent ($\alpha_2 = 0$). Thus

$$J_s^d = \frac{a_i - a_o}{\alpha_1^d} \tag{5}$$

and

$$Q^d = \frac{l_1}{2}\left(\frac{a_i + a_o}{\gamma_1}\right) \sim \frac{1}{2}\,\frac{l_1 a_i}{\gamma_1} \tag{6}$$

where the superscript d corresponds to the nonoccluded case.

For perfect occlusion ($\alpha_2 \to \infty$), we have

$$J_s \to 0 \tag{7}$$

and

$$Q^m \to \frac{l_1 a_i}{\gamma_1} \tag{8}$$

where Q^m is the maximum hydration. If α_2 is not all that different from α_1, we have an intermediate case. For a viscous hydrocarbon, we can assume* $D_2 \sim 10^{-8}$ cm²/sec, $l_2 \sim 40\mu$m, and $\gamma_2/\gamma_1 \sim 10$, and for the stratum corneum (8), let $D_1^w \sim 10^{-9}$ cm²/sec, and $l_1 \sim 10\mu$m. Thus, we have α_2/α_1^w

*The diffusion coefficient for a viscous hydrocarbon is approximated from the Stokes–Einstein equation, $D = kT/6\pi\eta r$ where k is Boltzmann's constant, T is temperature (30°C), is the hydrocarbon viscosity (taken to be 5 P as for castor oil), and r is the radius of water (taken to be 3Å). The ratio γ_2/γ_1, is a bit uncertain, but since skin hydrates well and water is not very soluble in hydrocarbons, a ratio of ten is not unreasonable.

~ 4, where α_1^w corresponds to the "wet" diffusion situation, i.e., $D_1 \sim 10^{-9}$ cm^2/sec. If we assume that $\alpha_1^d = 10\ \alpha_1^w$, we have

$$J_s^w = \frac{a_i - a_o}{5\alpha_1^w} = 2J_s^d \tag{9}$$

and

$$Q^w = 0.9\left(\frac{l_1}{\gamma_1}\right)\left(a_i + \frac{1}{9}a_o\right) \sim 0.9\,Q^m \tag{10}$$

Hence, we see that for a film that is sufficiently occlusive such that $\alpha_2 = 4\alpha_1$, we can hydrate the skin to within 90 per cent of maximum hydration. This increased hydration can then give rise to an increase in flux or TWL, which is consistent with the observed rise in TWL upon application of petrolatum to skin. In fact, from this analysis, a rise in TWL with an occlusive film is good evidence that the stratum corneum is being hydrated.

Conclusion

It has been observed that the insensible water loss of skin can increase when treated with occlusive agents. This increase is a logical consequence of the increase in diffusion coefficient of stratum corneum when it becomes hydrated. These results suggest that evaluation of cosmetic formulations on the basis of their effect on *in vivo* insensible water loss could easily be misleading with respect to skin conditioning. That is, a material which gives an increase in TWL may indeed be hydrating the skin to within a few percent of maximum hydration, and should not be eliminated as a poor conditioner on these grounds.

Acknowledgment

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New Lanolin Acid Quaternary Salts for use in Hair Treatment Preparations

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Presented May 29, 1975, Annual Seminar, St. Louis, MO.

Synopsis: The action of QUATERNARY AMMONIUM SURFACTANTS on HAIR has been studied for many years. Several of the characteristics, which are important in formulating with these SALTS, are dependent upon their molecular configuration. In this paper, lanolin compounds which essentially comprise QUATERNARY DERIVATIVES (QUATS) of LANOLIN ACIDS are described. The preparation of a derivative of lanolin consisting essentially of the reaction product of a lanolin acid and a specific diamine followed by quaternization is outlined. The chemical and physical properties of quats are briefly reviewed and compared with emphasis on these new lanolin acid derivatives, and their chemistry and processing is highlighted. Each of these quaternary salts was incorporated into hair conditioning preparations and evaluated on human hair.

Introduction

It has been known for a long time that quaternary ammonium surfactants display many unusual and desirous properties and functions (1). Much work has been done demonstrating germicidal activity (5), softening effects (2, 3), antistatic properties (4), substantive qualities, and other uses of these materials. Many of these properties find applications in cosmetics, where quaternary ammonium compounds are useful as preservatives (5), hair conditioning agents (6), emulsifiers (7), etc. However, it has long been known that these materials possess a relatively high level of toxicity both to the skin and eyes (8). Also, they have a low compatability level with other commonly used cosmetic materials—specifically anionic emulsifiers and surfactants (9).

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It was our goal in this study to develop a quaternary ammonium derivative, which would be less irritating, and yet, as chemically active as other common quaternaries presently used for hair treatment in the cosmetic industry.

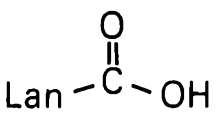
In this paper, we will chemically describe some new quaternary ammonium compounds, which are derived from a well established nonirritating (10) highly emollient material—lanolin acids. We will discuss some of their properties, specifically eye irritation, germicidal activity, and solubilities. Also, studies comparing two lanolin acid quaternaries with some other commercially used quaternary ammonium compounds in a shampoo and a cream rinse formulation involving salon testing of human hair will be presented.

Chemical Description

Lanolin, which is extensively used in cosmetic compositions, is generally considered to consist of a mixture of naturally formed esters derived from higher alcohols and higher fatty acids. By saponifying the lanolin esters with alcoholic alkali, one can separate the alkaline soaps of lanolin acids from the unsaponifiable portion containing lanolin alcohols. By acidification of the alkaline soaps, crude lanolin acids of the composition shown in Table I are obtained. These acids are refined through a distillation and deodorization process described in a U.S. patent.* The acids are then bleached or decolorized.

Table I

LANOLIN ACIDS:



where 'Lan' represents:

	%
n-alkanoic acids	7
iso-alkanoic acids	23
anti-iso-alkanoic acids	30
hydroxy-alkanoic acids	28
unidentified	12
	100%

*Richey, *et al.*, Pat. #3, 272, 850.

