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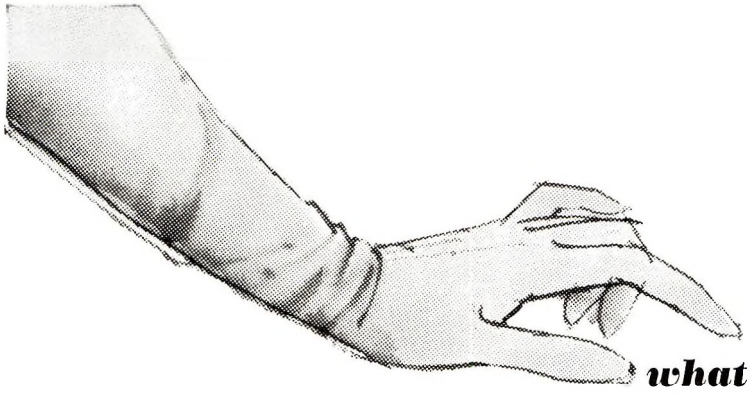

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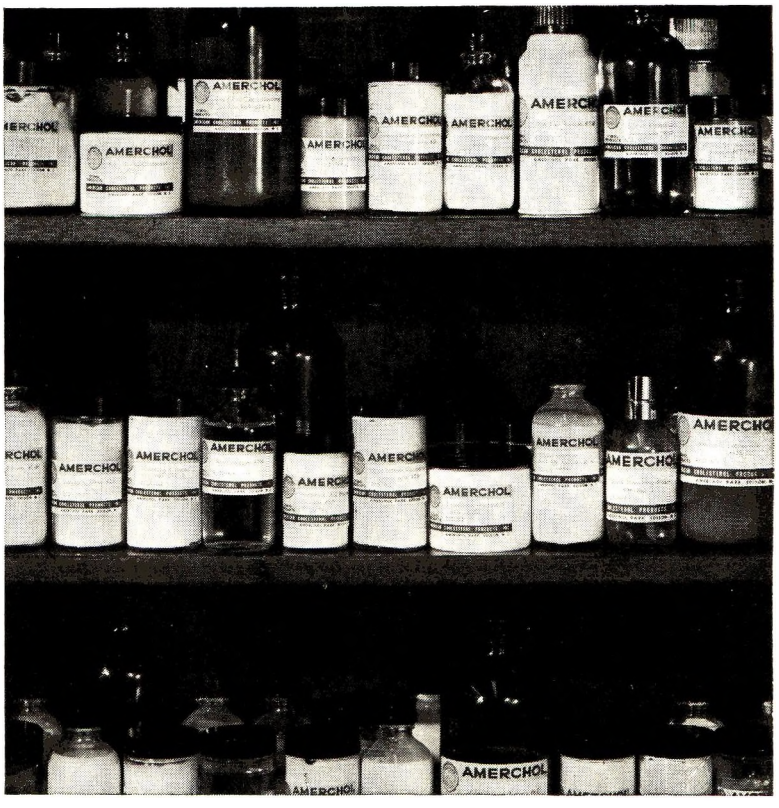

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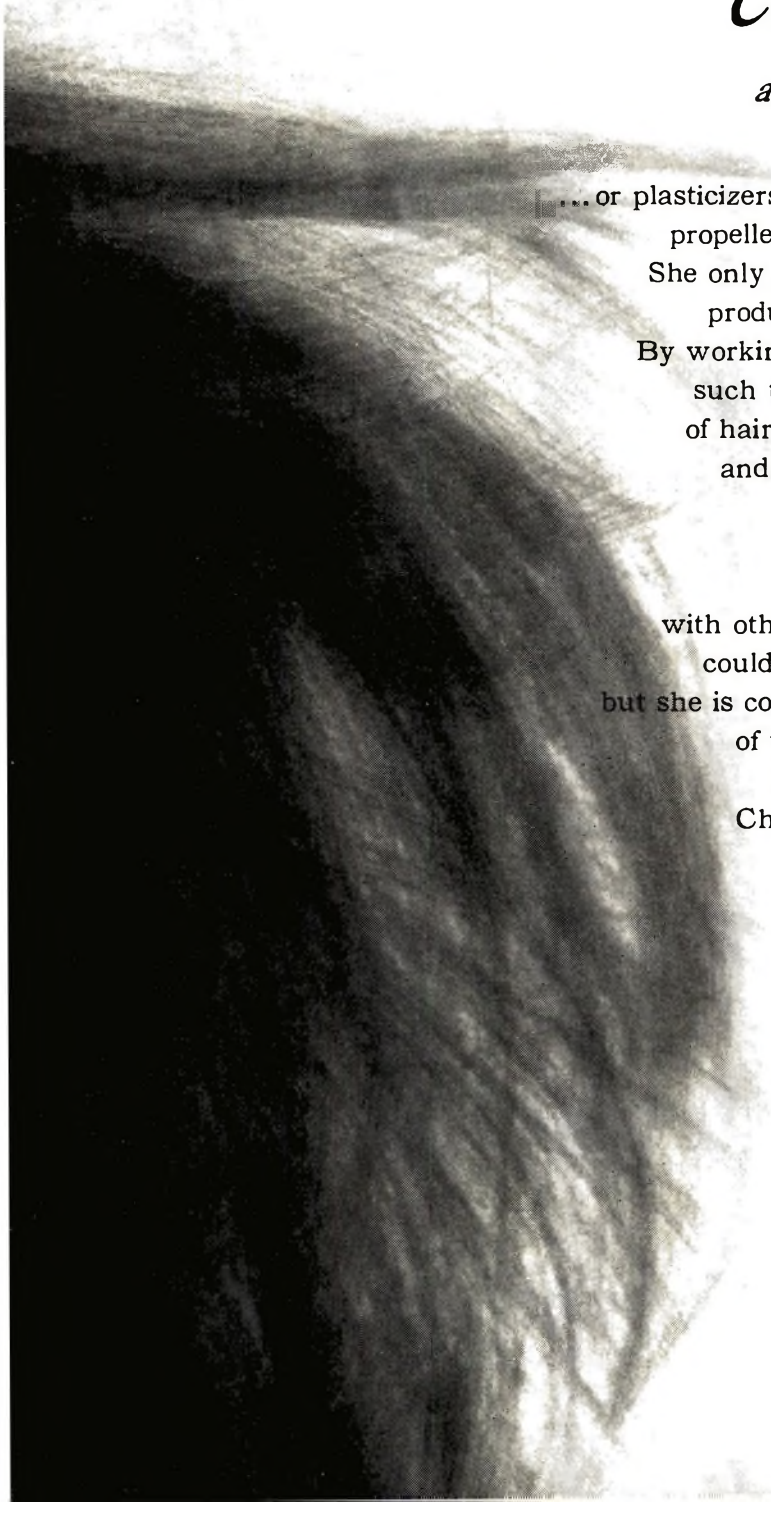

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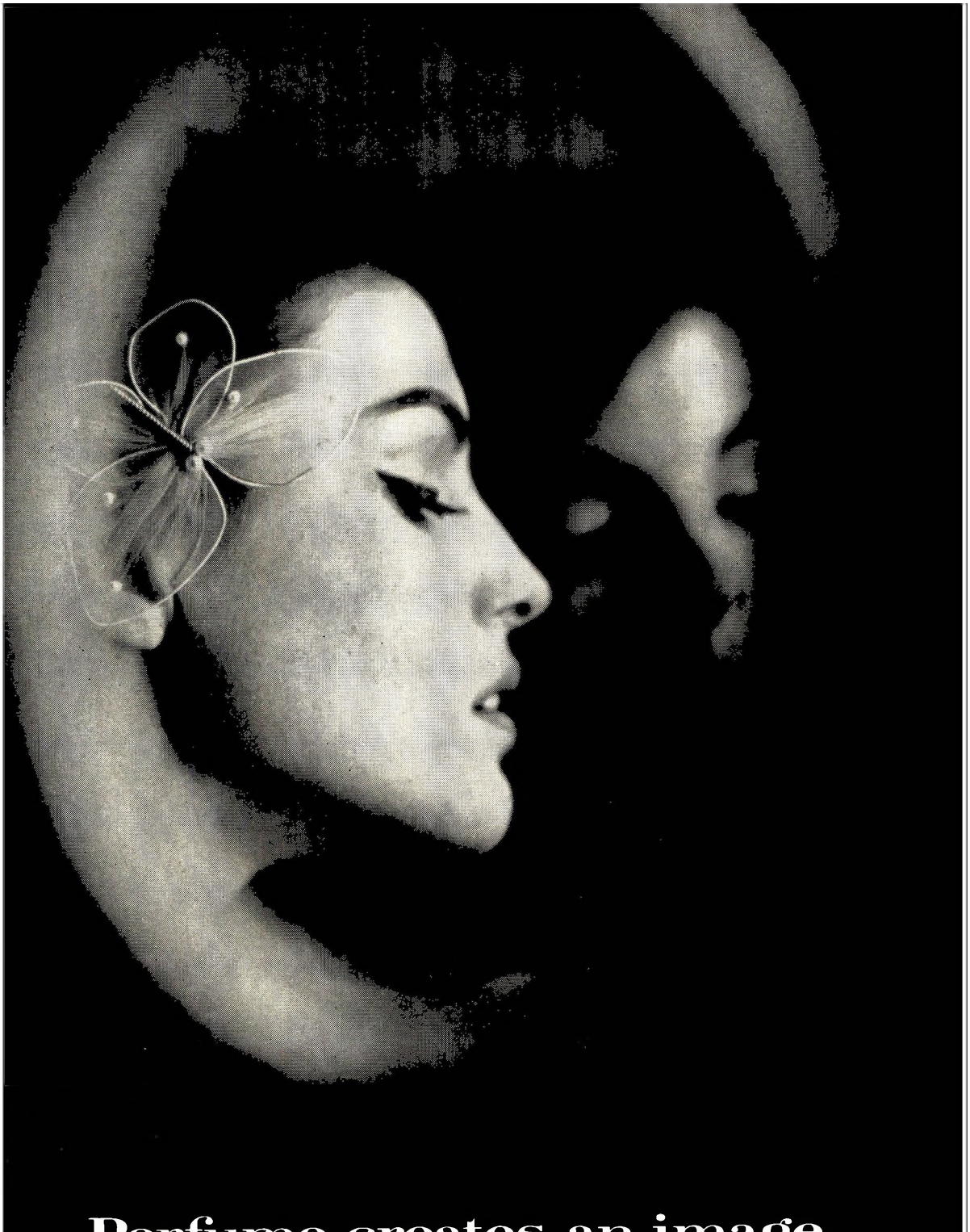

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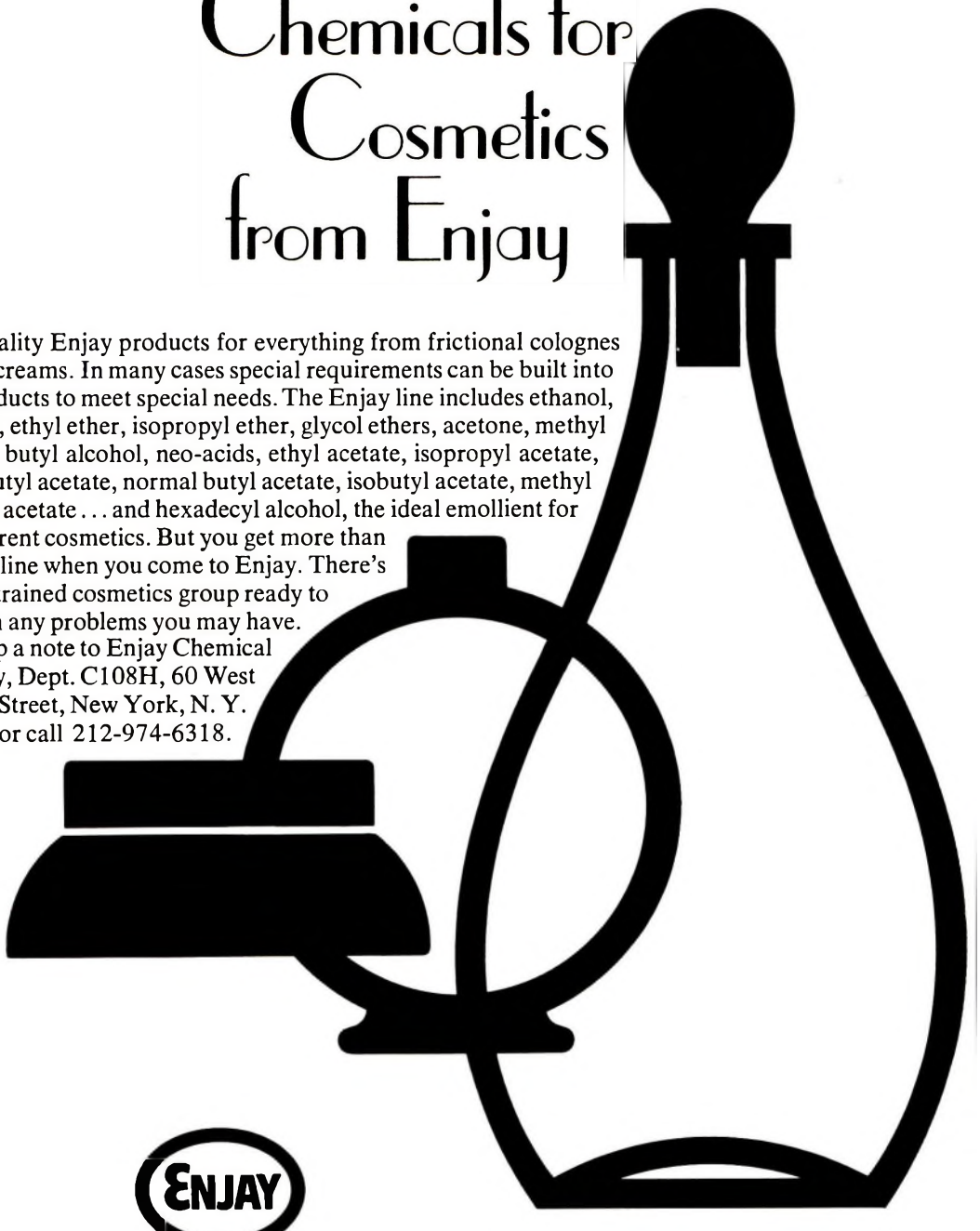

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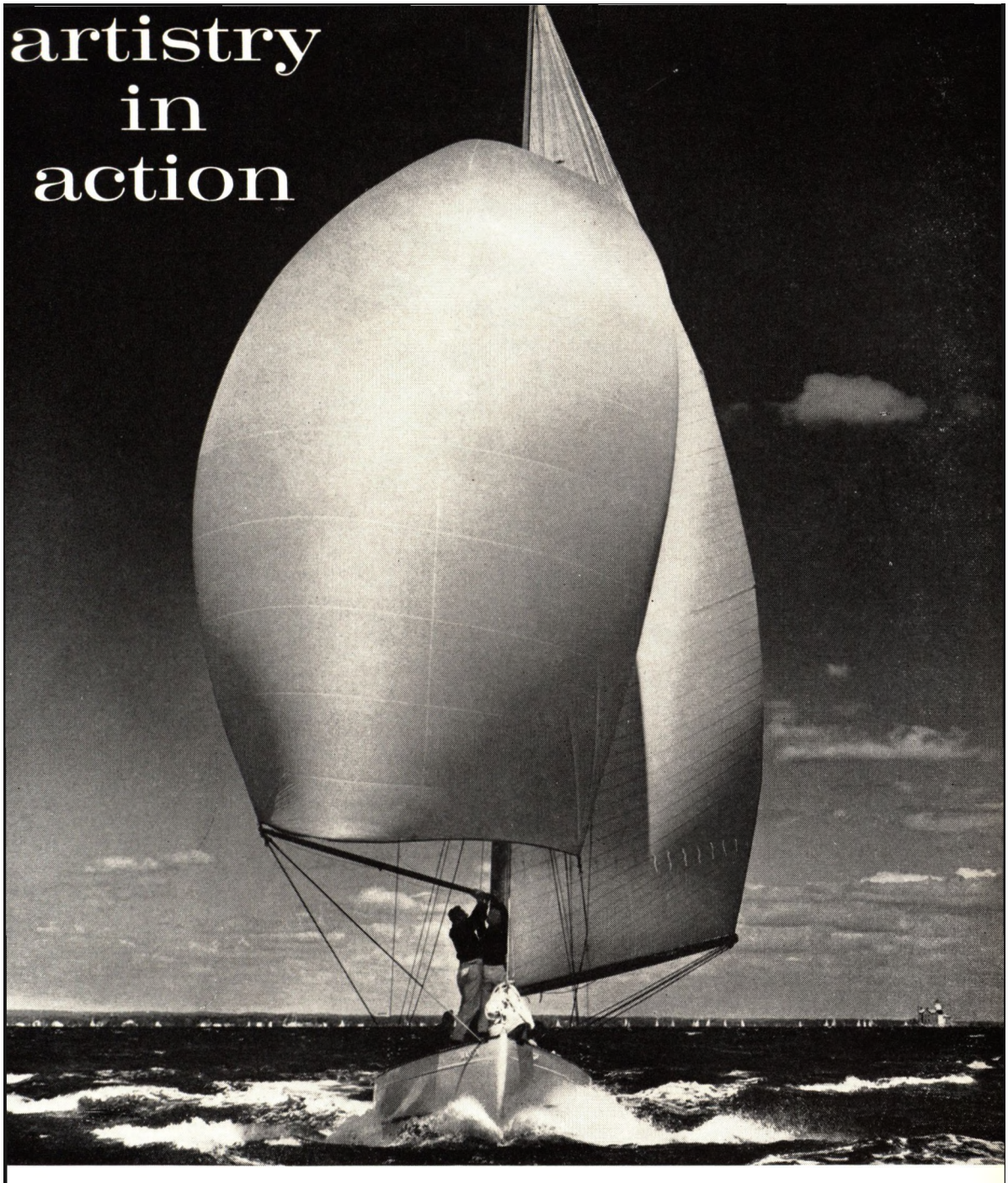

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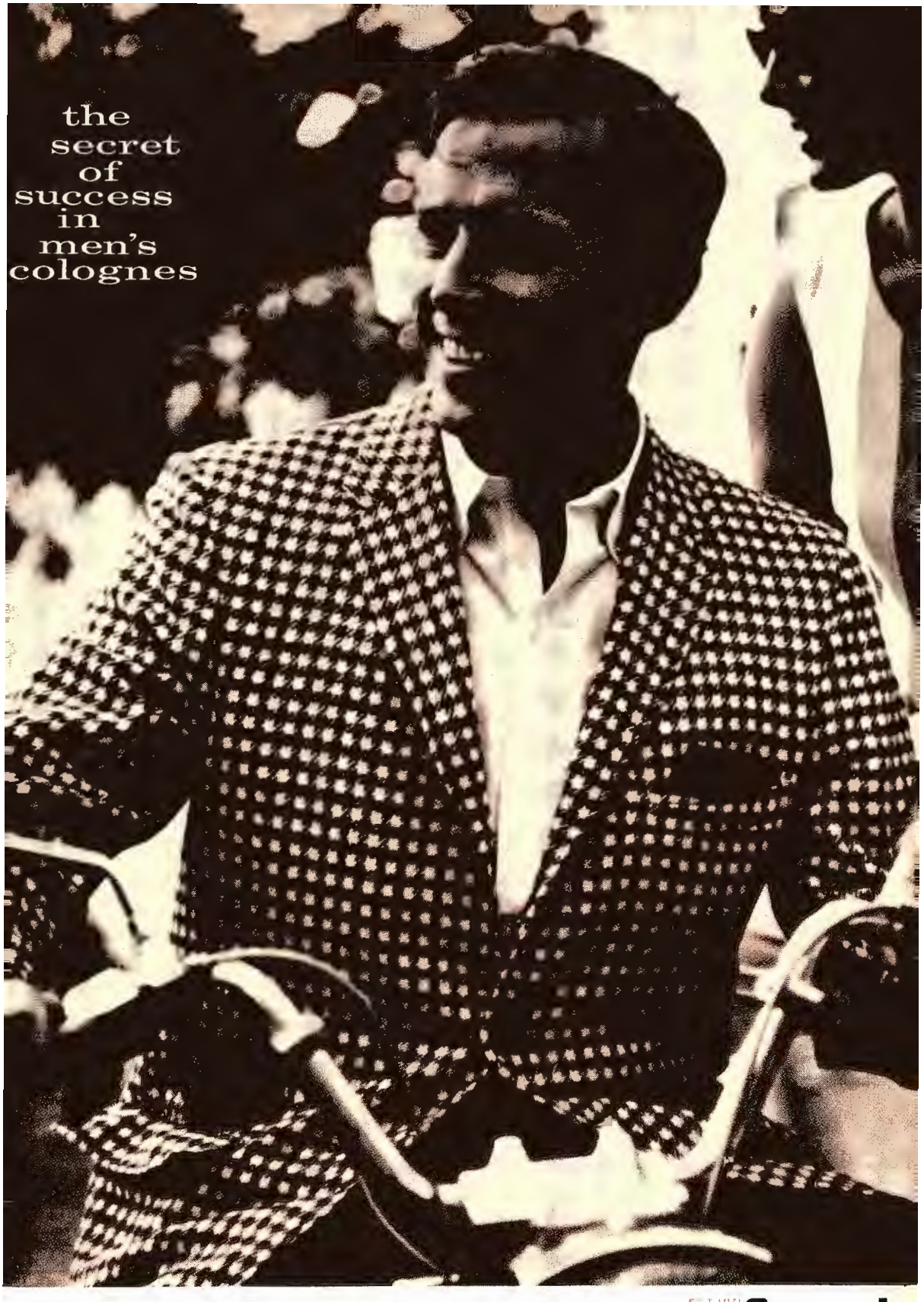

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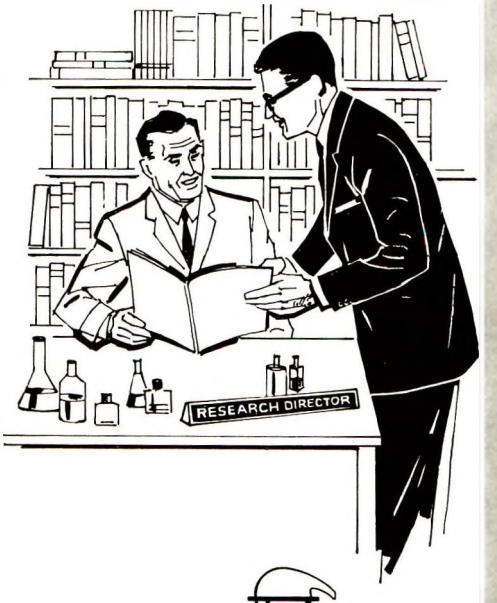

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INDEX TO ADVERTISERS

SYNOPSES FOR CARD INDEXES

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

Studies on the substantivity of collagen-derived polypeptides to human hair: S. A. Karjala, J. E. Williamson, and A. Karler. *Journal of the Society of Cosmetic Chemists* **17,** 513 (1966)

Synopsis—The sorption of collagen-derived peptides to human hair has been conclusively demonstrated. This proof of sorption can be applied only to peptides derived from collagen, since the procedure is based on the quantitative determination of a unique amino acid, hydroxyproline, which is present in large amounts only in collagen and in peptides derived from collagen. The sorption of collagen-derived peptides in general increases with increase in damage to the hair, with increase in concentration of peptides used, and with decrease in the molecular size of the peptides.

Temperature dependence of the mechanical properties of human hair in relation to structure: Ludwig Rebenfeld, Hans Dietrich Weigmann, and Cornelia Dansizer. *Journal of the Society of Cosmetic Chemists* **17,** 525 (1966)

Synopsis—The mechanical properties in tension of human hair were examined as a function of temperature in a buffer solution at pH 7.0 both in the presence and absence of a sulfhydryl group blocking agent. Untreated hair as well as hair that had been partially reduced to increase the free SH content was investigated. It was found that the elastic modulus, post-yield modulus, and fiber strength decreased with increasing temperature while extensibility increased. The turn-over point between the yield and post-yield regions was observed to undergo a transition at a characteristic temperature of 85.5°C. This transition temperature was decreased to 66.0°C for the partially reduced hair. The presence of the SH-blocking agent tended to decrease extensibility and increase the post-yield modulus but had no effect on the elastic modulus and strength. The results are explained in terms of a sulfhydryl-disulfide interchange mechanism whereby stressed disulfide bonds are relieved and transformed into three free positions. The transition temperature is associated with the stability of the disulfide bond and the onset of the SH catalyzed disulfide interchange.

The practical evaluation of shampoos: Marshall Sorkin, Bertram Shapiro, and Gus S. Kass. *Journal of the Society of Cosmetic Chemists* **17,** 539 (1966)

Synopsis—Appearance, performance during use, and effect on hair after use are the three major criteria by which shampoos should be evaluated. Within these three broad categories, 25 separate characteristics are enumerated. The importance of each of these and laboratory and beauty salon test procedures for evaluating shampoos are discussed.

Protection of cosmetic colors by means of U.V. absorbers: Willis G. Thomas, Jr. *Journal of the Society of Cosmetic Chemists* **17,** 553 (1966)

Synopsis—It is shown that nine commercially available ultraviolet light absorbers can be used to protect certified colors against fading. Such protection can be achieved by incorporating the U.V. absorbers into the product or into the coating of the package. Practical examples of both methods of protecting against fading are cited. The decision as to how the absorber is used depends on efficacy, the dye to be protected, safety, and costs.

LITERATURE SURVEY*

Analytical

Use of High Resolution Mass Spectrometry in the Study of Petroleum Waxes, Microcrystalline Waxes and Ozokerite. Reid, W. K., *Anal. Chem.*, **38,** 445–8 (March 1966).

Separation and Identification of Dyes from Cosmetics. Legatowa, B., *Roczniki Panstwowego Zakladu Hig.*, **16,** 453–9 (May 1965) (In Polish).

Complete Separation of Lipid Classes on a Single Thin-Layer Plate. Freeman, C. P., and West, D., *J. Lipid Res.*, **7,** 324–27 (March 1966).

Thin-Layer Chromatography of Phosphate Esters of Biologic Interest. Davidson, I. W. F., and Drew, W. G., *J. Chromatog.*, **21,** 319–23 (February 1966).

A Rapid Micromethod for Determination of Free Fatty Acids. MacKenzie, R. D., *et al.*, *Federation Proc. Abstr.*, **25,** 768 (March–April 1966).

A Method for Introducing Samples Into a Gas Chromatographic Column. Under, O. M., *et al.*, *Federation Proc. Abstr.*, **25,** 557 (March–April 1966).

Autotransfer Chromatography: Facile Two-Dimensional Chromatography in which the Stationary Phase is Changed. I. Autotransfer from Thin-Layer to Paper. Irvine, D. G., and Anderson, M. E., *J. Chromatog.*, **20,** 541–45 (December 1965).

Practical Aerosol Analysis. Reed, A. B., Jr., *Soap Chem. Specialties*, **42,** 130–32, 134, 171–72, 174 (February 1966).

Thermometric Titration of Cetyl Pyridinium Chloride. Weiner, N. D., and Felmeister, A., *Anal. Chem.*, **38,** 515–16 (March 1966).

Rapid Preparation of Fatty Acid Esters from Lipids for Gas Chromatographic Analysis. Metcalfe, L. D., *et al.*, *Anal. Chem.*, **38,** 514–15 (March 1966).

A Two-Dimensional Separation of Acid, Neutral and Basic Amino Acids by Thin Layer Chromatography on Cellulose. Bujard, El., and Mauron, J., *J. Chromatog.*, **21,** 19–26 (January 1966).

Estimation of Fatty Acid Composition by Gas Chromatography Using Peak Heights and Retention Time. Bartlet, J. C., and Iverson, J. L., *J. Assoc. Offic. Anal. Chemists*, **49,** 21–27 (February 1966).

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The Catalytic Effect of the Support on Terpene Compounds in Gas-Liquid Chromatography. Hayashi, S., *et al.*, *Bull. Chem. Soc. Japan*, **38,** 1824–31 (November 1965).

A Technique of Preparative Paper Chromatography. Pasieka, A. E., and Logan, J. E., *Can. J. Biochem.*, **44,** 149–53 (February 1966).

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Gas Chromatographic Identification and Determination of Barbiturates. Martin, H. F., and Driscoll, J. L., *Anal. Chem.*, **38,** 345–46 (February 1966).

Gas-Liquid Chromatographic Analysis of Long Chain Isomeric Glyceryl Monoethers. Wood, R., and Snyder, F., *Lipids*, **1,** 62–72 (January 1966).

Determination of Phenylmercuric Compounds in Fungicidal Preparations and in Paint. Hoffmann, E., and Saracz, A., *Textile Res. J.*, **36,** 428–30 (January 1966).

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Dr. Albert M. Kligman, Professor of dermatology in the School of Medicine and Graduate School of Medicine of the University of Pennsylvania, left, and Mr. William A. Mueller, President of the Society, right, after presentation of the Society of Cosmetic Chemists' 1965 Literature Award

The Twelfth Literature Award

The Twelfth Annual Literature Award of the Society of Cosmetic Chemists was awarded to Albert M. Kligman, M.D., Ph.D., Professor of Dermatology at the University of Pennsylvania. The presentation was made at the Literature Award Luncheon on May 10 at the Americana Hotel in New York City.

In presenting the award to Dr. Kligman, William Mueller, President of the Society of Cosmetic Chemists read the following citation:

"The Society of Cosmetic Chemists presents to Dr. Albert M. Kligman, M.D., Ph.D., the 1965 Literature Award in recognition of his achievements in the field of dermatology and in particular for his investigations concerning skin sensitization, the physiology of the sebaceous gland, and the properties of stratum corneum. His work is considered an outstanding contribution to Cosmetic Science."

Albert Montgomery Kligman, M.D., Ph.D.

A Eulogy by Walter B. Shelley, M.D.*

This is Albert Kligman day! We are all here to salute him, and it is my delight and joy to fire the first twenty-one guns. (Your thousand guns will follow.)

Albert is wonderful—a eulogist's delight. For those few of you who don't know him, I would like to paint his portrait. After eighteen years as a friend, colleague, confidante, and co-author, I would like to do this in oil, but your committee has allotted me only enough time for a water color. So, if you will pardon my quick brush, I will begin.

The brightest, gayest colors must be used to depict Albert's life. Nothing about him is ordinary, drab, or neutral. Although he hails to the title of Professor of Dermatology at the University of Pennsylvania and is completely indigenous to Philadelphia, his background sports at least a half dozen other professions. You would do well to consult this gentleman in such disparate fields as forestry, chemistry, mycology, psychoanalysis, hypnosis, and mushroom culture. Each he has mastered and enriched at various points in his half century stroll on our planet. Indeed, he remains an international authority on the care and feeding of mushrooms, having authored the only definitive monograph in this area.

Although his vocations are a *tour de force*, it is his avocations which leave one breathless. And I speak literally. For here is a man Kennedy would embrace with vigor. His early years in college found him captain of the Penn State gymnast team. Figure skating, ballet dancing, golfing, and skiing followed. Each was studied and performed with an intensity unmatched by others. Having mastered the land, he took to the water in a retrograde evolutionary manner, and we find him racing sails above and aqua-lunging below. As the year of affluence appeared, we saw Albert soar into the skies to acquire successively expertise in gliding, parachuting, flying his own plane, and more recently, balloon-

* University of Pennsylvania, Philadelphia, Pa.

ing! Every week of his life has been eventful as he searches out the physics of antigravity. The legends of his exploits, too, have enjoyed a logarithmic ascent. Given the time I could recount stories of his flying above the Atlantic with a gas tank registering zero, of his eighty mile an hour automobile accident, of near disaster in a blinding snow storm. But all this drama has left Albert unscathed, full of zest and *joie de vivre*. He has become an *objet d' art* of our department, and no foreign guest ever arrives without asking, "Do you think we could see Dr. Kligman?"

But, as your Society is so properly recognizing, Albert is more than a myth. He is in his finest flowering as a truly great teacher and researcher. Teaching is his greatest love, and I am certain that all who have heard his eloquent impassioned lectures would rank him as incomparable. He is a forceful, articulate, persuasive logician who attacks doubt and untruth with no concern for the source or consequences. His lectures are a daily delight to students who enjoy his antics, anecdotes, and thrusts at the ill-informed. His fame as an orator and scholar is such that a sampling of his recent speaking engagements includes Johannesburg, Cairo, Munich, London, and San Francisco. He obviously has seven-league boots and a voice to match. On a clear day, I have known him to give as many as eight thoroughly different sparkling lectures.

No account of Albert can evade the superlatives, and this is especially true in research. Hundreds of papers have flowed from his laboratory over the past twenty-five years. They have centered on disorders of hair, acne, fungous infection, poison ivy dermatitis (who can forget the Poison Ivy Picker of Pennypack Park in *Life* Magazine—in full page, too!), and now in his semi-centennial year, aging. Nothing cutaneous is foreign to his probing ceaseless curiosity. His most recent classics have included a definitive study of the magic penetrant, dimethyl sulfoxide, and an exquisite method of predictive patch testing.

Accolytes from the shores of Thailand to the halls of Lebanon have come to serve in his lab and to gather a lifetime of inspiration. But one of Albert's crown jewels has been the "Holmesburg Experiment." Here in a prison Albert has provided a new code of penal therapeutics, namely the involvement of prisoners in experiments for the common good of man. Nothing has given Albert more satisfaction than bringing prisoners to an awareness of their new significance in society.

Before putting my palette down, let me sketch Albert as a friend and a father. He is charitable and generous to a degree commensurate

with his total commitment approach in all fields. I know of no one with a deeper loyalty and kindness to his friends, his school, and his colleagues than Albert.

Albert's beautiful home reflects the love and affection he bestows upon his wife and three children. Living in regal splendor with his books, his collection of hats, and a multi-storied living room, Albert is the perfect host at many a distinguished dinner party. I should tell you Albert has been married twice—and his bride of both times is seated here to my left. Bea—also a physician worthy of eulogy in her own right—through an indescribable series of medical mishaps came so close to death that Albert commemorated her return to health by the moving ceremony of a second wedding.