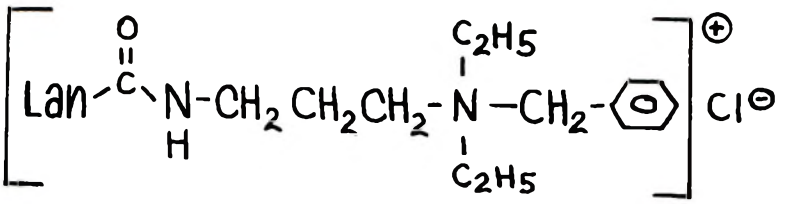


Figure 1. Structures of lanolin quaterniums

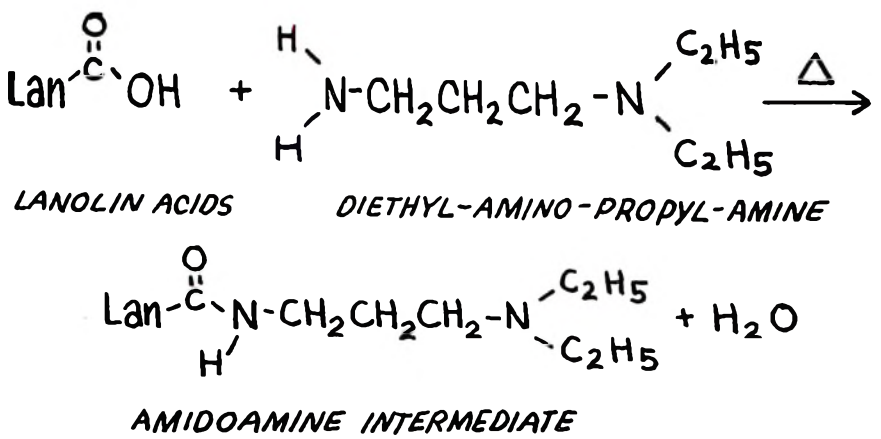


Figure 2. Preparation of intermediate

Apparently, the refining procedure eliminates a number of the more than 40 acids, which compose the crude lanolin acids. At any rate, the thus refined lanolin acids react with the amines described below and are then converted to the quaternary ammonium derivatives, which are also discussed below.

The general structural formulas of the lanolic acid quaternary ammonium derivatives are shown in Fig. 1. The quaternary compounds were prepared from a common amido amine intermediate. This intermediate was prepared by combining equimolar quantities of lanolin fatty acid and diethylaminopropylamine (as shown in Fig. 2.) Conditions for the reaction simply required heating to 150-160°C at first at atmospheric pressure for 2h, and finally under reduced pressure (0.1 mm Hg) for a period of about 3-4 h. The extent of reaction was followed by measuring evolved water and by a combination of acid and amine values.

The diamine required for reaction with the lanolin acid to form the intermediate must be a diamine having one of its nitrogen atoms bearing two substitutes (as shown in Fig. 3). In other words, one of the nitrogens of the diamine is a tertiary amine with no site available for reaction. The other nitrogen of the diamine is either a primary or a secondary amine and thus it becomes available, via one of its hydrogens, for reactions with a lanolin acid (11).

The quaternization of the amidoamine was carried out by combining equimolar quantities of the intermediate with a suitable quaternizing agent and heating to 110-120°C at atmospheric pressure for a period of about 4 h. The extent of reaction was measured by the decrease in amine value (reactions are shown in Fig. 4).

The choice of benzyl chloride as a quaternizing agent was based on the fact that analogous types of quaternaries are among the most common and comparisons to existing products could be made easily, without the fear of another variable. The choice of diethyl sulfate as the other quaternizing agent was more or less arbitrary, and any other suitable materials such as aliphatic hal-

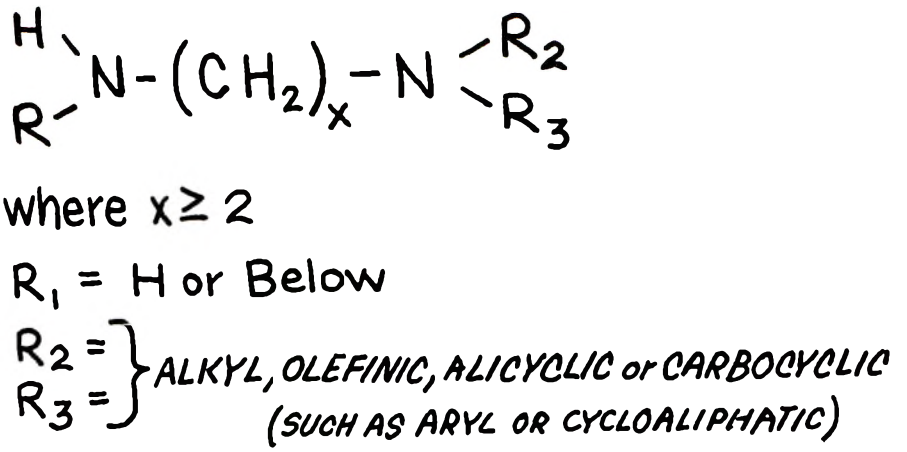


Figure 3. Required diamine

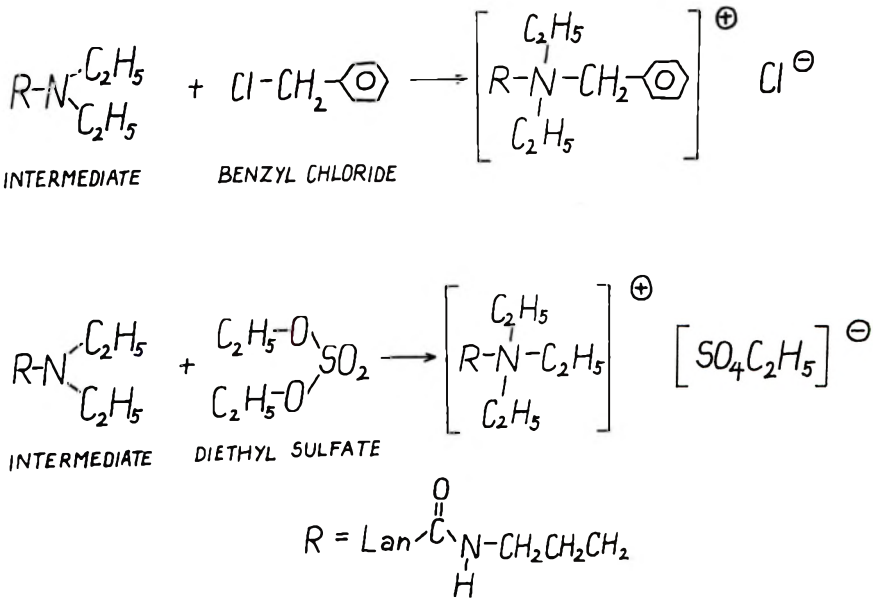


Figure 4. Quaternization

TABLE II
Typical Properties of Quats

	LanBAC	Stearalkonium Chloride	LanES	Quarternium 7
Form	Amber Semisolid	Creamy White Dispersion	Amber Very Viscous Liquid	Cream Colored Dispersion
Active content	81.9%	16.0%	76.3%	79.7%
Total chloride content	5.8%	–	N/A	7.8%
pH (1% aqueous sol'n)	6.2	3.0-4.0	5.0	3.4
Surface tension (1% aqueous sol'n (@ 25°C)	41.4 dynes/cm	34 dynes/cm	40.3 dynes/cm	–
Ross Miles Foam Data–				
Initial:	100 mm	50 mm	150 mm	150 mm
After 5 min:	80 mm	40 mm	110 mm	130 mm

ides, aromatic halides, or other aliphatic alkylating agents, such as ethylene chlorohydrin, could have been used. Among such halides and esters which may be used are methyl chloride, methyl bromide, butyl bromide, di-methyl sulfate, and the like (11).