The warmth of Albert's home life can be richly illustrated by a favorite story of mine. It seems that Albert addressed your group a few years ago, and a beautiful alluring woman whose identity must remain in the algebraic initials, Z. Z., was a co-speaker. After the conference, Albert was invited out by the glamorous Z. Z., but he declined saying he had to go back to Philadelphia to take his children to the Franklin Institute to see a performance—"Science Can Be Fun." Surely he deserves a special award for this.

If I close with a wistful stroke of the brush, it is but from dreamy envy of this superman. He leads us all in the pursuit of excellence. Ladies and gentlemen, I salute Albert the Great, Kligman.

Blind Man Dermatology

A. M. KLIGMAN, M.D., Ph.D.*

Presented at the Literature Award Luncheon, May 10, 1966, New York City

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The reader will not likely discern the intent of this little piece from the title. A sampling of my colleagues' guesses showed that I had succeeded in keeping them in the dark. Influenced by my past history in public speaking, they generally surmised that I was going to denounce dermatologists for being "blind," adding thereby a new dimension to the better known deficiencies of this sub-order of medical specialists. Neither I nor any other informed person can deny that dermatologists have keen eyes, though in some instances there is controversy concerning the adequacy of the connections between the retina and the brain. No, my sermon is not about sins on skin but secrets about skin.

Dermatologists are fond of pointing out that the skin is the largest and most visible organ in the body. Every recess can be minutely examined, not only with the eyes but with the fingers as well. For those who enjoy looking and touching, the skin is a playground. Our concern is more serious. How much learning, even at the elementary level of description, is possible in a school based on looking and touching?

However accessible the skin, this seeming advantage has not elevated dermatology to a premier position in biologic science. Indeed, this high visibility is, in my view, not a munificence but in fact a misfortune of the first magnitude. The skin is too obvious and too familiar. Just as it is the forbidden which excites the greatest curiosity, it is the hidden, the concealed which stirs the mind. What is inaccessible is challenging; easy seeing is sedating. Knowledge seems to be proportional to the barriers standing in the way of its acquisition. If size and accessibility were advantages, we should know little about those tiny tissues, the adrenal and pituitary, about which we probably know the most.

Dermatologists are wont to utter other propagandistic pronouncements which have the sound of validity but which, like most clichés,

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are not much more than noise. Novitiates are instructed that the skin is a window through which we may peer to obtain clues of systemic disease. This proposition is appealing to those externists who unconsciously wish to be internists or who feel obliged to explain that they are "real" doctors with far more than superficial interests. I personally find the crust as appetizing as the pie and do not need such rationalizations. A parallel exaggeration, equally popular, is the concept of the skin as a mirror, which reflects internal happenings. Here again we perceive the dermatologists' yearning for depth. If we search in the medical literature for the consequences of viewing the skin as a mirror, we find precisely what might be expected. What the dermatologist sees when he looks into the "mirror" is of course his own image. Such reflections confirm his own reality and importance. Instead of describing the skin, writers of this narcissistic bent mainly describe themselves. It does not avail much to think of skin as either a mirror or a window.

The skin is not a powerful reflector; moreover it is too turbid for the eye to penetrate its true depths. Besides, the eye is an organ more worthy of praise from the poets than scientists. In our more exuberant youthful days, Shelley and I wrote that the eye was "the supreme dermatologic instrument." Assertions of this kind confirm Montaigne's observation that it is easier to write luridly than accurately. The fact is, the limitations of the eye are prodigious. It enables us to perceive but a tiny fraction of the electromagnetic spectrum, from 4000 to 8000 A. Helmholtz, the renowned physicist, found numerous engineering faults in the construction of the human eye. Yet the eye is almost our exclusive means of obtaining diagnostic data whether we examine the skin grossly or microscopically. By way of contrast, think of the extraordinary array of exquisitely sensitive and complex testing procedures available to the internist, none of them dependent on the native sensing devices of the examining physician. In an up-to-date hospital one needs only to know how to write in order to place at his service the extraordinary technology of modern physics and chemistry. A mere listing of the routine diagnostic services available occupies a small volume. The dermatologist, of course, is not disbarred from using these tests, and, indeed, this is one of his chief strategies in the work-up of hospitalized skin patients. He can, in this way, establish that he is not merely an externist (an outsider) but an internist (an insider) as well. Although the "window" concept of dermatology is now fashionable, requiring that a profound search be made for evidences of internal involvement, I am of the opinion that only a small fraction, perhaps

not more than 5%, of dermatologic patients will be found to possess internal disturbances which are relevant to their skin diseases. Dermatologists, of course, must be cognizant of the possibility that the patient may have a systemic disorder in which the skin is participating, or indeed, that the patient may concomitantly have some unrelated internal disorder whose detection, cardiac or pulmonary disease, for instance, might be even more important than the skin manifestations. I am, however, proposing that the extensive and expensive work-up more or less as a matter of routine when there is no clue to suggest the possibility of internal disease is an action that is calculated, perhaps unconsciously, to be more helpful to the doctor than the patient. Once the biopsy is taken the average hospital has little more to offer in the way of studies directed to the skin itself with the exception of such elementary procedures as patch testing for contact allergy, photosensitivity and the like. If one can't study the skin in depth, one can at least call on the resources of the internist and request an evaluation of the heart, lungs, kidney, pancreas, bone marrow, blood, adrenals—the diagnostic possibilities are impressive and are very helpful in quieting the physician's anxieties concerning his credentials as a real doctor.

The pressing need is for a quantitative methodology which will portray and reveal the dynamic disturbances in the skin. It is not enough to classify and identify the disorder on the basis of its gross and microscopic attributes. We need to know a great deal more about functional derangements. The changes are often subtle and well below the level detectable by the eye. After a single modest ultraviolet exposure or even after so transient and trivial a reaction as a histamine wheal, the skin may remain abnormal for many months, though there is nothing to suggest this by appearance alone. Of course, one needs sensitive methods to appreciate these subtleties; in the case of ultraviolet light, a suitable reflection meter to demonstrate the persistence of venous congestion revealed by an elevated amount of reduced hemoglobin; after whealing, a means of measuring skin temperature with great accuracy to show that the affected site does not react in quite the normal way when it is again subjected to histamine whealing. The great French dermatologist, Gougerot, wrote a little volume, all but unknown in this country, dealing with the "invisible" or "silent" dermatoses relating to skin diseases which were hidden from view. He clearly appreciated that skin disease may involve more than meets the eye.

Now I shall reveal the meaning of my cryptic title, "Blind Man Dermatology." I believe that the golden age of dermatology is still

before us. To mine the treasure buried in skin disease will require the virtual elimination, though not necessarily the enucleation, of the eye as a diagnostic instrument. *The point of this essay is that dermatology will enter the privileged domain of modern medicine when a blind man will not in the least be compromised in the practice or investigation of skin disease.* I foresee the day when a blind dermatologist will have a good deal more "vision" than the best sighted of us now possess. Our happy blind man will rely on exteroceptive techniques that add immensely to what can be learned by looking. It is the utilization of instrumentation, gadgetry if you will, that will lead us to this kingdom.

What kind of measurements will provide the information we avidly desire? Galileo said, "Measure what you can measure, count what you can count, if there is no measurement, invent one." To specify measurements that will teach us more about the behavior of normal and abnormal skin requires an understanding of the complex nature of skin. It is in fact not a homogeneous organ; it varies from region to region and from the surface downward. It is not a simple tissue but a compound one with adnexal specializations such as sweat glands, hair, and sebaceous glands. It is divided into horizontal compartments, the epidermis, dermis, and subcutaneous tissues, each with its unique and different functions. It contains nerves, vessels, lymphatics, all in complex relationships. It is, in fact, not an organ but a series of organs, not a species but a genus.

A quantitative analysis of these diverse functions is entirely within reach of modern methodology. Each structure has attributes which can be characterized dynamically, that is, in terms of the function subserved. It would be tedious to do more than merely list some of the tools and methods which might provide a "profile" of the skin in health and disease. To name some of the more obvious activities which are susceptible to measurement:

(1) Skin blood flow, by determining clearance of a freely diffusable ion such as radio-sodium.

(2) Lymphatic flow by monitoring the rate of disappearance of radio-iodinated albumin.

(3) Epidermal replacement time by thymidine labelling of DNA in the nuclei of the germinative layer.

(4) Skin permeability by measurement of water diffusion rate utilizing electrical hygrometry; alternatively, one can determine the penetration and absorption of radio-active substances from the skin

surface by a variety of techniques employing gas flow chambers, scintillation counters, etc.

(5) Reparative activity after injuries ranging from simple Scotch Tape removal of the horny layer to full thickness excisions.

(6) Quantitative responses to physiologic and pharmacologic agents which elicit characteristic responses such as sweating, whealing, blanching, and erythema.

(7) Responses to allergenic and irritant stresses; *viz.* blistering produced by cantharidin, pustules to croton oil, necrosis after acids and alkalis, erythema to solvents, etc.

(8) Thermal, mechanical and radiation responses.

(9) Biochemical and histochemical analysis of scales, epidermis, dermis, etc.

(10) Physical measurements of hygroscopicity of the horny layer, "porosity" of the dermis, elasticity, thermal contraction, conductance, and impedance.

To these ten can be added, in logarithmic proportions according to one's lust for measurement, other items whose characteristics can be assessed without the use of the human eye.

I hope to be alive when the first blind medical graduate applies for residency training in dermatology; if he is as confident as I now am that sightlessness will be an inconvenience rather than a insuperable disability, the golden age will have begun.

New Members

Alperin, George, 49 Strawberry Hill Ct., Stamford, Conn. 06902
Anderson, Harold N., 266 Glen Ave., Glen Rock, N. J. 07452
Armstrong, Robert A., 549 W. Washington Ave., Chicago, Ill. 60606
Barba, Theodore L., 80-09 Thirty-fifth Ave., Jackson Heights, N. Y. 11372
Breier, Robert, 2047 Nostrand Ave., Brooklyn, N. Y. 11210
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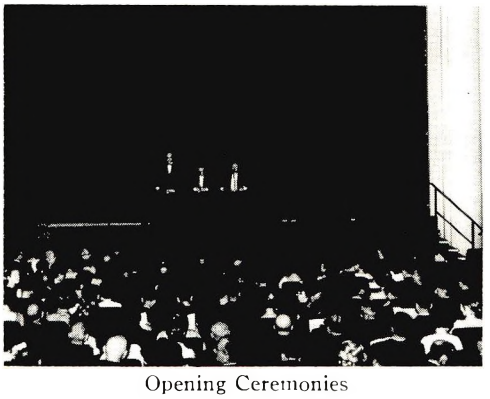
Williams, Richard G., Jr., 150 Causeway St., Boston, Mass. 02114
Wood, James W., 340 W. 86th St., New York, N. Y. 10024

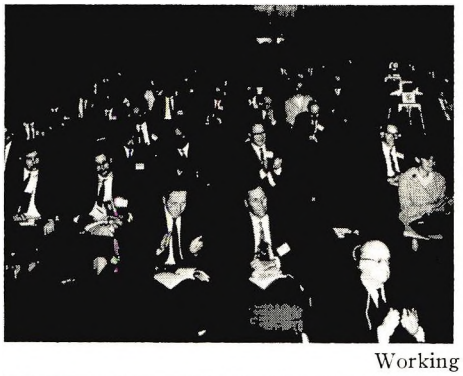
The Fourth Congress of Cosmetic Chemistry

The International Federation of Societies of Cosmetic Chemists, which comprises 14 national societies, held its Fourth Congress of Cosmetic Chemistry in Paris from June 27 to July 2.

The Congress was officially opened by Mr. A. E. Desperrois, President of the International Federation of Societies of Cosmetic Chemists, Mr. Charles de Chambrun, State Secretary for Foreign Trade, and by Mr. Charles Zviak, President of the French Society of Cosmetology, who noted, "Scientific and technical contacts, discovery of what men are thinking, their work—these are the reasons for International Congresses; these are the reasons for the Congress that we are going to conduct."



Opening Ceremonies



Working Sessions

Ballet

Bateau Mouche

During the Congress hundreds of cosmetic scientists from many countries and from many disciplines listened to the presentation and subsequent discussion of 27 original papers. The conferees also had a chance to exchange new ideas during more informal sessions and finally had an opportunity to become better acquainted during nonworking gatherings. Thus, the primary aims of the biannual congress of the I.F.S.C.C. were successfully met.

Obituary

Mr. Herman J. Amsterdam, Vice-President of International Flavors & Fragrances, Inc., died in Brooklyn on April 29, 1966. Mr. Amsterdam was born in New York City in 1905, graduated from George Washington University, and received his Masters' Degree from Columbia University in 1929. He taught at the Columbia University College of Pharmacy for 18 years. Since 1944 he had been associated with International Flavors & Fragrances. He was a trustee of the College of Pharmacy and served in its alumni association. He was a member of Delta Sigma Theta and Rho Pi Phi fraternities, of the AAAS, the ACS, the APhA, and of the SCC.

"Jerry" was President of the Society of Cosmetic Chemists during 1960 and had been active on many of its committees. Jerry's passing is a serious loss to the Society, and he will be remembered in years to come for his faithful service to the SOCIETY OF COSMETIC CHEMISTS.

J. Soc. Cosmetic Chemists, **17**, 513–524 (1966)

Studies on the Substantivity of Collagen-Derived Polypeptides to Human Hair

S. A. KARJALA, Ph.D., J. E. WILLIAMSON, B. S., and A. KARLER, Ph.D.*

Presented December 1, 1965, New York City

Synopsis—The sorption of collagen-derived peptides to human hair has been conclusively demonstrated. This proof of sorption can be applied only to peptides derived from collagen, since the procedure is based on the quantitative determination of a unique amino acid, hydroxyproline, which is present in large amounts only in collagen and in peptides derived from collagen. The sorption of collagen-derived peptides in general increases with increase in damage to the hair, with increase in concentration of peptides used, and with decrease in the molecular size of the peptides.

Introduction

During the past few years, considerable work has been done on the analysis of virgin hair and of hair modified in various ways. The first portion of a report by Freytag (1) on the effect of swelling agents on hair lists about 70 references on mechano-chemical, physico-chemical, and chemical procedures for the investigation of hair.

In the field of hair modification or conditioning, however, there are areas in which changes occur and must be evaluated on a subjective basis since objective means for measuring the modification are lacking. One of these areas is the problem of substantivity of additives to hair. In particular, this refers to the substantivity of proteins and polypeptides

* Wilson & Co., Inc., Chicago, Ill. 60609.

to hair. For the purposes of this investigation, substantivity is defined as the capacity of a substance to be sorbed to a surface. If sorption is only on the surface, it is referred to as adsorption, while if the substance penetrates the surface, the phenomenon is referred to as absorption. The general term sorption, covers both effects. In cases of true sorption a substantial portion of the substance is retained by the surface, with little or none of the substance being detectable by chemical or physical means in the rinse water when rinsings are carried out with a solvent in which the substance is highly soluble. This definition of sorption does not include precipitation reactions such as that described in a patent (2) in which a protein, insoluble in water at its iso-electric point, is dissolved in alkaline solution and then precipitated on the hair by acidification.

The use of proteins in cosmetics for hair and other applications has been reviewed by deNavarre (3) and Burnett (4), but thus far no data have appeared which demonstrate conclusively that the proteins, or polypeptides derived from them by chemical or enzymatic hydrolysis, are in fact substantive to hair. Herd and Marriott (5) have pointed out that, on the basis of radiochemical studies, the sorption by hair of the amino acids methionine and tyrosine from shampoos can be demonstrated, but, although it is suggestive, it is not proof that polypeptides will be sorbed in similar fashion.

Nelson and Stewart (6) studied the adsorption of radioactive sodium *N*-lauroyl and *N*-palmitoyl sarcosines on proteins, including casein, gelatin discs, and human hair. Considerable variance was found in human hair, probably due to variance in the physical and chemical properties of the hair. They report that 0.06–1.88% of *N*-lauroyl sarcosine and 1–2% of *N*-palmitoyl sarcosine were adsorbed by different types of human hair.

Methods and Results

A comparison of the amino acid composition of the various proteins which have been used as hair modifiers, such as hair (and wool) hydrolysates, milk, blood, proteins, egg albumin, etc., with that of human hair indicates that they all contain the same amino acids, differing only in the relative amounts of each. However, when collagen-derived polypeptides are used, a distinct difference arises, due to the presence in collagen of a unique amino acid, hydroxyproline (at a level of approximately 10%). All other normal proteins contain little, if any, of this amino acid. Although keratin is formed upon skin areas high in col-

lagen, and possibly from a collagen precursor, Flesch (7) indicates that during keratinization the only definitely established changes are a disappearance of hydroxyproline and an inconstant and variable rise in cystine content. Keratin, on the basis of numerous analyses, has been shown to be free of hydroxyproline.

Thus, the qualitative demonstration of the presence of hydroxyproline in hydrolysates of hair strands treated with a solution containing collagen-derived polypeptides and thoroughly rinsed in an appropriate solvent would be definite proof that the polypeptide is indeed substantive to hair.