The resulting experimental lanolin quaternaries are dark amber materials ranging in viscosity from a thick liquid for the ethosulfate derivatives, to a hard brittle solid for the benzyl chloride derivative. Since these quaternium

salts are soluble in water, aqueous solutions ranging in activity of 10 to 25 per cent offer an easier means of handling these materials.

Typical specifications of these lanolin quaternaries are compared to two other commercial quaternary ammonium compounds (Quaternium 7 and Stearalkonium Chloride) in Table II.

Analytical Procedures

Various procedures were used to support evidence of our reactions. The structure of the lanolin acid amidoamine intermediate was confirmed by infrared analysis. The acid carboxyl absorbance was absent and was replaced by absorbition in the region 1640 cm^{-1}, which is indicative of amides. Also, the so-called Amide II band appearing near 1550 cm^{-1} was observed. The absence of unreacted primary amine was determined titrametrically (12). Quaternary activity was determined via a titration with tetraphenyl boron (13).

Physical Properties

I. Compatability with Anionic Surfactants

Experimental—10 per cent active solutions of Triethanolamine (TEA) Lauryl Sulfate. Sodium Laureth Sulfate (3 moles of ethylene oxide (ETO)), Quaternium 7, Stearalkonium Chloride, the experimental lanolin benzyl chloride quat (LanBAC) and the experimental lanolin ethosulfate quat (LanES) were prepared. The pH of these solutions were adjusted to 4 with citric acid. (The pH of the Quaternium 7 and the Stearalkonium Chloride solutions were under 4, so that these were not adjusted.) Blends were then prepared by adding 1, 5, 10, 15, and 20 g of cationic solution to 99, 95, 90, 85, and 80 g of an anionic solution. The solutions were warmed on a steam bath when necessary to obtain clarity. The resulting 40 solutions were then set aside for 2 weeks.

Results—Formation of either a cloud, haziness, or a precipitate in the solutions was taken as an indication of incompatability (14). Those solutions, which remained clear were taken to be compatible. The results are summarized in Fig. 5.

It was found that upon mixing, both lanolin acid quaternary ammonium derivatives formed clear solutions without warming. Also, the lanolin quaternary salt solutions showed superior compatability in an anionic medium to the other two cationic ammonium compounds tested.

Blends of the 10 per cent active cationic solutions and 10 per cent active anionic solutions were prepared by adding 5 parts of the cationic solution to 95 parts of the anionic solutions. These blends were further diluted to yield a total 1 per cent active solution of surfactant. Ross-Miles foam tests were run on the anionic solutions alone and the various blends of the cationic-anionic blends. Foam height measurements were taken initially and after 5 min. The resulting data demonstrated tht the lanolin derived quaterniums interfered

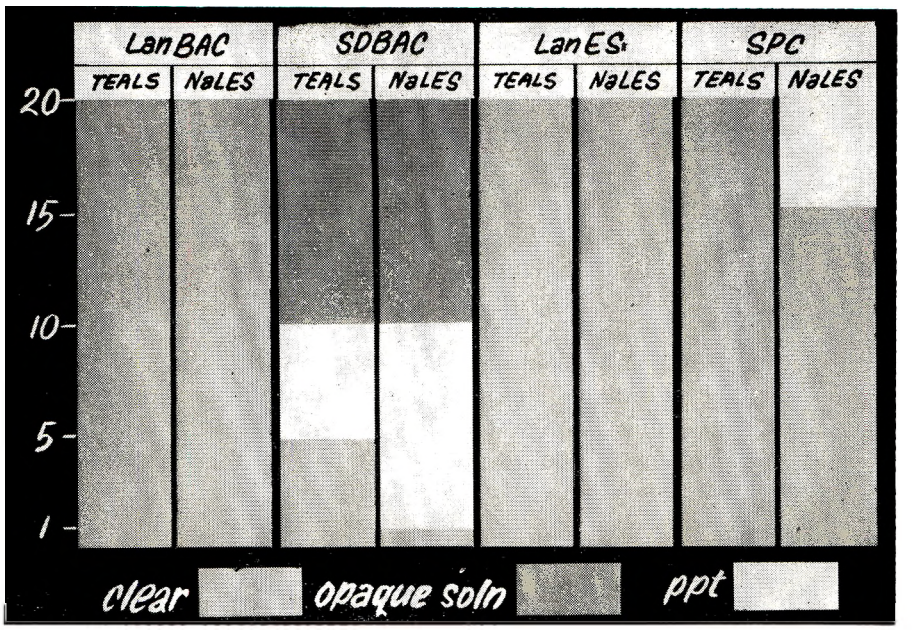


Figure 5. Compatability with anionics

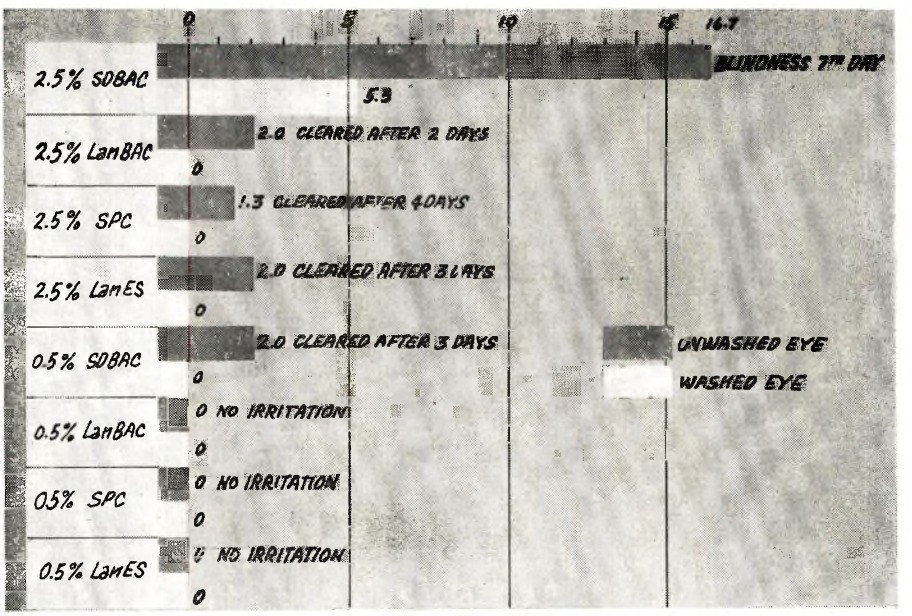


Figure 6. Draize eye irritation scores

with the foaming power of the anionics less than the Quaternium 7 and the Stearalkonium Chloride. This again demonstrated higher compatability between the cations of the lanolin quaterniums in solution with the anions of the detergent salts.