Although procedures for measuring hydroxyproline involving oxidation to pyrrole and developing a color by reaction of the pyrrole with *p*-dimethylaminobenzaldehyde have been known for thirty years, it was not until 1950 that Neuman and Logan (8) developed a reliable analytical procedure. The method was improved by Prockop and Udenfriend (9) and the specificity increased by oxidizing with chloramine-T instead of hydrogen peroxide, by removing some interfering materials by toluene extraction after oxidation, and by extracting the pyrrole into toluene after the heating period (during which the pyrrole carboxylic acids formed in the oxidation step are converted by decarboxylation into pyrrole). The color reaction is then run in toluene solution. Udenfriend and co-workers in 1964 (10) discovered a collagen-like protein in plasma and also detected an interfering substance which gave a color by this analytical procedure. The interfering material was retained on a cation-exchange column from 1*N* HCl but was eluted with 3*N* HCl, whereas the hydroxyproline was eluted with 1*N* HCl. The shade developed by the interfering material was somewhat different from that with hydroxyproline, and the absorption maximum was at a different wavelength.

Comparative radiochemical procedures (10) have shown that all of the color produced in the reaction from material capable of being eluted from the cation-exchange columns with 1*N* HCl is attributed to hydroxyproline. This color reaction thus appears to be specific for this amino acid. Repeated analyses of individual strands of hair by the above method, as described below, gave consistently nil for hydroxyproline.

Most of the work to be reported was done on virgin brown DeMeo Blue String* human hair. Individual strands or groups of strands

* DeMeo Co., 135 Fifth Avenue, New York, N. Y. 10010.

weighing approximately 1–10 mg were coiled in loose circles of about 1 cm diameter, so the strands could be handled more readily and weighed on a microbalance. In all cases, the weight changes as a result of treatment were determined, using a Cahn Gram Electrobalance.* After the coils were prepared and prior to any treatment, the strands were washed by immersion in a nonionic detergent, Triton X-100,† rinsed thoroughly with distilled water, dried in an atmosphere of 52% relative humidity, weighed, and processed.

Standard solutions of hydroxyproline and of collagen-derived polypeptides and the hair strands after various treatments were hydrolyzed by the method of Udenfriend *et al.* (10), together with suitable blanks and control hair strands, with several slight modifications in procedure. The samples, in 1 ml of water, were treated with 2 ml of saturated $Ba(OH)_2$ and autoclaved at 15 lb pressure for 16–18 hours. It was found later that comparable results could be obtained in much shorter time by use of the Castle portable autoclave,‡ operating at 25 lb pressure for two hours. This method of hydrolysis was used in all subsequent work. The cooled tubes were treated with $6N$ H_2SO_4 until colorless to phenolphthalein and then back-titrated with diluted KOH to a faint pink color. The $BaSO_4$ precipitates did not interfere with the analysis. The tubes were analyzed by Procedure I of Prockop and Udenfriend (9) without separating the $BaSO_4$, after adjustment of the pH to 8 by treatment with 2 ml of pyrophosphate buffer (0.2M solution, pH 8.0) and 1.0 ml of 0.02M chloramine-T solution. After standing for 20 minutes, oxidation was stopped by the addition of 1.0 ml of 3.6M sodium thiosulfate solution, and the solutions were saturated with KCl by addition of the dry salt. The samples were then treated with 5 ml of toluene, agitated well with a Vortex mixer and centrifuged if necessary. The toluene was drawn off and discarded to eliminate certain toluene-soluble impurities which yield colors with Ehrlich's reagent. The tubes were then capped and the pyrrole carboxylic acids converted to pyrrole by heating in a boiling water bath for 25 minutes. After the tubes were cooled, 5.0 ml portions of toluene were added to each tube, and the solutions were mixed well on a Vortex mixer, centrifuged if necessary; finally 3.5 ml aliquots of toluene were drawn from each tube. The toluene solutions were then treated with 1.5 ml of Ehrlich's reagent in absolute alcohol, prepared as described in Reference 9. The color values

* Cahn Instrument Co., Paramount, Calif.

† A product of Rohm and Haas, Philadelphia, Pa.

‡ Ritter Company, Inc., Rochester, N. Y.

were read after 15 minutes at 560 mμ on a Beckman Spectrophotometer and corrected to the initial 5 ml volume of toluene used for extraction.

Control analyses gave hydroxyproline values similar to those obtained by alkaline hydrolysis. In these the collagen-derived polypeptides were treated with 6*N* HCl in heavy walled glass tubes; frozen in dry ice/alcohol and sealed in a vacuum; autoclaved at 15 lb pressure for 16–18 hours; cooled and evaporated to dryness; and analyzed by the above procedure. Since alkaline hydrolysis is much easier to run when large numbers of analyses must be made, this procedure was used

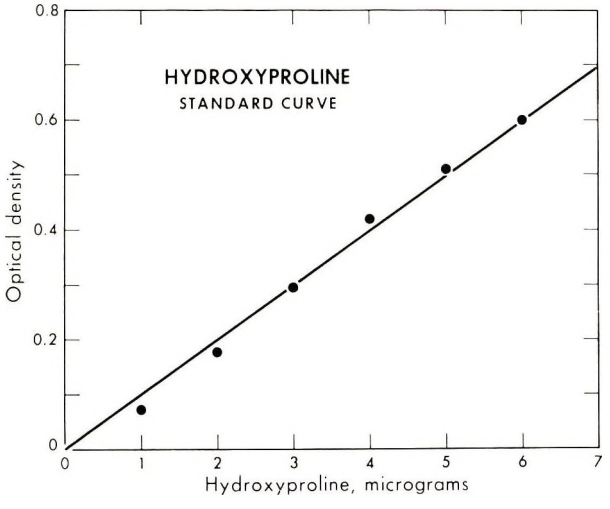


Figure 1. Standard curve for hydroxyproline assay using Ehrlich's reagent (at 560 mμ)

in all cases. The standard curve obtained on standard hydroxyproline samples closely paralleled the reported one (9). This curve is shown in Fig. 1.

Several runs of collagen-derived polypeptides were analyzed by absorption on ion-exchange columns from 1*N* HCl and elution with 1*N* and 3*N* HCl. No indication was found of any interfering substances absorbing at the wavelength reported for the nonhydroxyproline component in the fraction eluted in 3*N* HCl.

The hydroxyproline content of the peptides shows a slight drop with decrease in molecular weight of the peptide from 11.3% for 75 Bloom gelatin, 11.1% for solubilized gelatin, to 10.5, 9.8 and 9.8% respectively for cosmetic polypeptides of formol nitrogen values of 9, 12.6, and 17, as shown in Fig. 2. This suggests that there may be a

selective loss of hydroxyproline as the molecular size is decreased. Formol nitrogen values are a rough measure of the molecular size of the peptides, since these values represent the percentage of nitrogen present as free amino groups relative to the total nitrogen. In the quantitative determination of the amount of collagen-derived peptide sorbed, in which the hydroxyproline and not the peptide is measured, it becomes necessary to know the history of the peptide sorbed and to analyze a sample for its hydroxyproline content. In the case of the peptides studied, a rough average of 10% hydroxyproline was usually taken.

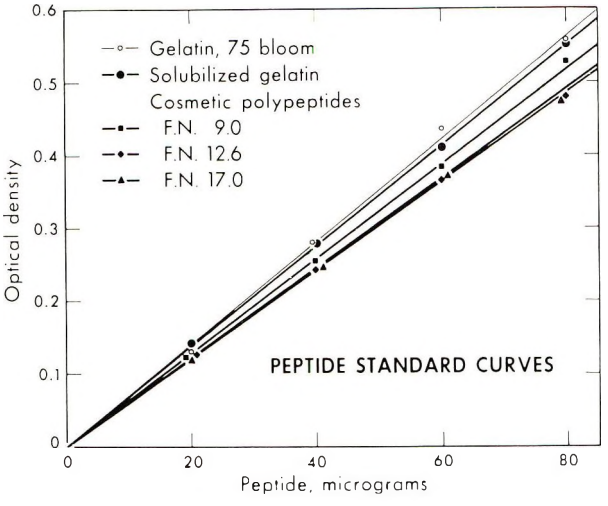


Figure 2. Standard curves for the collagen-derived peptides used in this investigation. The F.N. values refer to the formol *N* value of the peptides

The wide variance in the properties of hair, as pointed out by Nelson and Stewart (6), precludes the absolute comparison of sorption under different conditions by separate strands of hair. However, in general, it can be stated that sorption increases with increase in concentration of the peptide and with a reduction in molecular size of the peptide. Sorption also increases with increase in damage to hair. Less peptide is sorbed on virgin hair, more is sorbed on bleached hair, and still larger amounts are sorbed on hair subjected to cold-wave treatments, especially if the peptide is present in both the thioglycolate and bromate solutions. Repeated simulation of cold-wave treatments appears to increase sorption still more, probably as a result of increased damage to the hair under these conditions.

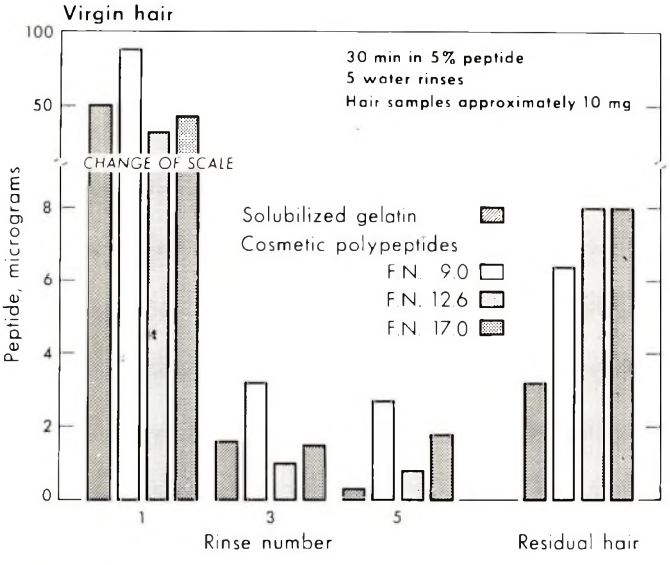


Figure 3. Sorption of peptides (5% in water) on virgin hair

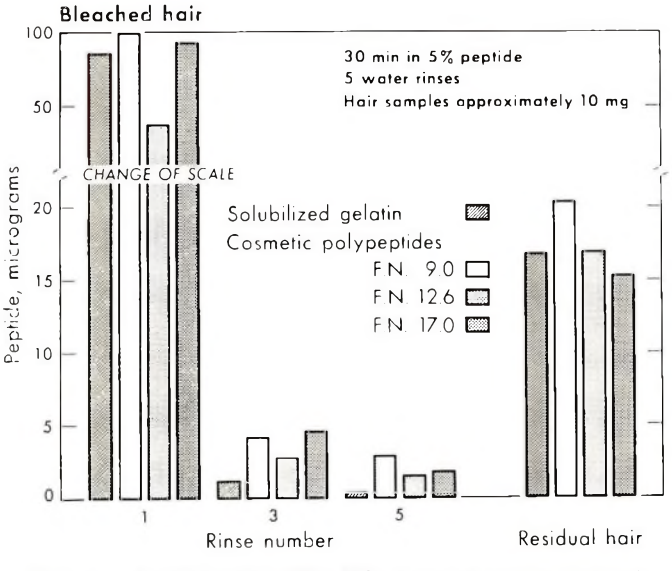


Figure 4. Sorption of peptides (5% in water) on bleached hair

All samples of hair were first subjected to a preliminary rinse in a nonionic detergent, Triton X-100 in 1% concentration. The strands were then rinsed thoroughly with distilled water, blotted on cleansing tissue, and dried in a cabinet maintained at 52% relative humidity prior to weighing. Bleaching was carried out at room temperature for one hour with 6% hydrogen peroxide solution containing 50 volumes of peroxide solution and 1 volume of concentrated ammonia followed by rinsing with water. Peptide and thioglycolate (6%, pH 9.4) treatments and combined treatments with the two reagents were conducted for 30 minutes, while the bromate oxidation procedure was limited to 5 minutes. The volume/weight ratio when no thioglycolate was used was approximately 500 to 1 (5 ml bleach solution for 10 mg hair samples). When thioglycolate was used, the hair samples weighed approximately 1 mg; in these experiments the volume/weight ratio of both bleach and thioglycolate solutions was approximately 5000 to 1. For the analysis of the strands for peptide sorption, the strand was removed from the particular treatment solution, blotted on cleansing tissue, and immersed in 2 ml of distilled water for 5 minutes with occasional agitation, after which it was removed, blotted again, and placed in a second 2 ml portion of water. This process was generally repeated five times for hair strands which had been in solutions with a peptide concentration of 10% or less and ten times for those in peptide concentrations over 10%. The rinsings in each run were saved, and the first, third and fifth rinses, or the first, fifth, and tenth rinses in the higher peptide concentrations, were analyzed for hydroxyproline, together with the analysis of the residual hair after the rinsing procedure.

Studies on the sorption of peptides on virgin and on bleached hair were made on loops of combined strands with a total weight of approximately 10 mg, but peptide sorption in the case of thioglycolate treated hair was easily demonstrable on single strands weighing approximately 1 mg. The results obtained are illustrated in the following figures.

Figures 3 through 8 are bar graphs showing the amount of peptide in the rinse waters, as calculated from the hydroxyproline found, as well as the amount of peptide remaining on the hair. The vertical scales are different for each graph, in order to emphasize the amounts of collagen-derived protein remaining on the residual hair as contrasted with the amount found in the total volume of each specific rinse solution.

In the case of virgin and bleached hair not treated with cold-wave solution, the results are reported as μg of peptide sorbed per 10 mg sample of hair, as shown on Figs. 3 and 4. In the case of more highly damaged

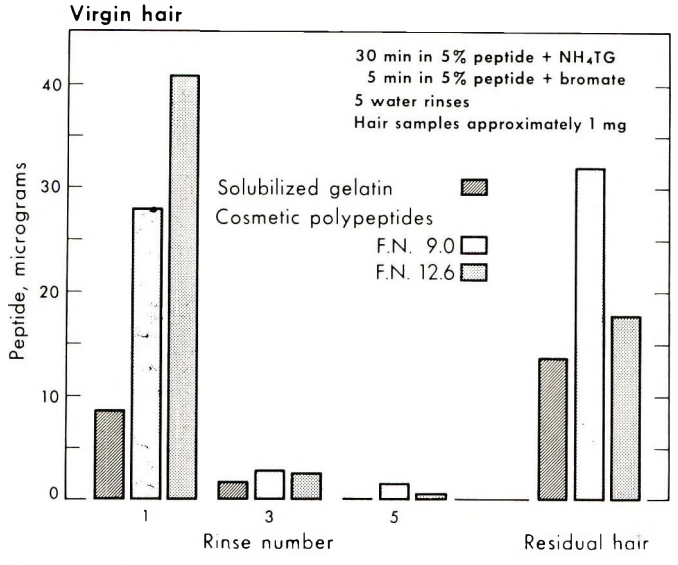


Figure 5. Sorption of peptides (5% in cold waving chemicals) on virgin hair

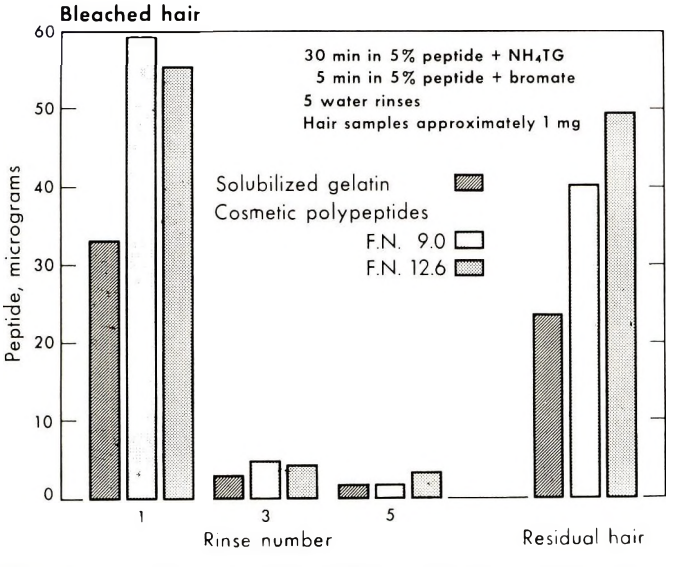


Figure 6. Sorption of peptides (5% in cold waving chemicals) on bleached hair

hair, a single strand weighing approximately 1 mg was used, and the peptide sorbed was calculated on this basis.

Figure 3 shows the sorption of peptide on virgin hair in 30 minutes from a 5% peptide solution, while Fig. 4 depicts sorption on hair bleached for one hour in 6% hydrogen peroxide. On each of the graphs, each set of four similarly marked bars represents a single experiment, using one of the peptides listed and one group of hair strands (or individual strands), with the first three bars showing the amount of peptide released

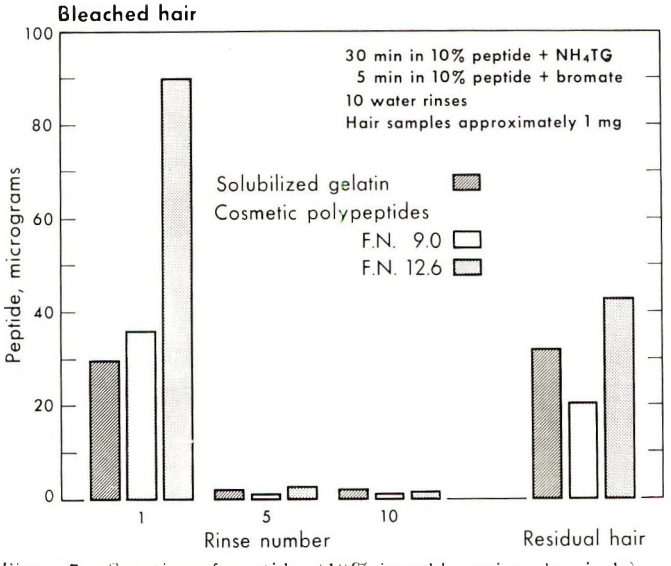


Figure 7. Sorption of peptides (10% in cold waving chemicals) on bleached hair

from the hair in the rinsing series while the last bar of each experiment demonstrates the amount of peptide remaining on the hair after the rinsing procedure.