II. Eye Irritation

Experimental—0.5 and 2.5 per cent active solutions were prepared for the Quaternium 7, Stearalkonium Chloride, LanBAC, and LanES. The resulting 8 solutions were submitted to an outside laboratory for Draize Rabbit Eye Irritation tests. Six normal healthy albino rabbits were used in this experiment. The animals were divided into 2 groups of 3 animals each. Group 1 had 0.1 ml of the test solution instilled into the right eye with no further treatment. Group 2 had 0.1 ml instilled into the right eye followed 4 sec later by washing out with 20 ml of lukewarm water. The untreated left eye of each animal served as its own control. Both the treated and control eyes were examined every 24 hours for 4 days and then again on the seventh day. The scores recorded were made according to the Draize scale for scoring occular lesions (15).

Results—As can be seen in Fig. 6, the lanolin quaternaries proved to be less irritating than the other two cationic salts used in the test. The LanBAC was shown to be less irritating than Stearalkonium Chloride at 5 times the concentration of Stearalkonium Chloride.

III. Germicidal Activity

Experimental—In this experiment, 2 aspects of a germicidal activity were studied—namely, the zones of inhibition and the plate count reduction. Five per cent active Quaternium 7, Stearalkonium Chloride, LanBAC, and LanES were prepared and submitted to an outside testing laboratory for these tests. The solutions were diluted 1:5 for both determining the zones of inhibition and for the plate count reduction, so that the results shown in Table III are for 1 per cent active quaternary solutions.

For the zones of inhibition, the quaternaries were tested against two organisms: Staph aureus ATCC* 6538 and Strep pyogenes ATCC* 8668. In the plate count reduction, the test organism was Staph aureus ATCC 6538. A 24-h broth culture of the test organism was diluted 1-10 with sterile distilled water before use. One ml of the diluted test organism was added to 9ml of the sample and stored at 37°C. At 2, 5, 10, 15 minutes, 1 and 4 h 1 ml of the sample was plated out with Tryptic Soy Agar. The plates were incubated at 35°C for 48 h.

Results—As can be seen in Table III, the two experimental lanolin quaternaries exhibited larger zones than either of the two commercial quaternaries against both test organisms. The plate count reduction showed the two lanolin quaternium salts to be as effective as the Stearalkonium Chloride, and more

*American Type Culture Collection, Washington, D.C.

Table III

GERMICIDAL ACTIVITY

ZONES OF INHIBITION:

QUAT (1% ACTIVITY)	ORGANISM	
	S. Aureus	S. Pyogenes
STEARALKONIUM CHLORIDE	3.4 mm	3.9 mm
Lan BAC	4.8 mm	5.5 mm
QUATERNIUM 7	2.7 mm	4.4 mm
Lan ES	6.4 mm	5.2 mm

PLATE COUNT REDUCTION: (% Reduction)

	TIME (MIN)					
QUAT (1% activity)	2	5	10	15	1 hr.	4 hrs.
STEARALKONIUM CHLORIDE	99.99+	99.99+	99.99+	99.99+	99.99+	99.99+
Lan BAC	99.99+	99.99+	99.99+	99.99+	99.99+	99.99+
QUATERNIUM 7	80.00	95.67	99.98	99.99+	99.99+	99.99+
Lan ES	99.99+	99.99+	99.99+	99.99+	99.99+	99.99+

effective than Quaternium 7. Stearalkonium Chloride, along with the 2 lanolin quats, achieved a 99.99+ per cent reduction in plate count in under 2 min, while Quaternium 7 required 15 min to achieve this plate count reduction.

IV. Applications

Shampoo Study—In developing a shampoo for a study of this type, we wanted a low pH clear simple formula with as few ingredients as possible so as not to interfere with the conditioning properties of the quaternaries during their evaluation. We desired though, a formula which would foam well, clean well, and be acceptable to the consumer (panelist) An amphoteric was used for the bulk of the detergent action. A small amount of TEA lauryl sulfate was added to boost the foaming. An amide level of 5 per cent was used to provide a suitable viscosity and add to foam stability. A total 3–per cent active quaternary was used (see Table IV). This formula provided a clear liquid shampoo of moderate viscosity.

Table IV

Low pH Quaternary Shampoo

	WT. %
Amphoteric-10	30.00
TEA — Lauryl Sulfate (40%)	8.00
Quaternary (10% active Solution)	30.00
Lauramide DEA	5.00
Propylene Glycol	6.50
Deionized Water	20.20
Perfume	0.30
	100.00

PROCEDURE:
Heat and mix the first four ingredients to 70°C until clear and homogeneous. Let cool and adjust the pH to 5.0 with lactic acid. Add perfume — the mass is now cloudy. Add the propylene glycol and mix until clear. Add the rest of the water.

Two shampoos were prepared. The first contained the LanES quaternium and the other contained Quaternium 7. Half-head studies involving 6 subjects were employed to evaluate the shampoos. The right side was reserved for the LanES shampoo and the left side for the Quaternium 7 shampoo. The subjects were all females in their mid-teens with shoulder length or longer virgin hair. Experiments were performed in the beauty salon of a well known testing agency.

In the procedure used, the hair of the subject was first examined for color, texture, condition, and length. The hair was parted in the middle and combed out. One side was wetted, then washed with a measured amount of one of the shampoos. The other side was also wetted and washed with a measured amount of the other shampoo. At this point, foam quality and quantity were observed. Then the head was rinsed and washed again in the same manner. After the final rinse, the hair was evaluated with a wet comb. The tangles were combed out with the large teeth of a comb and then with the small teeth. Ease of combing, hair conditioning effects, and slip were then evaluated by the subject, operator, and observer. The hair was set with rollers and the subject was placed under the dryer until the hair was thoroughly dry. After completion of the drying, the rollers were removed and the hair was combed out. The hair was again evaluated by the subject, operator, and observer for conditioning, sheen, manageability, softness, degree of static charge, curl retention, and any other properties which appeared to be either exceptional or poor.

Table V

Quaternary Creme Rinse

	WT. %
Quaternary (10% active solution)	30.00
Glycerol Stearate, SE, acid stable	1.50
Hydroxypropyl Methylcellulose (1% solution)	40.00
Deionized Water	28.00
Perfume	0.50
	100.00

PROCEDURE:
Heat the GMS and water together to 75°C and let cool to 30°C with slow continual stirring. Add the other ingredients and package.

pH was adjusted to 5.5 with Lactic Acid.

Results—In all 6 cases, the 2 shampoos used were very similar as far as foam quality and quantity are concerned. If anything, the right (LanES) side produced a tighter bubble, which gave the appearance and feel of a thicker creamier lather. Both shampoos rinsed equally well. During the wet comb evaluation, the left side (Quaternium 7) excelled. In 4 cases out of 6, the left side combed out easier with less tangles and had more slip, which allowed the comb to glide through the hair easier. After comb out, the right (LanES) side generally felt as if it had a slightly greasy film remaining.

After setting and drying, the right (LanES) side was preferred for sheen, manageability, and body. Both shampoos controlled fly away well; in only one case, the subject preferred her right over her left side in the fly away evaluation.

In general, marked distinctions between the two shampoos did not exist. Differences were very small in most cases, thus showing the LanES to be as effective as the Quaternium 7.