As can be seen, approximately 3–8 μg of the different peptides are found sorbed on 10 mg of the virgin hair, and 15 to 20 μg are sorbed to 10 mg of the bleached hair. It is clear that even after five rinses, under conditions which give a more effective rinse than a simple running water procedure, appreciable amounts of peptides remain sorbed to the hair strands.

Figure 5, which shows the effect of 5% peptides in the presence of both ammonium thioglycolate and sodium bromate, demonstrates clearly how much more peptide is sorbed when the hair is damaged in this way; the sorption reaches 10–30 μg per mg of hair. The third and fifth rinses are essentially free of peptide. On bleached hair treated in

the same way (Fig. 6), the sorption of peptide is practically doubled, with very little peptide being demonstrable in the rinse water.

Figures 7 and 8 present results when 1 mg samples of bleached hair were treated with 10 and 20% peptide, and then rinsed ten times as described previously. The peptide concentration reaches a low value around the fifth rinse and appears to remain at this level. After ten rinsings,

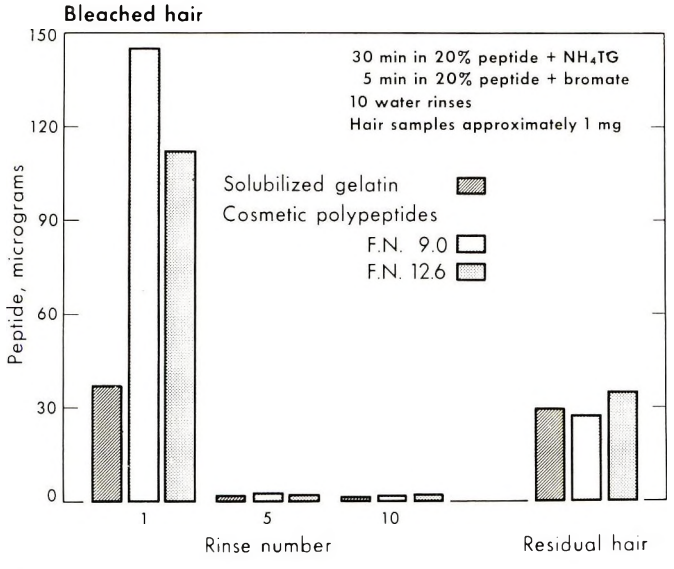


Figure 8. Sorption of peptides (20% in cold waving chemicals) on bleached hair

the peptide level of the hair is generally equal to or slightly less than the amount left on after five rinsings after treatment with 5% peptide. It is certainly true that with a sufficiently large number of rinses essentially all of the peptide could possibly be removed in time. This concept is now under investigation, namely, to determine whether a point can be reached at which no further traces of peptide can be detected in the rinse waters, while definite amounts can still be found in the hair.

Discussion

Some of the graphs, for example, Figs. 5 and 7, deviate from the generalization proposed earlier that the lower the molecular size of the peptide the greater the sorption. This can be explained only in terms of the wide variations in properties of individual hair strands.

Weight differences as a result of sorption of peptides on virgin or bleached hair are generally too small to register even on a sensitive

microbalance. These differences are detectable on thioglycolate treated strands, but the inherent variability of individual hair strands makes it difficult to obtain consistent quantitative results. This problem is being studied intensively at present, and the data obtained will be presented in a future paper. It is also planned to study the physical properties of human hair, particularly its tensile strength after treatment with reagents containing peptides, and the electrical properties of hair to determine how these properties change after hair modification.

This method of demonstrating peptide substantivity is a direct method but is applicable only to peptides derived from collagen. Another useable direct method would be: to obtain randomly-labelled radioactive skin from an animal; carry a segment of the skin through the same general hydrolysis treatment to reduce it to the peptide stage; dilute it with nonradioactive peptides; and measure the amount sorbed by the normal procedures used in radioactivity studies.

An indirect means for measuring substantivity, and one upon which some preliminary work has begun, is the measurement of dye adsorption. Differences in amounts of dye adsorbed could be related to differences in the nature of the hair surface after peptide treatment. This method would be applicable to proteins and peptides other than those derived from collagen.

It might be pointed out that, although in general the sorption of peptides increases with decreasing molecular size of the peptide, this does not necessarily mean that the lower peptides will be preferable in cosmetic formulations to the higher peptides. This preference must be based on a purely subjective evaluation during actual use of formulations containing the different peptides.

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Temperature Dependence of the Mechanical Properties of Human Hair in Relation to Structure

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Presented December 1, 1965, New York City

Synopsis—The mechanical properties in tension of human hair were examined as a function of temperature in a buffer solution at pH 7.0 both in the presence and absence of a sulfhydryl group blocking agent. Untreated hair as well as hair that had been partially reduced to increase the free SH content was investigated. It was found that the elastic modulus, post-yield modulus, and fiber strength decrease with increasing temperature while extensibility increased. The turnover point between the yield and post-yield regions was observed to undergo a transition at a characteristic temperature of 85.5°C. This transition temperature was decreased to 66.0°C for the partially reduced hair. The presence of the SH-blocking agent tended to decrease extensibility and increase the post-yield modulus but had no effect on the elastic modulus and strength. The results are explained in terms of a sulfhydryl-disulfide interchange mechanism whereby stressed disulfide bonds are relieved and transformed into stress free positions. The transition temperature is associated with the stability of the disulfide bond and the onset of the SH catalyzed disulfide interchange.

Introduction

Human hair is constantly subjected to a variety of chemical actions and mechanical forces which may have significant effects on its structure and properties. These chemical actions and mechanical forces are operative even under normal daily conditions involved in hair grooming and environmental exposure. The chemical actions may result in deep-seated alterations in the hair's molecular structure or in

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its extremely complex supermolecular organization. The mechanical forces result in permanent or temporary deformations and may also manifest themselves in various forms of hair damage, particularly in the scalar surface structure.

The chemistry of human hair was recently discussed by Whewell (1) who related the setting characteristics of hair to its chemical structure. The supermolecular or fine structure of animal fibers in general was recently summarized by Rebenfeld (2) and reviewed more extensively by Lundgren and Ward (3). In brief, keratin fibers are visualized as being composed of high molecular weight polypeptide chains which are intramolecularly stabilized into α-helices. The polypeptide chains are composed of some 21 amino acids of which the disulfide-containing amino acid, cystine, is certainly one of the most important. The α-helices are further wound around each other in the form of a multi-stranded rope which is referred to as a protofibril. These elements of structure are aggregated into microfibrils, which are considered to be the key structural elements in keratin fibers. The protofibrils are arrayed in each microfibril in a characteristic "9 + 2" arrangement wherein 9 protofibrils are disposed in the periphery of each microfibril and two protofibrils are in the center. The microfibrils are considered to be composed of fully crystalline α-helices; their structure is stabilized by a variety of intramolecular and intermolecular forces, including hydrogen bonds, van der Waals forces, dipolar interactions, and hydrophobic bonds. The microfibrils are embedded in a matrix which is amorphous and presumably composed of randomly coiled polypeptide chains. It is felt that a large proportion of the sulfur-containing proteins are in the matrix, which is therefore highly cross-linked through the amino acid cystine. The microfibrils, which may be further associated into macro-fibrils, are the actual building blocks of which the ortho- and para-cortical cells are composed.

The mechanical properties of a fiber or a hair are most easily determined in axial tension, in view of its geometric shape. The stress-strain curve of any material is a graphical record of the stress which develops in the material as it is deformed under closely specified experimental conditions. The shape of the stress-strain curve frequently provides a ready means of predicting the behavior of the material under use conditions and of interpreting the structure of the material in relation to its mechanical properties.

When a keratin fiber is stretched in water the stress-strain curve reveals three distinctly different regions, as shown in Fig. 1. In the

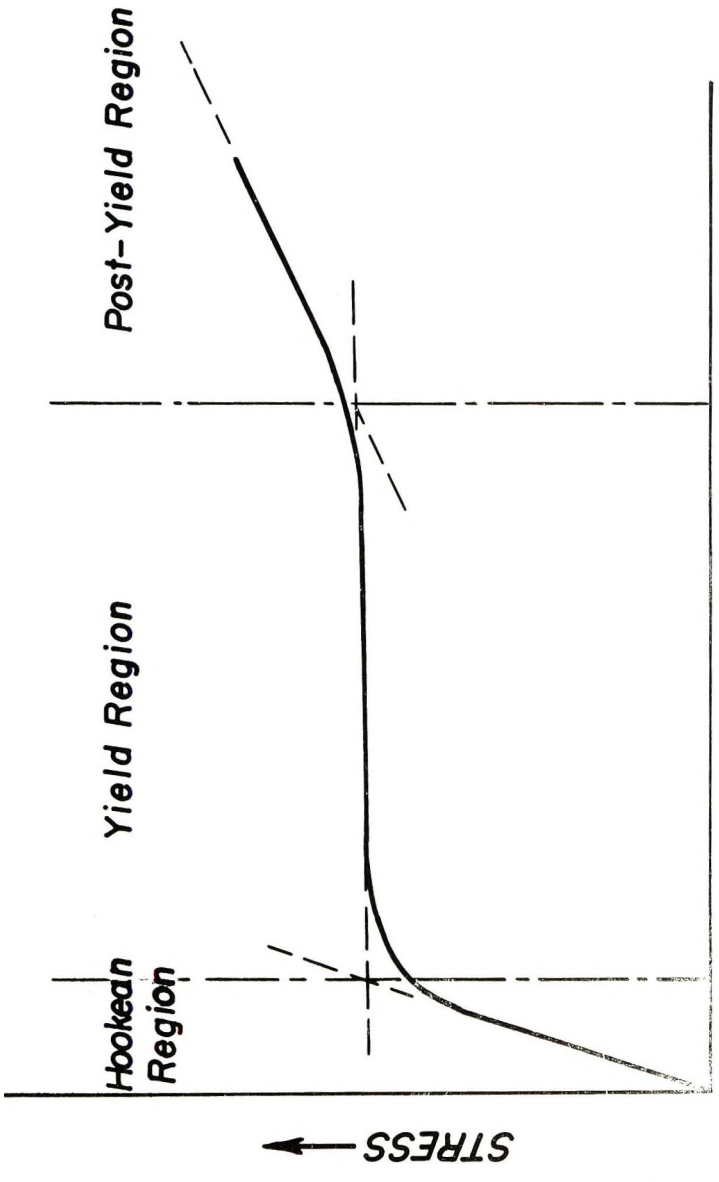

Figure 1. Schematic stress-strain curve of a single human hair

Hookean region the stress is approximately linearly related to the fiber strain, reflecting a bond angle deformation in the microfibrils. At a certain strain, usually 1–2%, the fiber yields, and the α-helices in the microfibrils begin to unfold (4) into a sheet-like β structure. Before the α-β transformation, which would cause a fiber extension of over 100%, is completed the stress suddenly increases sharply, and the fiber breaks

at an extension of approximately 50%. Considerable disagreement exists about the structural and molecular interpretation of the post-yield region, but it is generally agreed that this region of the stress-strain curve is an indication of the involvement of disulfide cross-links in the deformation process (5, 6).

It has been shown in the case of wool fibers that a chemical modification involving a reduction of some of the disulfide crosslinks has a significant effect on mechanical properties, as revealed by the stress-strain curve (7). These effects on mechanical properties are particularly evident at higher extensions and must be attributed, at least in part, to the free SH groups arising from the partial reduction of the disulfide bonds rather than to the attendant decrease in cross-link density. If the free SH groups are blocked by reaction with a suitable reagent, such as methyl iodide or N-ethyl maleimide (NEMI), the properties are to a large extent recovered. Such observations have been used to indicate the importance of a sulfhydryl-disulfide interchange mechanism whereby stressed disulfide bonds react with free SH groups to assume stress-free positions. The importance of the sulfhydryl-disulfide interchange has been shown in relation to keratin fiber mechanical properties, stress relaxation, settability, and supercontraction.

The temperature dependence of the mechanical properties of wool fibers has recently been discussed by Weigmann *et al.* (7) in relation to the sulfhydryl-disulfide interchange. These workers have shown that the elastic and post-yield moduli decrease with increasing temperature and that partial reduction of disulfide bonds has an effect not only on the shape of the stress-strain curve but also on the nature of the temperature dependence. A transition temperature which was strongly dependent upon the free SH content was observed and was interpreted as indicating the onset of a chemical flow process in the matrix.

The purpose of this paper is to present some new data on the temperature dependence of the mechanical properties of human hair and to indicate the importance of the sulfhydryl-disulfide interchange mechanism in relation to the deformation characteristics of hair.

Experimental

Single hairs, randomly chosen from a solvent-extracted sample, were mounted on tabs at a gauge length of 2 in; and the cross-sectional area of each specimen was determined by means of a vibroscope (8) at 21 °C and 65% R.H. The hairs were then placed in a jacketed cell which was

heated by circulating oil from an external bath and extended to break on an Instron tensile tester at a rate of extension of 50% per minute. The stress-strain curves were determined in a phosphate buffer solution of pH 7.0 and, in separate experiments, also in the presence of NEMI (1.3×10^{-2} N). A partial reduction of the disulfide bonds was achieved by reaction with sodium thioglycolate solution, as previously described (9). The mechanical properties of the reduced hair were determined in the same manner as the untreated, both in the presence and absence of NEMI in the buffer solution at pH 7.0. For comparison purposes the mechanical properties of a fine, highly crimped Merino wool, subsequently referred to as IWS Wool C, were also determined under the same conditions. Each experimental datum in the figures and tables is the mean of five determinations. The cystine content (10) and the sulfhydryl content (11) were determined by previously described experimental methods.

Results and Discussion

The cystine and sulfhydryl contents of the untreated and reduced human hair and of the untreated wool sample are presented in Table I.

Table I
Chemical Properties

	Cystine Content (%)	Sulfhydryl Content (μmole/g)
Human hair		
Untreated	17.6	10.1
Reduced	17.0[a]	63.0
IWS wool C	12.3	14.1

[a] Calculated.

The human hair sample has a higher cystine content than the IWS Wool C, indicating a higher cross-link density which is consistent with previous experiments on this sample that characterized it to be essentially an all para-cortex hair (12). The wool sample is known to be bilaterally asymmetric, containing approximately equal quantities of ortho- and para-cortex. The sulfhydryl contents of the two samples are approximately equal, and it should be noted that less than 1% of the total sulfur in these keratin samples is in the form of free SH groups. A low level of reduction of the human hair was achieved, as indicated by the small decrease in cystine content, although the SH content increased

by a factor of six. One may, therefore, conclude that the cross-link density of the reduced human hair was not significantly decreased; changes in mechanical properties must, therefore, be attributed largely to the increase in the free SH content.

The following parameters were used to characterize the various regions of the stress-stain curve shown in Fig. 1: Elastic modulus or initial stiffness obtained from the slope of the Hookean region, the modulus of the post-yield region, the extension to the post-yield region

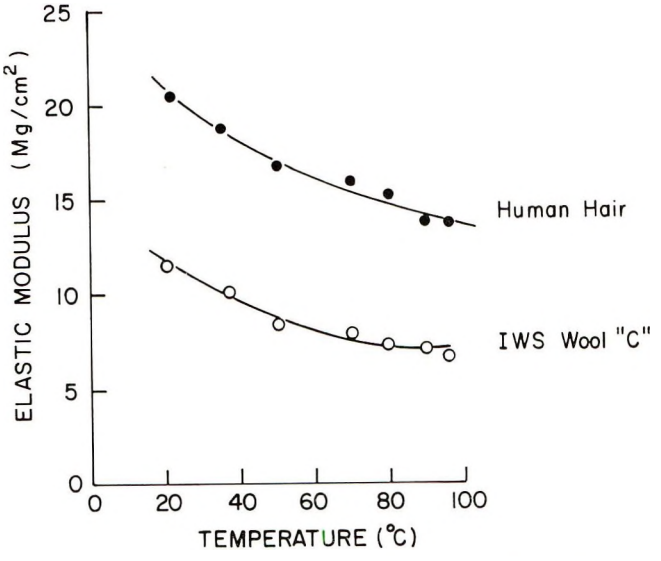

Figure 2. Tensile stiffness as measured by the elastic modulus of human hair and wool fibers as a function of temperature. Average values over all conditions

taken as the turnover point between the yield and post-yield regions, the strength of the hair taken as the stress at the point of rupture, and finally the total extensibility of the hair at the break.