Creme Rinse—The formula employed for this study was simple but effective in pointing out the differences between the LanBAC and the Stearalkonium Chloride. The formula is shown in Table V. The small percentage of gum was added to provide a viscosity sufficient to improve the formula's stability.

Experimental—Half-head tests were employed to evaluate the two products. Six females in their mid-teens, with long virgin hair were used. The hair was washed twice with a commercial bland shampoo, then parted in the middle of the head. The Stearalkonium Chloride creme rinse was used on the left side and the LanBAC creme rinse was used on the right side. The rinses were diluted 10 to 100 ml at the salon and applied to the hair. The full 100 ml was

used on each side. This was followed by a thorough rub in for approximately 3 min and then a thorough rinse. A wet comb evaluation was followed by a set and drying. The curlers were removed and a final evaluation of the hair was carried out.

Results—Both rinses applied equally well and rinsed out well. The left (Stearalkonium Chloride) side was preferred by all in the wet evaluation for ease of combing and amount of slip on the hair. In some cases, the right (LanBAC) side yielded a lesser amount of tangles.

After setting and drying, the right (LanBAC) side was preferred by 5 out of the 6 females for sheen, fluffiness of the hair, manageability, feel, and body. As in the shampoo study, the lanolin quaternary was preferred in the final evaluation, although it suffered somewhat in the wet comb evaluation.

Summary

In this paper, we presented two new quaternary compounds derived from lanolin acids. We discussed their method of preparation and described other derivatives that could be prepared. It was demonstrated that their use in shampoo and creme rinse formulas compared with commercially available compounds of this type. Lower eye irritation scores and higher germicidal activity were presented along with an experiment demonstrating greater compatibility with anionic surfactants. (Received July 15, 1975)

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Hair Body

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Synopsis: HAIR BODY can be defined as the STRUCTURAL STRENGTH and RESILIENCY of a HAIR MASS. The definition conforms to the qualities assessed subjectively by hair cosmetic users. Five groups of fundamental parameters govern the mass structural strength of hair: hair density on the scalp, material stiffness, diameter, configuration of the fibers, and fiber-fiber interactions. The potential influence of hair cosmetics on hair body can be systematically analyzed by deducing their effects on these separate fundamental parameters. It is proposed that current cosmetic products are effective in modifying hair body through only the last two factors: fiber configuration and fiber-fiber interactions.

I. Introduction

Terms like *body* and *texture* have gained greatly in their importance to hair cosmetics during the last few years. All major hair care product categories—shampoos, conditioners, setting aids, sprays, waves, bleaches, and dyes—tend to promise these characteristics to the consumer.

The terms have magic qualities because they represent much sought after properties and because they refer to some intangible characteristics which have not yet been defined. The aim of this paper is to offer a physical definition for hair body, analyze its component parameters, and discuss how different types of products assist in realizing it.

II. Discussion

A. *Definition*

Women tend to judge hair body either by visual or tactile characteristics. According to the visual evaluation, a head of combed-out hair has body if it shows high elevation over the crown and significant lateral displacement at the sides, conversely, when the mass of hair closely follows the shape of the skull on the top and sides under its own weight, it is interpreted as lacking

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body. In tactile evaluation, a mass of loose hair is usually compressed and relaxed, if it is firm and resilient, the rating is positive.

While considerable differences exist both in methods and ratings, a common characteristic can be found in all cases: hair body is associated with mass structural strength and resiliency. On the basis of this, it is proposed that: body is a measure of a hair mass's resistance to, and recovery from, externally induced deformation.

Some of the words of this definition must be emphasized. First, body always refers to a hair mass even if one may extrapolate to it from single fiber properties. Secondly, body is a quantitative characteristic and, therefore, the word measure must be included in the definition. Hair with no body means that some or all of the fundamental parameters which contribute to the mass strength are present at low levels only.

The above definition satisfies the characteristics which are judged by the visual method of body determination according to the following. The emerging angle of hair fibers is high in relation to the skin. Consequently, the fibers would keep pointing in a substantially radial direction with regard to the skull in the absence of outside forces. The continuously acting external modifier is the gravitational force. Depending on the balance between structural strength and resiliency of the hair on one hand, and the gravitational load on the other, the hair mass may show more or less elevation bulkiness. The word bulkiness is used here in terms of its textile definition, meaning low structural density.

In connection with the hand compression method of body evaluation, it is evident that strength and resiliency characteristics are appraised and, therefore, it fits the above given definition for body as well.

B. *Component Factors in Hair Body*

The above definition equates body with the resilient strength of a hair mass under static and dynamic conditions. The resilient strength of any multicomponent engineering structure, which a hair mass is, is influenced by a number of independent parameters. In the most basic form, five such parameters need to be considered: fiber density on the scalp; bending and torsional stiffness and resiliency of fibers; fiber diameter; fiber configuration; and fiber-fiber interactions.

1. *Fiber density on scalp:* Fiber density is an important factor in modifying both structural volume and resiliency of hair mass over and at the sides of the head. When all other factors are equal, the volume of a fibrous mass is a linear function of the number of fibers in it. This correlation is satisfactory to indicate the direction of the influence, but it must not be applied quantitatively to the elevation of hair over the head. The main reason is that the hair mass density decreases with increasing distance from the skin for any fiber density at the roots. The structural stabilization—originating from fiber-fiber

interactions and fiber stiffness—decreases with the density. Complete mathematical models, incorporating all variables, are not yet available. When only the density gradient is taken into account, it is easy to show that the fiber mass elevation increases with the square root of the hair density at the skin level.

The increasing structural resiliency of a denser head of hair can be associated with the following facts: the number of contact points between fibers is higher and the segmental fiber length between supporting contact points is lower. In addition, the angle of contact between neighboring fibers is lower in regions near the scalp. For these reasons, a larger portion of the load is supported by material compression, instead of bending or torsional resistance of the fibers.

The most closely fitting industrial example for the importance of fiber density in a loose fibrous mass is that of a pile carpet. The packing density is of great importance for the resilient strength of these structures.

While the on-head fiber density influences the visual hair body evaluation very strongly, it is probably a secondary characteristic in the hand compresson method which measures intrinsic parameters for the mass structure.

2. *Bending and torsional stiffness and resiliency:* The second group of parameters for hair body involves mechanical characteristics—specifically the modulus and yield stress—of the component fibers in bending and torsional modes. Tensile behavior does not play a significant role in hair body. The weight of even a 100-cm long fiber is in the 10^{-3} g range. This is 3 to 4 orders of magnitude smaller than the yield force of an average fiber in the dry state. However, this load is more than enough to cause torsional and especially bending deformations. The bending deformation gains added importance as it increases with the third power of the segmental length of a beam, which a fiber represents:

$$S = k \frac{f l^3}{M r^4} \tag{1}$$

where S equals bending flexure; k equals numerical constant; f equals force; l equals length of beam; M equals Young's modulus; and r equals radius of beam.