In Fig. 2 are shown the initial stiffness or elastic modulus values for the human hair and the wool fibers as a function of temperature. The values shown are averaged over the several experimental conditions since neither the presence of NEMI in the pH 7.0 buffer solution nor the partial reduction of the human hair had a significant effect on the elastic modulus. The data for the human hair are shown in Table II. The elastic modulus decreases with increasing temperature for both fiber types, and it should be noted that the modulus of the wool fibers at any given temperature is lower than that of human hair, which is consistent

with the lower cystine content and therefore the lower cross-link density of the wool. Since the initial Hookean region of the stress-strain curve is associated with bond angle deformation and polypeptide chain stretching processes, it is to be expected that an increase in temperature would weaken the intermolecular attractive forces, resulting in a decreased modulus.

Table II

Elastic Modulus (kg $\times$ 10^{-3}/cm^2) of Human Hair

	Untreated		Reduced	
Temperature	pH 7.0	NEMI	pH 7.0	NEMI
21°C	21.2	20.8	20.6	19.4
35	18.0	19.8	19.6	18.0
50	17.0	16.4	17.0	16.5
70	16.7	16.2	16.2	15.1
80	15.5	15.7	15.5	14.9
90	13.9	14.6	13.0	13.8
96	13.8	15.6	12.8	13.1
Pooled 95% c.l.	2.6	1.8	1.3	1.1

Table III

Post-Yield Modulus (kg $\times$ 10^{-3}/cm^2) of Human Hair

	Untreated		Reduced	
Temperature	pH 7.0	NEMI	pH 7.0	NEMI
21°C	5.25	5.72	4.14	4.07
35	4.90	5.22	3.82	3.82
50	4.53	4.37	2.94	3.79
70	3.63	4.24	2.03	3.38
80	2.74	3.67	1.57	3.23
90	1.57	2.91	1.47	2.62
96	1.55	2.28	1.32	2.20
Pooled 95% c.l.	0.56	0.46	0.23	0.28

The post-yield modulus of the untreated human hair is shown in Fig. 3 as a function of temperature. This modulus also decreases with increasing temperature to extremely low values at the higher temperatures. Blocking of the free SH groups in the untreated hair by performing the experiment in the presence of NEMI increases the post-yield modulus at all temperatures, although the nature of the temperature-dependence remains unchanged. This clearly indicates that the post-yield region of the stress-strain curve involves the stretching of high sulfur-containing domains in the hair, presumably the matrix,

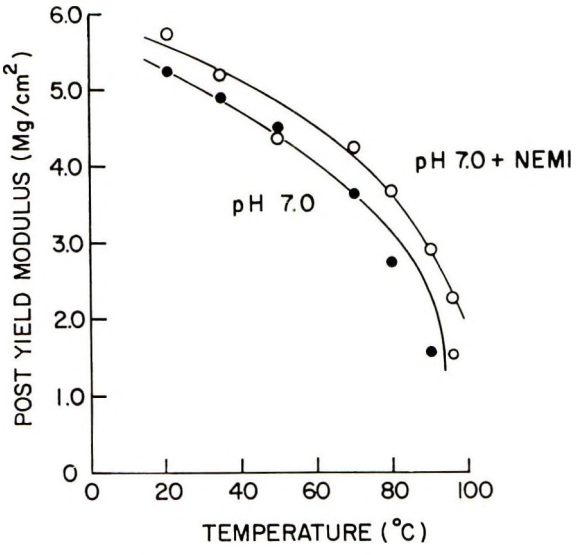

Figure 3. Post-yield modulus of human hair as a function of temperature

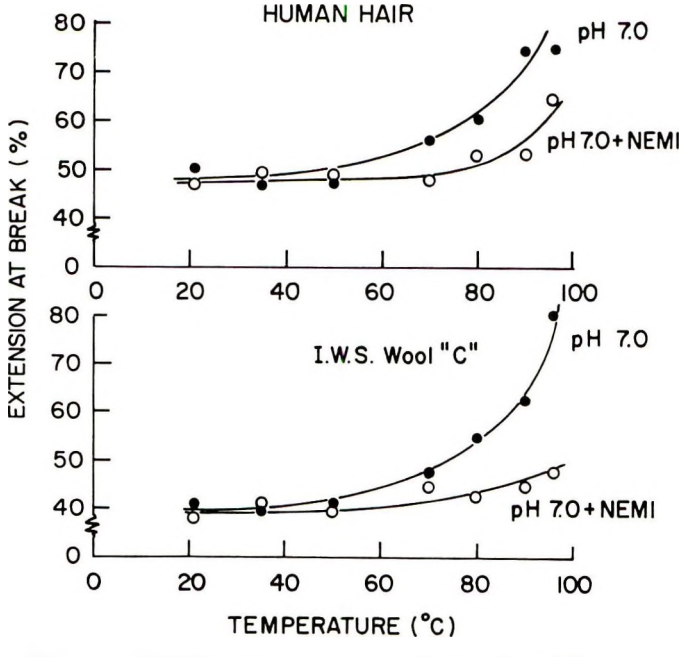

Figure 4. Extension at break of human hair and wool fibers as a function of temperature

and that the stresses on the disulfide bonds in these domains are relieved by an interchange mechanism catalyzed by free SH groups. This is further substantiated by the post-yield modulus values of the reduced human hair which are shown in Table III. The reduction causes a decrease in the post-yield modulus at any given temperature which is largely eliminated by the presence of NEMI. The increased SH content arising from the reduction catalyzes the interchange, thereby decreasing the post-yield modulus; but blocking of the free SH groups with NEMI again increases the modulus value, since the stressed disulfide bonds can no longer be relieved via an interchange. At each temperature and under comparable experimental conditions the wool fibers have a lower post-yield modulus, but the temperature dependence and the effects of blocking free SH groups with NEMI are the same for both fiber types.

The extensibility of the untreated human hair and IWS Wool C fibers as a function of temperature are shown in Fig. 4 in the presence and absence of NEMI. In both fiber types the extension at break increases only at the higher temperature levels, which is to be associated with a characteristic transition temperature to be discussed later. The effect of blocking free SH groups is to decrease extensibility which is consistent with the prevention of the interchange mechanism as a means of relieving stress and allowing a chemical flow process to be operative. Reduction of the human hair increases the extensibility by a significant amount, as is shown in Fig. 5.

The strength dependence of both fiber types on temperature is shown in Fig. 6. The strength decreases with increasing temperature, reflecting the thermal disruption of some of the intermolecular attractive forces. As is shown in Table IV, neither the presence of NEMI nor the partial reduction had a systematic or significant effect on the strength of the hair.

The extension at the turnover point from the yield to the post-yield regions is a particularly interesting and revealing parameter obtainable from a keratin fiber stress-strain curve. The temperature dependence of this parameter for the untreated human hair is shown in Fig. 7. In the absence of NEMI the extension to the post-yield region is essentially constant up to a characteristic temperature and then increases rapidly as the temperature is further increased. A transition temperature (T_{tr}) can be determined from the intersection of these two temperature dependencies. In the case of the untreated human hair sample this transition temperature has a value of 85.5°C. In the

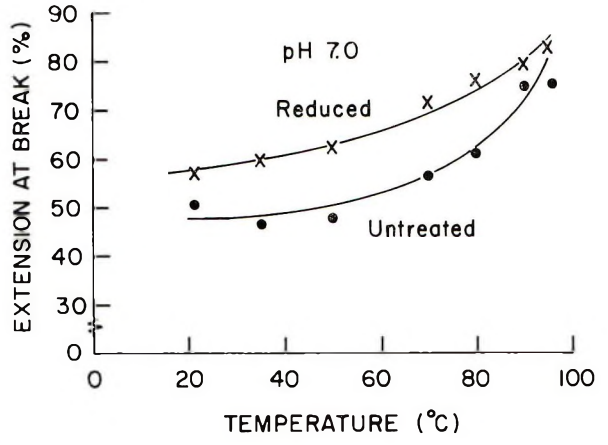

Figure 5. Extension at break of untreated and reduced human hair as a function of temperature

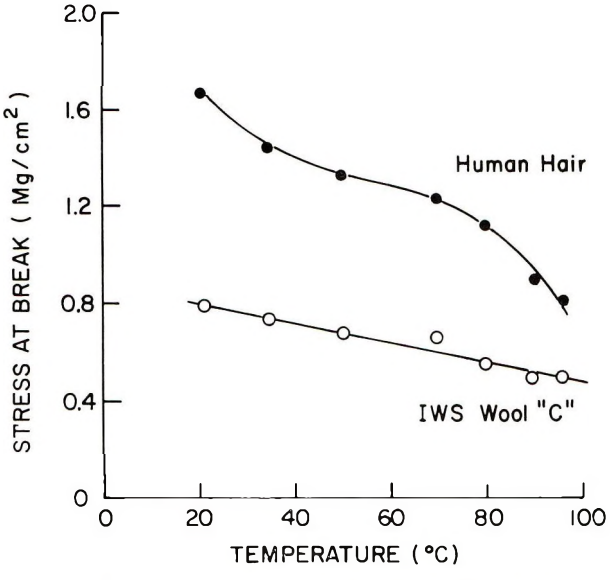

Figure 6. Strength as measured by the stress at break of human hair and wool fibers as a function of temperature. Average values over all conditions

presence of NEMI such a transition temperature is not observed within the temperature range of the experiments. Clearly, the transition temperature must be associated with the sulfhydryl-disulfide interchange, which is prevented by blocking SH groups with NEMI. Similar

curves are shown in Fig. 8 for the reduced human hair, where it can be seen that a transition temperature of 66.0°C was found in the absence of NEMI; however, no transition temperature was observed when the free SH groups were blocked with NEMI. Analogous curves for IWS Wool C are shown in Fig. 9. A summary of the transition temperature values in relation to chemical structure of the keratin fibers used in these experiments, along with some comparable values obtained in an earlier investigation, are shown in Table V.

Table IV

Stress at Break (kg × 10^{-3}/cm²) of Human Hair

	Untreated		Reduced	
Temperature	pH 7.0	NEMI	pH 7.0	NEMI
21°C	1.71	1.60	1.66	1.66
35	1.32	1.61	1.61	1.21
50	1.28	1.46	1.30	1.27
70	1.43	1.30	1.06	1.14
80	1.25	1.33	0.84	1.06
90	1.01	1.07	0.62	0.87
96	0.78	1.11	0.54	0.82
Pooled 95% c.l.	0.29	0.22	0.13	0.18

Table V

Transition Temperatures and Sulfhydryl Content of Keratin Fibers

	Sulfhydryl content (μmole/g)	T_{tr} (°C)
Human hair		
Untreated	10.1	85.5
Reduced	63.0	66.0
IWS Wool C	14.1	75.0
B. A. Fleece Wool (7)		
Untreated	12.4	72.0
Reduced	200.9	15.0

It is quite evident that a negative correlation exists between the sulfhydryl content and the transition temperature. This correlation is particularly significant when one considers that keratin fibers of different origin are being considered.

The dependence of the transition temperature on the SH content clearly indicates that a disulfide-sulfhydryl interchange is responsible for the control of deformations beyond 30% strain. In this region of the stress-strain curve the deformation of the matrix or other sulfur-

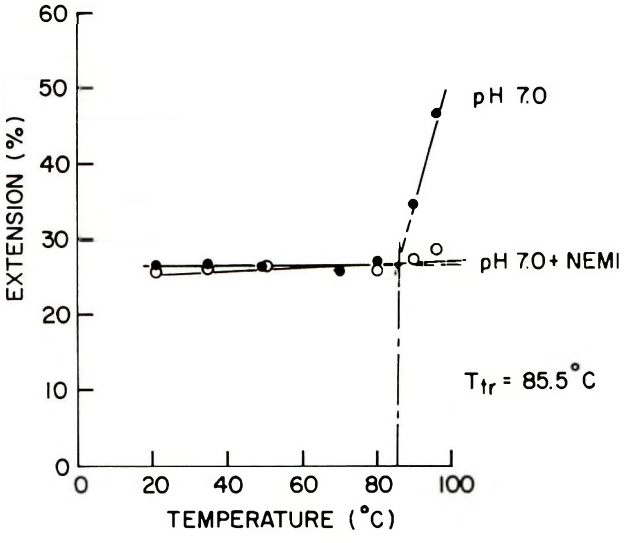

Figure 7. Extension to post-yield region of human hair as a function of temperature

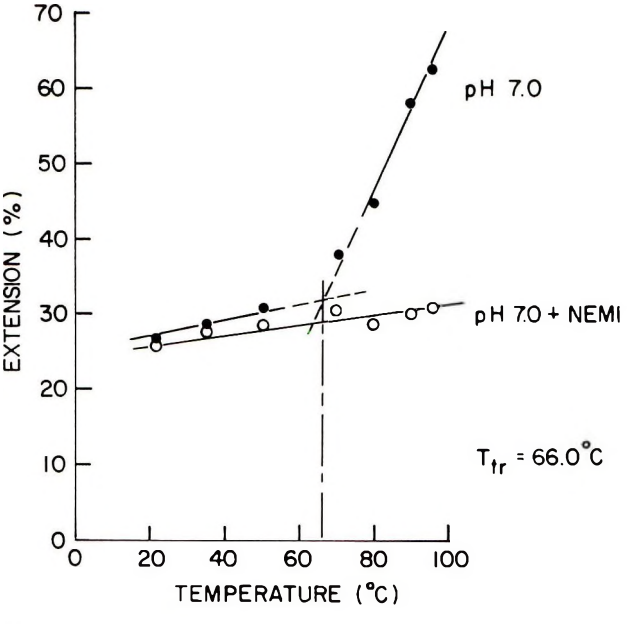

Figure 8. Extension to post-yield region of reduced human hair as a function of temperature

containing domains starts to contribute to the over-all process. It has been suggested that this apparent second-order transition temperature indicates a transition of the fiber from a glassy to an elastomeric state (13); however, the interpretation of thermal transitions in stressed systems is rather complicated and not necessarily analogous to unstressed systems. If one considers the transition to be a glass transition, one would have to visualize parts of the fiber in a glassy state which, under stress at a certain temperature, are transformed to an

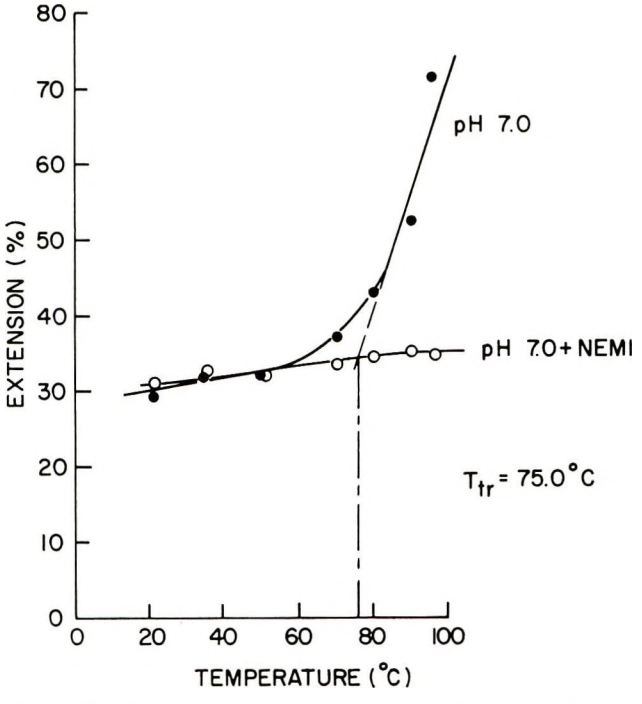

Figure 9. Extension to post-yield region of wool fibers as a function of temperature

elastomeric state. This behavior would have to be connected with the matrix since the microfibrils are presumably crystalline and would show a crystal-melt transition rather than a glass-elastomer transition. If it is assumed that this transition is connected with the matrix, the question arises whether a highly water-swollen matrix can exist in a glassy state at these temperatures. Of course, if the matrix is considered not to be homogeneous, with regions of high and low cross-link density and correspondingly low and high water contents, then it is conceivable that certain regions of the matrix may exist in a glassy state.

It is not necessary, however, to postulate a heterogeneous matrix in an explanation of the observed transition. This transition may be entirely connected with the stability of the disulfide bond and the onset of a disulfide interchange which is catalyzed by SH groups. In an untreated human hair, for instance, the disulfide cross-links reach such a degree of instability at 85.5°C that the restrictions for mobility of the chain segments in the matrix are decreased to a critical level, and the viscoelastic behavior of the matrix shows a rapidly increasing flow component with increasing temperature. In a partially reduced human hair this critical instability is reached at a lower temperature, in view of the higher free SH content.

In general, the results of this study have shown that the mechanical properties of human hair are strongly temperature dependent and that many of its viscoelastic characteristics can be interpreted in terms of a sulfhydryl-disulfide interchange as a means of relieving stressed disulfide bonds. It should be noted that the properties of human hair are significantly affected by even low levels of reduction, particularly at the higher strains in view of the important catalytic effects of free SH groups.

Acknowledgment

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The Practical Evaluation of Shampoos

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Presented December 1, 1965, New York City

Synopsis—Appearance, performance during use, and effect on hair after use are the three major criteria by which shampoos should be evaluated. Within these three broad categories, 25 separate characteristics are enumerated. The importance of each of these and laboratory and beauty salon test procedures for evaluating shampoos are discussed.