A second characteristic within this group is the resiliency of the fibers, describing the balance between elastic and plastic behavior. Overall, the higher the stiffness and resiliency of the fibers, the higher the body of the hair mass, when other characteristics are equal.

3. *Fiber diameter*: This parameter often reaches a dominant position, because as mentioned before, hair body is associated mostly with torsional and bending deformations of the component fibers. Both the bending and the

torsional stiffness of beams increase with the fourth power of the diameter, as is shown by equations (1) and (2):

$$\theta = k \frac{C\,l}{M\,r^4} \qquad (2)$$

where θ equals twist; k equals numerical constant; C equals force couple; l equals length of beam; M equals modulus of rigidity; and r equals radius of beam.

The theoretical value of a sixteen-fold increase in body with a two-fold increase in diameter has been measured by us on certain fiber arrays. This factor is one of the most important in determining natural hair body, both by the visual and tactile methods, because the fiber diameter variation is significant among individuals. Again, carpets provide a descriptive example for this characteristic: fine merino wool is rather unsuited for carpet making in contrast to a coarse South African wool. For equivalent compressive strength and resiliency of a carpet, more wool—by weight—of the former than of the latter type is needed.

4. *Fiber configuration*: The term fiber configuration primarily refers to curliness versus straightness and, secondly, to the array of the fibers. To some extent, the angle of hair fibers relative to the skin belongs to this category. Curly or crimped fibers increase the bulk volume of a fiber assembly; that is, they provide stabilized structures at lower density. An appropriate example is that all bulky knit fabrics rely on crimped fibers. In the case of wool, the crimp is natural, while for continuous filament synthetic fibers, it has to be processed into the yarns separately. Two basic factors are operational when the stabilized bulkiness of a fiber mass is due to curl. One is that a curved object creates a prohibited space—larger than its own material volume—which other bodies cannot easily enter. Secondly, curved fibers establish contacts with larger numbers of neighboring fibers than straight ones. An extreme example for curl induced bulkiness and resilient strength in hair is the natural or Afro style. This cannot be achieved with straight hair without resorting to other stabilizing treatments.

5. *Fiber-fiber interactions:* The last major factor is the surface interaction between fibers, which determines the ease or difficulty of fiber displacement within the mass structure. The structural strength of any multicomponent system, and, therefore, the body of a hair mass, depends on the effective stabilization of the component units relative to each other. When applied to hair, this overall parameter includes a number of basic factors: material frictional characteristics and surface roughness of the fibers themselves, lubricity, shear resistance, and the adhesiveness of any surface coatings under the static and dynamic conditions operating on a hair mass. It is safe to state that the stronger the surface interaction between contacting fibers, the higher the hair body.

In our view, the concept of hair body, as defined above, is exhaustively described by these five variables. The variables are causatively independent of each other, but synergism can exist. For example, fibers of higher material moduli or larger diameter can enhance the structure stabilization by surface interaction as well, because they are able to support higher normal forces. This, in turn, results in greater frictional immobilization.

According to the above given interpretation of hair body, none of the five variables have exclusive influence on the overall behavior. Therefore, any specified level of body, if a quantitative scale existed, could be obtained by a nearly infinite number of variations among the five factors. Obviously, when a given body level is achieved by different combinations of the fundamental parameters—for instance, a decreasing fiber diameter is balanced by increasing hair density—some other perceptible hair mass characteristics will change. These changes, however, belong to second-order behavior patterns, specifically to texture qualities.

C. *Cosmetic Products and Hair Body*

The specific influence of cosmetics on hair body is best discussed by analyzing the changes in the five basic parameters caused by different cosmetic products.

It may be stated summarily that cosmetics—according to the current definition of the term—cannot directly influence any of the five parameters so far as the biological synthesis of the fibers is concerned. Compositions or treatments which could grow denser, stronger, thicker, curlier, or rougher hair would be outside the field of cosmetics. Therefore, the discussion needs to involve only those effects of cosmetics which occur on grown hair.

Cosmetic products can have only indirect and/or negative effects on fiber density. The on-head fiber number can be considered as a kinetic equilibrium determined by the rate of new fiber growth on the one hand and the rate of fiber elimination on the other. As mentioned above, fiber growth rate is not a cosmetically solvable problem. The rate of fiber attrition, however, can be influenced to some degree. Treatments or products, which result in more difficult combing, accelerate the rate of fiber elimination, thereby reducing the fiber density to a lower steady-state level. Lubricants, on the other hand, delay the mechanical fiber removal and assist in the maintenance of marginally higher fiber densities. Nonetheless, these effects are secondary, and it may be stated that cosmetics do not significantly influence hair body through modification of the fiber density on the scalp.

The modulus or stiffness of polymeric materials can be increased by chemical treatments. This has been achieved on natural fibers, including keratin fibers, by cross-linking, or by introducing bulky side groups. However, the nature of the reactants and/or the reaction conditions are such that, at present, these methods cannot be used for on-head treatments. No current cosmetic products increase body by this method. Conversely, some cosmetic

products decrease the level of cystine cross-links in hair. These include bleaches and especially bleaches followed by permanent waving. Their influence on the dry modulus—and on whatever segment of body is derived from the modulus—is negligible, because the cystine cross-links are not important load bearing elements in dry fibers within the Hookean range

The moduli of the fibers can be influenced by internal or external deposition of nonreactive materials as well. The resulting systems are composite structures with increased final fiber volumes, therefore, these will be discussed in connection with the fiber diameter effects.

A specific case of modulus change occurs when the hair is swollen by liquids which interfere with the internal salt and/or hydrogen bonds of the fibers themselves. Wetting of intact hair by water decreases the modulus by nearly an order of magnitude. The wet modulus of an oxidatively modified hair is even lower. While the modulus reducing effect of fiber swelling liquids must be kept in mind when hair compositions are formulated, the fact in itself is of little importance for the present purpose. Hair body refers primarily to the dry and not to the wet state of the hair. The overly high softness of extensively bleached or bleached-waved wet hair may present problems during a shampoo and wet comb-out, but it does not translate to the dry behavior. Overall, it may be concluded that present day cosmetic products and processes can influence hair body only marginally through modulus modification.

Body modification through fiber diameter increase can be accomplished by internal or external deposition of foreign materials. High levels of internal polymer deposition have been accomplished both on wool and cut hair, with significant increases in body type characteristics. While processes are available for the deposition of solids, mostly polymeric materials, they are not presently utilized in cosmetic products for reasons already mentioned. On the other hand, materials of small molecular weight which are sorbed by the hair —such as alcohols, amines, etc.—most often act as plasticizers, therefore, defeat the original purpose of increasing body.

Only solid materials need to be considered for external deposition which can act as load bearing elements. While setting lotions and gels meet this requirement, the approach has serious limitations. The coating thickness must be very limited, if the natural fiber surface and topography are to be maintained. Consequently, hair body can be increased by surface deposition only if the coating is continuous and its stiffness is significantly higher than that of the fibers. In this case, the composite material—keratin core and external coating—has high bending stiffness. A specific case is when the solid deposit acts as an adhesive on heavily surface damaged fibrillated fibers. Through adhesively joining these splintered surface units to the main fiber body, they recover their load bearing ability in fiber deformation.

Based on the above, it can again be concluded that current cosmetic products do not increase hair body significantly by increasing the diameter of the fibers. Even in the case of setting gels, the effectiveness is not due primarily to this parameter.

Fiber configuration and array represent an area through which hair body is often increased. The higher the curl level and the greater the disorientation of the fibers, the greater will be the bulkiness and, thereby, the body. Permanent waving solutions and setting lotions and gels operate by this mechanism. All wet hair treatments can operate through this method, as they provide the opportunity for obtaining a temporary water set in the desired configuration. Prior chemical treatments, such as bleaching or waving, which increase the fiber swelling in water improve the water settability further and, therefore, increase the temporary body characteristics. For the sake of completeness, it must be mentioned that some hair care appliances (i.e., curling devices and even hand-held driers) belong to this category. Hand-held driers, in the normal mode of operation, provide water set to the hair at a high angle relative to the skin and reduce the level of configurational conformation among neighboring fibers.

The factor through which cosmetic products most often influence hair body is the fiber-fiber interaction. No cosmetic treatment leaves the fiber surface unmodified relative to its starting condition.

The products which most drastically increase hair body by this mechanism are sprays and polymeric setting lotions. These form rigid joints between contacting fibers which are similar to welding in steel structures. In order to overcome the segmental stabilization of involved fibers, the joints must be broken. Even when this is achieved, subsequent fiber displacement is still resisted as long as laterally extending asperities of the broken joints remain on the fibers. Therefore, the structural strength of a sprayed hair mass decreases with comb-out, but does not sink back to its original presprayed level until the residues are fully removed, for instance, by shampooing. The opposite case—a lowering of body—can be accomplished by surface coating when the deposit is a lubricant with low static frictional coefficient. Quaternary ammonium components behave this way. The shear strength of fiber joints is very low in this case, therefore, the fibers will displace, even under very low external forces and occupy lower-energy positions. With this treatment alone, a bulky high-bodied structure cannot be achieved when all other parameters are equal. Other surface deposited materials can achieve intermediate positions between these extremes. Generalizations, according to conventional classification of materials, must be avoided. Oil, grease, and wax-type components of shampoos, rinses, and conditioners, which are lubricants in the everyday use of the word, can increase hair body. They form adhesive joints between contacting fibers with finite well measurable strength. The bonding strength de-

rives both from surface tension and from static shear rigidity of the thin films. The kinetic frictional resistance of these joints is often low, allowing easy combing, but their static strength is considerable—in the range of a few milligrams. The layer thickness, especially for long hair, must be controlled because, in the case of overloading, the hair mass may compact and settle under its own weight. Chemically active hair cosmetics—bleaches, permanent waves and oxidative dyes—increase the material frictional coefficient and the surface roughness of the fibers and thereby reinforce the fiber-fiber interactions. This results in increased body.

III. Conclusions

It is possible to assign physical interpretation to a cosmetic term such as hair body which is logical and self-consistent in scientific meaning and correlates with the linguistic use pattern of the word. Furthermore, it is possible to break down the complex body characteristics into fundamental, single parameter, physical factors. The body attributes of hair cosmetics can be studied systematically, by evaluating their effects on these fundamental factors. It is, of course, quite easy to design measurements for directly assessing the influence of cosmetics on the complex phenomena, and we have used such techniques for body determination for some years.

Obviously, the present discussion represents a single viewpoint and further discussions by individuals from different areas of the fiber and cosmetic fields would be highly desirable to achieve a consensus on, and a better definition of, these rather important terms.

(Received June 3, 1975)

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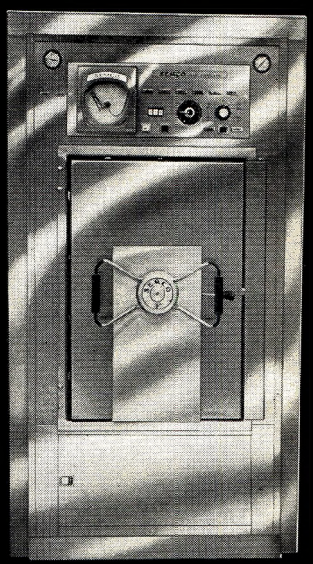

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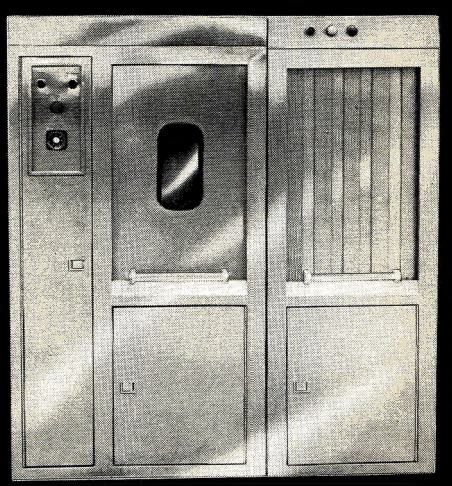