Introduction

The development of a shampoo that can win a significant share of a highly competitive market is not a simple task. Even though a shampoo is more or less a rather prosaic toiletry, many of its qualities, or lack of these qualities, can affect the consumer either favorably or adversely. The chances of developing a utility shampoo with a significant innovation are rather remote. The term utility shampoo is used to differentiate between the general use shampoo and those which are more specifically defined, such as antidandruff shampoos, color shampoos, etc. In order to produce a successful shampoo of the utility type, it must have a quality of excellence built into it. This quality of excellence is almost always a total combination of many factors, some of which are immediately obvious to the consumer and many of which are not.

The consumer reacts to a shampoo at three different times. The consumer will be considered to be female, since almost all of the general use family shampoo is purchased by a feminine member of the family.

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It is true that her decision is influenced by advertising, packaging, brand name, and reputation of the manufacturer—and, perhaps a great deal more than one would like to admit, by price. Her first real impressions are established when she picks the package off the shelf. If she is favorably impressed at that time she may buy and use the shampoo. Her decision whether to purchase the product again is influenced twice more. How did the shampoo perform, and how did it leave her hair?

Most discussions of shampoo performance found in the literature are limited to evaluation of foaming qualities, manageability, and detergency. There are many other factors that contribute to a quality shampoo, which have been delineated in 25 distinct categories. Every shampoo under development and all competitive shampoos are evaluated against this check list. Many of the qualities can be measured by well-established laboratory procedures. Others must be evaluated by specially devised techniques. And still other qualities can only be determined subjectively, and here experience and a thorough understanding of shampoos are invaluable.

Details of the formulation or composition of shampoos will not be considered. Instead, the major objective is a discussion of the practical evaluation of the 25 characteristics or qualities which enable the chemist to determine whether or not a shampoo has that certain "quality of excellence," as measured by the consumer. These qualities are reviewed not necessarily in order of importance; nor are they studied in the order shown; and many of them are interrelated.

The methods of evaluation as described in this paper apply to a clear liquid shampoo although similar criteria may be applied to a liquid lotion or a cream shampoo.

The 25 shampoo qualities can be divided into three broad groups. This is primarily a check list designed for the fairly rapid evaluation of large numbers of shampoos on a routine basis. The first group concerns the appearance of the product itself in the bottle and includes the following nine qualities for evaluation:

1. Clarity
2. Viscosity
3. Color
4. Color stability
5. Cloud point
6. Clear point
7. pH

8. Fragrance
9. Sterility

The second group of qualities relates to or is directly concerned with the actual performance on the hair and includes:

10. Foam production—hard water
11. Foam production—soft water
12. Foam production—hard water plus soil
13. Foam stability
14. Foam texture
15. Speed of foam production
16. Rinseability
17. Fragrance of lather

The third group of characteristics concerns the effect of the shampoo on both the hair and skin. Here the following qualities are evaluated:

18. Combability of wet hair
19. Combability of dry hair
20. Static electricity of the hair
21. Fragrance of the hair
22. Hair gloss
23. Effect on artificial hair color
24. Staining of bleached or permanent waved hair
25. Feel on hands

Shampoo Evaluation

Clarity

From a consumer point of view, the general outward appearance of the shampoo is the first contact with the product itself, stripped of its outer covering of label and package. For this reason it is most important that a clear shampoo be manufactured with maximum care. A shampoo with sparkling clarity has obviously greater consumer appeal that one that is hazy.

The danger in formulating clear shampoos is loss of clarity with aging, a fairly common defect. Only thorough stability testing of the shampoo will reveal this problem so that measures can be taken to solve it. Among the factors contributing to loss of clarity are temperature, perfume, water hardness, contamination by microorganisms, and water-insoluble fatty compounds used as hair conditioning agents.

Cloud point and clear point evaluations are important in order to maintain clarity under a range of colder-than-normal temperatures.

The cloud point is the highest temperature at which the shampoo will cloud or haze when cooled. The clear point is the lowest temperature at which the product will clear when warmed from a chilled opaque condition. They are not always the same. Clarity, insofar as cloud and clear points are concerned, should be maintained at about a maximum of 10°C. This should insure clarity in stores and homes under average conditions of temperature.

Viscosity

Liquid shampoos comprise the largest share of the shampoo market, with clear liquid shampoos accounting for better than 50% of the market. Among the most important characteristics of these products is viscosity which may range from water-thin products to viscous liquids. There are both psychological and practical advantages to relatively high viscosity liquid shampoos. They often imply a high concentration of shampoo ingredients plus a richness that is usually associated with hair conditioning and management. There is also a practical value. High viscosity liquid shampoos can be poured into the palm of the hand for application to the hair, thus eliminating dripping through the fingers or down the face and neck.

A desirable viscosity range will vary between 500 and 1500 cps. Shampoos having viscosities below this level tend to be runny; and if the viscosity is over 2000 cps., they may not pour too well. Maintaining viscosity within a close range over a long period of time can sometimes be a problem. Here again, stability testing is of utmost importance.

Color

A shampoo may be uncolored, or it may have certified color added. The color of a shampoo is dictated by esthetic considerations, packaging, and subtle psychological factors. The market to which it is directed is also a factor. A shampoo for men may be blue, green, amber, or gold, or it may be colorless, but pink would be a doubtful choice. There has been a transition over the years in the colors which the consumer prefers. Until recent years liquid shampoos were usually amber, yellow, or orange. More recently, green and blue shampoos have become popular. Clear, colorless shampoos are also on the market. Such shades as lavender and red and deep colors are particularly unacceptable.

Color Stability

In selecting the color to be used, color stability or instability can become a problem. Many of the certified dyes used are sensitive to light, pH, and other chemical factors. It should be unnecessary to state that every shampoo should be thoroughly tested for light stability. Since it is not always convenient to set the product in the sun and since the results are not reproducible, a commercial "fadeometer" may be used to determine color stability. In such equipment the shampoo is exposed to high intensity ultraviolet light under controlled conditions. A minimum exposure of six hours with negligible or no color change is usually considered acceptable.

Incidentally, one of the pitfalls to be avoided in light exposure studies is to test the shampoo in a container made from the same material as the ultimate package. It is not unusual to find a color that may fade in glass but is stable in a given plastic and *vice versa*. With the de-listing of many certified colors, the problem of finding a suitable color that is stable to light has increased. The use of ultraviolet absorbents in the shampoo can be extremely helpful in improving the light stability of fugitive colors. Some container manufacturers are coating their glass or plastic bottles with ultraviolet absorbents which serve the same purpose.

A third area where the color of a shampoo should be evaluated is one that is frequently overlooked. Some hair, and this is especially true of bleached and permanently waved hair, is quite porous and may absorb the color from the shampoo. Here again, pH and chemical composition of the product may be contributing factors. Only thorough testing on laboratory hair swatches and subsequent application to subjects with bleached or permanently waved hair will determine whether this problem exists.

pH

The pH of a shampoo may have definite effects upon its properties. Most liquid shampoos today are formulated to have a pH between 6.5 and 8.5. Within this range a suitable viscosity and clarity can usually be achieved, as well as good stability and lathering properties. A few generalizations can be made concerning the effects of pH on a typical clear shampoo formulation:

1. Shampoos formulated on the high side of the pH range will exhibit a greater degree of foaming and cleansing as well as a greater ability to strip the natural oils from the hair.

2. Conversely, shampoos on the low side of the range will generally leave the hair in better condition with a greater degree of manageability and combability.
3. Shampoos with pH's above and beyond the high side of the range can cause eye irritation more readily than those within the range.
4. It is easier to maintain clarity on the high side of the pH range.
5. Viscosity generally increases as the pH is lowered. This is especially true of alkylolamide-lauryl sulfate shampoos.

pH can, therefore, be considered as a key factor in formulating a product to suit the consumer's desires. Although she may never have heard of the term, pH can affect the appearance, efficacy, and residual performance of a shampoo.

Fragrance

The fragrance of a shampoo is a most important quality. It can add a touch of cosmetic elegance to the product plus an air of distinction. It can significantly influence the consumer whether or not to purchase the product initially or to repurchase it. It is the authors' opinion that a shampoo fragrance should be a light and clean bouquet; but the perfume type will be dictated by whether the shampoo is marketed primarily to women, men, children, or for family use.

The shampoo fragrance should be evaluated critically at three different stages. First, the product itself in the bottle. A buyer will often remove the cap and sniff the product at the shelf or counter. Does it have a light refreshing scent with high appeal? Is the shampoo free of a chemical or detergent odor; is it effectively masked? Does the fragrance appeal to the consumer group to whom the shampoo is directed? The fragrance at point of purchase can often make or prevent a sale.

The second time that the fragrance may elicit a response from the consumer is during application to the hair. The use of hot water plus the fact that shampoos are often applied to the hair in a confined area, such as the bathroom or shower, can result in a fragrance change noticeable in the lather and in the atmosphere. The fragrance should retain its basic characteristics without becoming overpowering.

The third important stage is the fragrance of the hair after shampooing. The hair should retain an almost imperceptible scent. Certain perfume types should be avoided, such as heavy, sweet types which tend to cling to the hair. Hair that has been bleached or permanently waved

tends to retain more of the fragrance than chemically untreated hair. Also, hair that has been shampooed with products containing amphoteric surfactants often retains more fragrance than when anionic surfactants are used.

Sterility

For some reason cosmetic chemists often disregard or minimize the potential problem of shampoo contamination by microorganisms. They would not consider marketing a cream or lotion that is inadequately preserved, but shampoos are often found without preservatives. There is a mistaken notion that, since sulfated lauryl alcohol and sulfated ethers are considered antagonistic to bacterial and fungal growth, no contamination problems exist in shampoos. Several investigators (1, 2) have shown that this is only partly true, and shampoos are often found that give high bacterial counts—particularly of gram-negative bacteria. This has been confirmed by the authors' experience over the years. Contamination by microorganisms poses not only a health hazard but can cause changes in the shampoo, such as malodor, turbidity, and viscosity changes. On the other hand, it is also possible to find grossly contaminated products without visible signs of change.

All shampoos must be preserved not only for original freedom from contamination but also must be protected against the possibility of future contamination when the package is opened and reopened for use. Many preservatives are available for use in shampoos today, and their incorporation is fairly simple; however, their effect on certain organisms may either diminish in time or cause the generation of resistant strains. Thus, even after many years of preservation by specific agents have passed safely, a periodic investigation should be undertaken to determine whether the preservatives are still effective. Freedom from microorganisms not only depends on adequate preservation but also upon uncontaminated raw materials—particularly water. Vitally essential are strict sanitary measures during manufacture. Constant diligence is required, and development production shampoos should be routinely subjected to bacteriological evaluation.

Foaming

To the consumer, foaming or lathering action is one of the most important aspects in determining the quality of a shampoo, and the measurement of foam has received much attention in the literature. The volume, foam structure, foam viscosity, and foam stability are also

important criteria by which the consumer judges the shampoo even though she may not realize it. Undoubtedly, techniques to measure and evaluate foaming qualities are important. Normally, such measurements are first performed in the laboratory and then in actual use on models. There have been many laboratory techniques developed over the years to measure foam, some of them highly sophisticated. The authors use a very simple technique which requires only a 500 ml glass stoppered cylinder and a device to revolve or agitate it. This very simple method has been widely criticized, and there are more precise procedures (3–5). For practical purposes and after thousands of foam

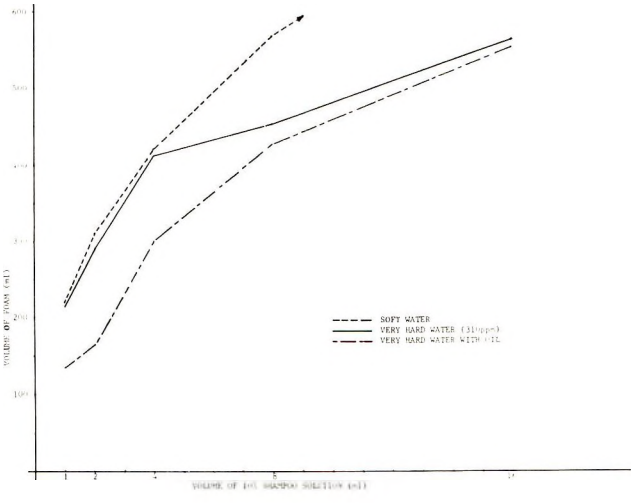

Figure 1. Foam curves of a commercial shampoo (Shampoo A)

tests, this technique has been found to meet the following conditions: It is fast, it is reproducible, and it reflects the performance of the shampoo on the hair.

First, 10% dilutions of the shampoo in either soft water or water of known hardness are prepared. Increasing increments of the diluted shampoo are pipetted into the cylinder, diluted with water of required hardness to a fixed level, and then rotated for a precise number of times. The foam volume is recorded, and the bubble structure and foam stability are examined. Three foam curves are plotted for every shampoo: A soft water dilution; a dilution with water of known hardness; and a dilution of water with known hardness plus the addition of 1 ml of olive oil. The foam determination in the presence of oil fairly accurately

reflects the performance of the shampoo on the first lathering. During the first lathering the foam is often depressed because of sebum, hair dressings, and other cosmetic products which may be on the hair. The hard and soft water curves represent the range of water hardness used by consumers throughout the country and can be a major factor in the type of foam developed. Figure 1 illustrates these three foam curves of a nationally advertised brand of shampoo. Figure 2 shows the foam curves in very hard water (310 p.p.m.) of two popular shampoos. This significant difference in foam production of shampoos A and B is also evident when the two shampoos are actually applied to the hair of a subject using a "half-head" technique.

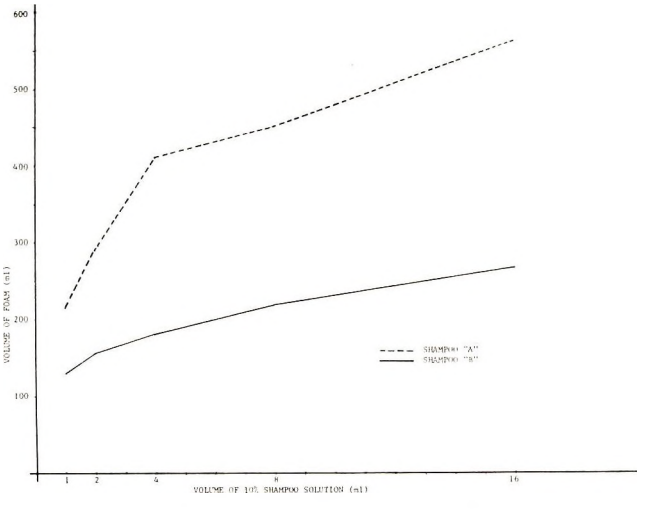

Figure 2. Comparison of the foam volume of two shampoos in very hard water (310 ppm)

The most important test in evaluating shampoo performance is to shampoo a variety of hair types under controlled conditions and observe the results. The recommended method is the "half-head" technique which involves parting the hair down the center and shampooing each half simultaneously with two different shampoos. The "half-head" technique is commonly used with many hair preparations such as hair sprays, wave sets, hair dressings, etc. With these, "half-head" testing is simple and easy, but it is not quite so simple with a shampoo.

The reasons for "half-head" testing are quite obvious. No two heads of hair are the same. The hair varies in texture, length, condition, sebum and soil content, and presence of cosmetics. Therefore, compar-

ing Shampoo A on one head with Shampoo B on another head is rather meaningless, especially if only subtle differences exist. One must then rely on memory and, therefore, cannot compare the results of a head shampooed with product A and subsequently treated with shampoo B. A skilled beautician can apply two shampoos to the same head and, if done on a number of heads, obtain meaningful and reproducible results.

Two shampoos are applied to dampened hair in equal amounts (from glass hypodermic syringes for accuracy and convenience) to both sides. The lather is worked up as uniformly as possible on both sides of the head and the various lathering and foaming qualities observed, including the speed at which the lather develops, the so-called "flash-foam" characteristics. A second lather is worked up, again using syringes for accurate dispensing of the shampoo, and the evaluation is repeated. Very often the second lather is allowed to remain on the hair for three to five minutes and foam collapse, if any, noted. The shampoos are rinsed from the hair and the rinsing characteristics observed. It has been found that some shampoos rinse very rapidly while others continue to produce foam for several minutes during the rinsing procedure.

The foam texture is also examined during these tests. Foam made up of large, thin bubbles is not desirable; neither is foam made up of very small bubbles, which tend to make the foam feel like a cream.

Incidentally, one observation made during these "half-head" tests is frequently overlooked. How does the shampoo feel on the hands during application? Does the shampoo impart the desirable soap-like lubricity, or does it impart a raspy harsh feel to the hands? The consumer has been conditioned to the feeling of lubricity or slip that is always characteristic of soap and most shampoos. With the current trend to shampoos of lower pH, this quality can be lost. A shampoo of pH 6.0 to 6.5 can lack this feeling of lubricity on the hands, but the problem can be resolved by skillful formulation.