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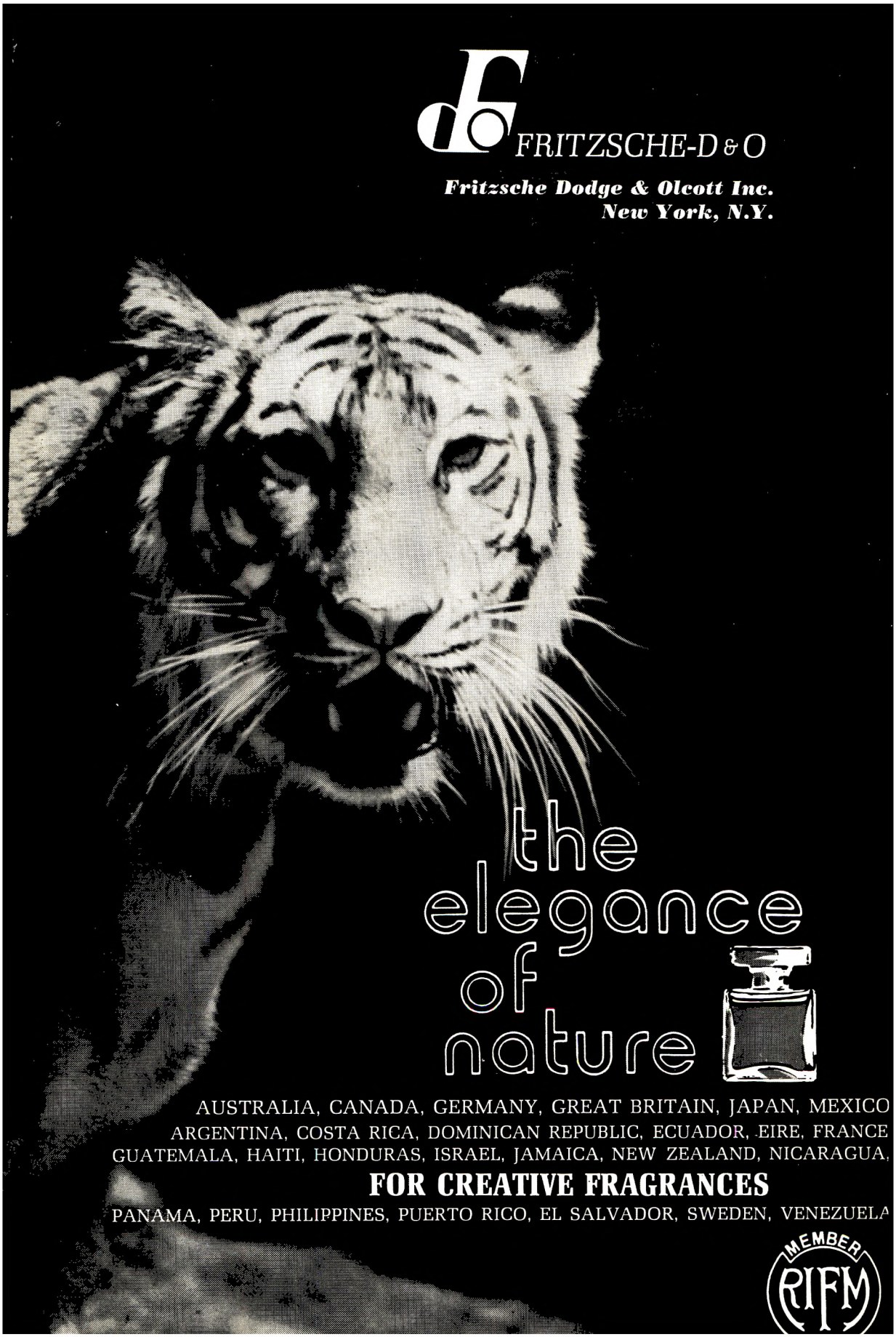
A MESSAGE FROM THE EDITOR OF THE JSCC

As you know, The Journal of the Society of Cosmetic Chemists, along with all other publications, has been faced with increasing production costs over the past year. The cost of paper along with printing costs have increased to the point where some action must be taken in order to insure the continued scientific and technical integrity of The Journal. The Publications Committee has been considering this problem for the past several years and has found it necessary to increase its subscription rate to non-members, increase its advertising rates as well as to increase the total number of pages of advertising copy. We have now reached the point where we can no longer increase the number of advertising pages without proportionally increasing the number of pages devoted to scientific and technical articles. To do so would drastically change the nature of our Journal to the point where it would lose much of its professional status.

Therefore, in order to increase the number of pages devoted to scientific and technical papers, the Board of Directors have approved the institution of a modest page charge to be assessed each author of a published paper. While these page charges will be waived by the business office in cases of undo hardship, it is expected that sufficient income will be received so as to insure the continued viability of scientific and professionals journals.

If we recognize that publication is one of the goals of research, then the cost of publication should be included as part of the research funding.

Sincerely,
John J. Sciarra, Ph.D.
Editor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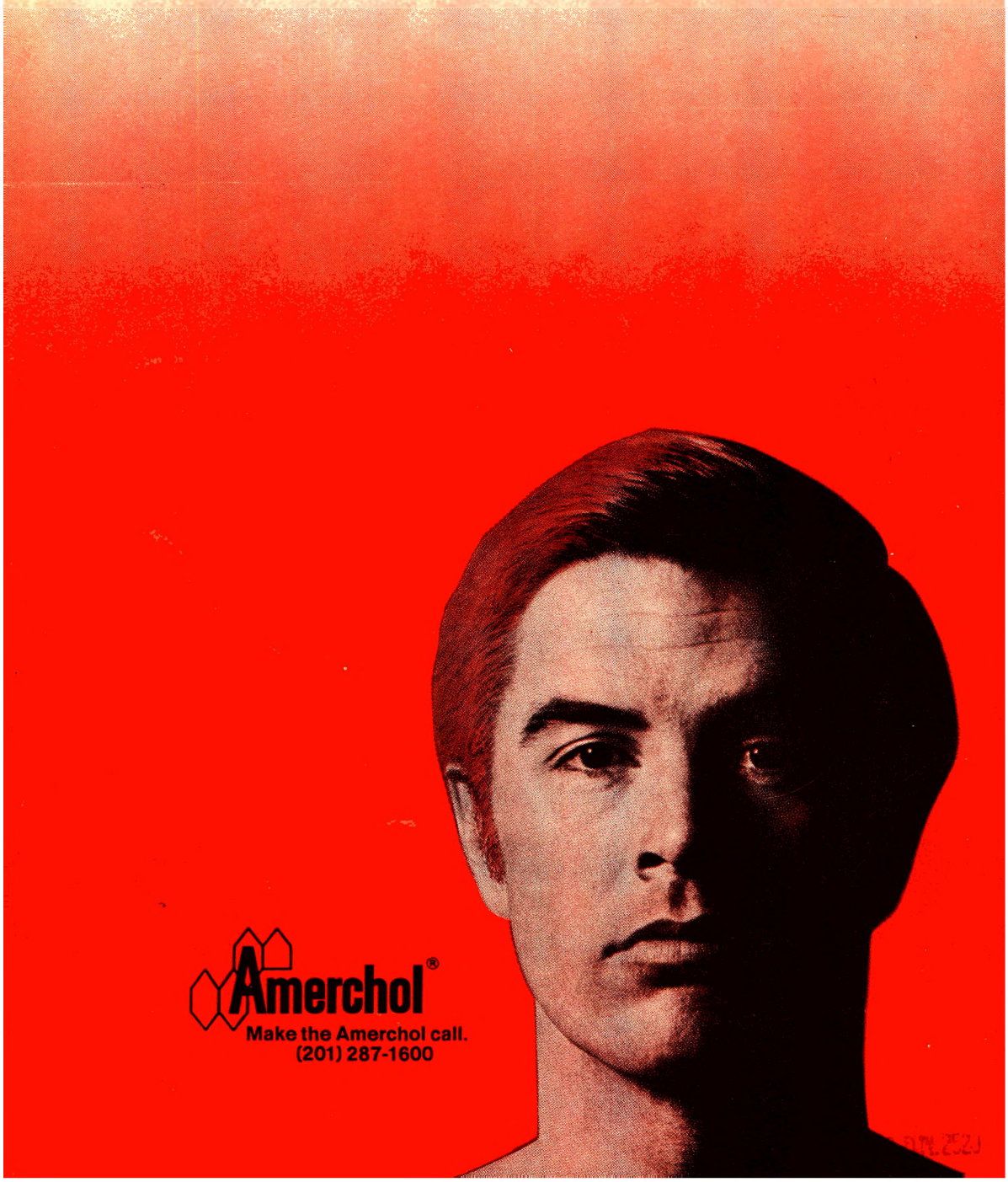

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