Manageability

Perhaps one of the most abused words used in shampoo advertising is "manageability" or "conditioning." Such claims are frequently made for shampoos, even though they do not exist. However, they are meaningful to the consumer and are, therefore, important to the chemist. Just what do these words mean? A healthy, normal head of hair is one that is easily combed when either wet or dry. This is due to natural secretions which coat the hair with a lubricating film, eliminate

CLINIC SHAMPOO TEST

Date _____ Subject _____ Ph. _____

DESCRIPTION OF HAIR

Short _____ Medium _____ Long _____
Tinted _____ Bleached _____ P.W. _____ Date _____

Dry _____ Normal _____ Oily _____

Fine _____ Medium _____ Coarse _____

Good _____ Fair _____ Poor _____

Date of Last Shampoo _____ Shampoo Used _____

LEFT		RIGHT
_____	Shampoo Used	_____
_____	Dilution	_____
_____	Amount	_____
1st Slow Av. Fast	Foaming	1st Slow Av. Fast
2nd 1st Little Av. Heavy	Volume	2nd 1st Little Av. Heavy
2nd 1st Thin Av. Thick	Density	2nd 1st Thin Av. Thick
2nd		2nd
0 1 2 3 4 5	Collapse	0 1 2 3 4 5
0 1 2 3 4 5	Rinsability	0 1 2 3 4 5
0 1 2 3 4 5	Feel-Wet	0 1 2 3 4 5
0 1 2 3 4 5	Combability-Wet	0 1 2 3 4 5
0 1 2 3 4 5	Feel-Dry	0 1 2 3 4 5
0 1 2 3 4 5	Combability-Dry	0 1 2 3 4 5
0 1 2 3 4 5	Static Charge	0 1 2 3 4 5
0 1 2 3 4 5	Body	0 1 2 3 4 5
0 1 2 3 4 5	Sheen	0 1 2 3 4 5

Other Comments _____

Call Back Comments _____

Date _____

Figure 3. Beauty Clinic form

static charges, and impart gloss or sheen. Many shampoos will completely strip the hair of sebum and other natural secretions, with the result that the wet hair snarls or tangles and is difficult to comb. The dry hair is often lustreless and also difficult to comb. A strong static charge results in "fly-away" or hair difficult to hold in place.

There are two solutions to this problem. One is to formulate a shampoo with reduced detergency. The shampoo will remove surface soil on the hair and most—but not all—of the sebum coating. The amount of natural oils remaining on the hair is sufficient to impart some

degree of "manageability." A second solution is to compound a shampoo that will cleanse the hair but still leave a film on it to serve temporarily as a conditioning agent until natural scalp secretions are replaced. The authors doubt that most so-called "conditioning agents" incorporated in shampoos are deposited on the hair. There are, however, substantive materials which are useful for this purpose.

After the hair has been thoroughly rinsed and towel dried, it is again parted down the center and combed (using two identical clean combs) by both the beautician and the chemist, and differences in combability are noted. No other cosmetic products are used on the hair when shampoos are evaluated. When dry, the hair is again checked for dry combability, gloss, and static charge. Excellent methods have been devised for the measurement of static charge on hair (6, 7) but for routine purposes visual observation is sufficient. All beauty clinic observations are recorded on the form shown in Fig. 3. A subjective rating system is used whereby many of the characteristics discussed above are scored from 0 to 5, with 0 being very poor and 5 very good. In a series of tests on a shampoo, using suitable controls, meaningful observations are readily made as to the performance characteristics.

Effect of Shampoo on Hair Color

In view of the tremendous growth of hair coloring, the possible effects of shampoos on artificially colored hair cannot be ignored. Specialty shampoos have been developed for use on color treated hair, but utility shampoos should also be checked. This is routinely performed in the laboratory and in the beauty clinic on hair that has been colored with oxidation dyes and with semi-permanent dyes. In the laboratory, the AATCC Launderometer as modified by Goldemberg (10) is used. Observations of loss of color during shampooing and of color changes are made. Here again the "half-head" technique is useful because color changes and attrition of color may be due primarily to the color and not to the shampoo.

Concluding Comments

There are additional shampoo qualities that require evaluation, and omission of these from the list of 25 characteristics does not necessarily minimize their importance. Safety to the consumer is of paramount importance, and certainly no shampoo should ever be marketed that is a sensitizer or an irritant to the eyes or skin. Factors that contribute to

such hazards are well known, and methods to detect them are in widespread use.

Detergency has not been listed as an important consideration for routine evaluation. Although excellent methods have been reported for the measurement of detergency (8, 9), some cosmetic chemists are of the opinion that a shampoo should not be so powerful a detergent as to strip all natural secretions from the hair and scalp. Modern shampoos are based on surface-active agents that perform this task adequately for all practical purposes. The latitude for degree of detergency is fairly wide. When one considers that most heads of hair are shampooed with two applications of shampoo, the factor of detergency becomes relatively unimportant.

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Translations Available

English translations of the following papers may be obtained by writing to Mr. Robert A. Kramer, Evans Chemicals, Inc., 250 East Forty-third Street, New York, New York 10017.

"Studies of the Phenomenon of Permanent Waving of Human Hair," by Dr. Hans Freytag.

"Alteration of Hair Keratin by Cosmetic Processing and Natural Environmental Influences," by Dr. Peter Berth and Dr. Gunter Reese.

"New Information about the Morphological Structure of the Hair," by Dr. Rudolf Randebrock.

"The Application of the Analytical Methods of Sulfur Chemistry to Permanently Waved Hair," by Prof. Dr.-Ing. Helmut Zahn, Dr. Tarsilla Gerthsen, and Dipl.-Chem. Marie-Luise Kehren.

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Protection of Cosmetic Colors by Means of UV Absorbers

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Synopsis—It is shown that nine commercially available ultraviolet light absorbers can be used to protect certified colors against fading. Such protection can be achieved by incorporating the UV absorber into the product or into the coating of the package. Practical examples of both methods of protecting against fading are cited. The decision as to how the absorber is used depends on efficacy, the dye to be protected, safety, and costs.

Introduction

The utility of many organic colorants employed in cosmetic products is restricted by their instability on exposure to light. This instability normally evinces itself as fading and is caused primarily by wavelengths within the ultraviolet portion of the electromagnetic spectrum, although wavelengths in the visible light range of the spectrum also may be responsible. Adequate protection of many of these colorants against harmful radiation can be provided by ultraviolet absorbers. The information to be presented will demonstrate this ability and, it is hoped, assist in the intelligent selection and usage of ultraviolet absorbers to combat color fading of cosmetic products.

To protect the certified cosmetic colors against light induced fading, ultraviolet absorbers can be employed in either of two ways:

1. By direct incorporation of an absorber into the composition, the color of which is sensitive to light.

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2. By incorporation of an absorber into a transparent coating to be applied over the clear container holding the colored product; or, if a clear plastic container is used, by incorporation into the body of the container.

Each method has its advantages and disadvantages which will become evident with the information to follow.

Before proceeding with the data, it would be well to define the term "ultraviolet or UV absorber" and to dwell briefly on some of the aspects of ultraviolet absorption. An ultraviolet absorber is a substance capable of absorbing large quantities of ultraviolet radiation which can convert this radiation into a harmless form of energy, heat, and which is not altered or destroyed in the process. A UV absorber should:

1. Absorb large quantities of ultraviolet radiation
2. Be stable toward ultraviolet radiation
3. Be soluble in the medium in which it is incorporated
4. Possess little or no color
5. Be heat stable
6. Exhibit low volatility
7. Be nontoxic
8. Be nonreactive toward the medium in which it is incorporated

Few, if any, absorbers possess all of these desirable properties to the fullest extent.

Ultraviolet absorption follows the Beer-Bouguer law which in one of its forms is stated as:

$$A = Klc,$$

where A = absorbance or optical density, K = the specific extinction coefficient, l = path length or cell thickness (cm), and c = concentration of absorber (g/l). The absorption curve of a UV absorber (shown in Fig. 1) demonstrates how the law works. This curve for Uvinul ®* D-49, 2,2′-dihydroxy-4,4′-dimethoxybenzophenone, was obtained at a concentration of 0.025 g/l in methanol using a 1 cm cell thickness. The curve exhibits two absorption maxima, one at 284 mμ and the other at 340 mμ. Since the earth's atmosphere filters out radiation from the sun below about 290 mμ, the maximum at 284 mμ is of no importance with respect to natural sunlight; however, other sources of ultraviolet radiation such as fluorescent lamps do emit below 290 mμ, and this

* ® "Uvinul" is a registered trademark of the General Aniline & Film Corporation.

second maximum then may become useful. By substituting in the Beer-Bouguer expression the absorbance value for any specific wavelength along the curve together with concentration and cell thickness, the specific extinction coefficient or K value of the absorber can be

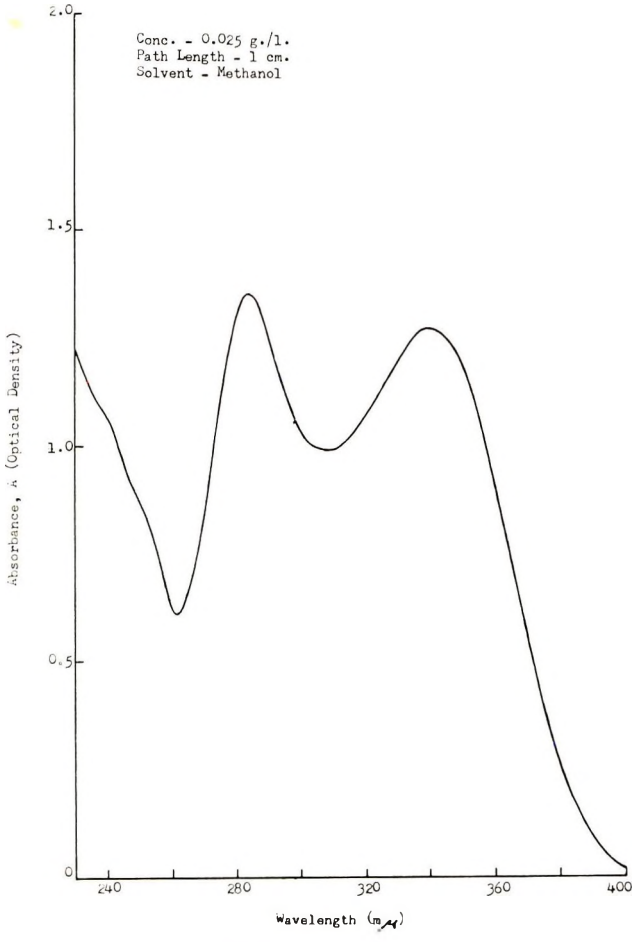

Figure 1. UV absorption curve for Uvinul D-49

calculated for that particular wavelength. The extinction coefficient is a constant and remains the same for the absorber in that same medium and at that particular wavelength regardless of path length or absorber concentration. Thus, K can be used as a means of describing the absorptive capacity of UV absorber. Normally K is cited for the absorbance maximum nearest 400 mμ, the beginning of the visible

light spectrum. For example, in the case of Uvinul D-49, $K_{340\ m\mu}$ = 50.8 in methanol. In selecting a UV absorber for an application it is usual to pick one which has an absorbance peak at or near the wavelength or wavelengths toward which the material to be protected is most sensitive.

Use of UV Absorber in Composition

With the above as a basis, the actual effectiveness of UV absorbers in protecting some of the organic colorants commonly used in cosmetics against light fading can be assessed. The first area to be covered is the method in which the absorber is incorporated directly into the composition, the color of which is to be protected. To illustrate this

Table I
UV Absorbers

UV Absorber	Absorber Structure	Specific Extinction Coefficient (K) at Absorbance Maximum Nearest Visible
Uvinul 400	2,4-dihydroxybenzophenone	$K_{321\ m\mu}$ = 53.2 in methanol
Uvinul M-40	2-hydroxy-4-methoxybenzophenone	$K_{323\ m\mu}$ = 44.8 in methanol
Uvinul D-49	2,2′-dihydroxy-4,4′-dimethoxybenzophenone	$K_{340\ m\mu}$ = 50.8 in methanol
Uvinul D-50	2,2′,4,4′-tetrahydroxybenzophenone	$K_{346\ m\mu}$ = 60.0 in methanol
Uvinul 490	Mixture of Uvinul D-49 and other tetra-substituted benzophenones	$K_{340\ m\mu}$ = 51.2 in methanol
Uvinul N-35	Ethyl 2-cyano-3,3-diphenylacrylate	$K_{303\ m\mu}$ = 47.4 in methanol
Uvinul N-539	2-Ethylhexyl 2-cyano-3,3-diphenylacrylate	$K_{302\ m\mu}$ = 36.2 in methanol
Uvinul MS-40	2-hydroxy-4-methoxy-benzophenone-5-sulfonic acid	$K_{324\ m\mu}$ = 23.6 in methanol $K_{320\ m\mu}$ = 24.4 in water
Uvinul DS-49	Sodium 2,2′-dihydroxy-4,4′-dimethoxy-5-sulfobenzophenone	$K_{333\ m\mu}$ = 6.3 in methanol $K_{332\ m\mu}$ = 17.4 in water

procedure, the effect of addition of varying amounts of nine different UV absorbers on the light stabilities of eleven certified colors in solution was studied. In Table I are listed the absorbers and in Table II the colors which were investigated. The absorbers are represented by two structural classes, the substituted benzophenones and the substituted acrylonitriles, exhibiting absorbance maxima nearest the visible ranging from 300 to 345 mμ. The colors were recommended by a leading supplier as being among those most widely employed in cosmetics. As carriers for the dyes and absorbers three solvent systems were used,

90/10 and 50/50 by weight mixtures of SDA-40 anhydrous ethanol and water and water alone. The latter two systems were found necessary for one dye and one absorber not soluble in the 90/10 system. All colors were tested at 0.001% (by weight) concentration with the exception of D&C Yellow No. 8 which was studied at a level of 0.005%. The UV absorbers were evaluated at 0.05, 0.1, and 0.2% (by weight) concentrations. Testing was carried out by exposing clear flint glass bottles containing the color/absorber solutions in an Atlas Model FDA-R single carbon arc Fadeometer operating at a 145°F black panel temperature until significant differences were noted. Periodically

Table II
Certified Colors

Certified Color No.	Structural Type	Common Designation	Color Index No.
D&C Violet No. 2	Anthraquinone	Alizurol Purple SS	60725
FD&C Blue No. 1	Triarylmethane	Brilliant Blue F.C.F.	42090
Ext. D&C Green No. 1	Nitroso	Naphthol Green B	10020
D&C Green No. 5	Anthraquinone	Alizarin Cyanine Green F	61570
D&C Green No. 8	Pyrene	....	59040
FD&C Yellow No. 5	Monoazo	Tartrazine	19140
D&C Yellow No. 8	Xanthene	Uranine	45350
FD&C Red No. 3	Xanthene	Erythrosine	45430
D&C Red No. 17	Diazo	Toney Red	26100
D&C Red No. 19	Xanthene	Rhodamine B	45170
D&C Red No. 22	Xanthene	Eosin YS	45380

during exposure samples of each solution were withdrawn for comparison with the unexposed control. Table III through XIV list the results of the experimentation. Each table represents a single certified color with the exception of Table XIV based on data in which Uvinul DS-49, a water-soluble absorber, was tested in conjunction with all the colors except D&C Green No. 8 in aqueous solution. Several broad conclusions can be drawn from these results:

1. UV absorbers are effective in protecting many organic colorants against fading caused by ultraviolet radiation. The degree of protection conferred is dependent upon the particular dye under consideration, the absorber employed, and the concentration of the absorber.

2. While near UV absorbers, i.e., those having an absorption peak at a wavelength approaching 400 mμ, generally are more effective than absorbers showing peak absorption farther down the UV spectrum, this does not hold true for all certified colors.

3. Increasing the concentration of a UV absorber does not necessarily result in a proportionate increase in the degree of protection afforded a color.

4. A factor limiting the amount of the more highly colored UV absorbers which can be used with a dye is the change in original color brought about by addition of the absorber. This in turn is dependent upon the hue of the dye, the concentration of the dye, and the hue of the absorber. Since most UV absorbers are faintly yellow, dyes giving violet, blue, and red hues are most easily discolored by addition of the absorbers while dyes giving green, yellow, or orange hues are less susceptible to discoloration.

In addition to these general conclusions which will apply for any absorber/color system, there are certain specific conclusions which, while they apply to the particular system under discussion, may or may not be valid for all systems.

1. Taking into consideration not only the degree of protection against fading afforded a dye by an absorber, but also any change in hue of the dye solution caused by addition of the absorber, the following UV absorbers were found to perform best with the listed certified colors:

D&C Violet No. 2: 0.1% Uvinul 400 (Table III).
FD&C Blue No. 1: 0.05% Uvinul D-50 (Table IV).
Ext. D&C Green No. 1: 0.05% to 0.1% Uvinul D-49 or 0.05% Uvinul 490 (Table V).
D&C Green No. 5: 0.1% Uvinul 400 (Table VI).
D&C Green No. 8: 0.05% to 0.1% Uvinul DS-49 (Table VII).
FD&C Yellow No. 5: 0.2% Uvinul 490 or 0.1% Uvinul D-50 (Table VIII).
D&C Yellow No. 8: 0.2% Uvinul D-49 or 0.1% Uvinul D-50 (Table IX).
FD&C Red No. 3: 0.2% Uvinul D-49 (Table X).
D&C Red No. 17: 0.1% Uvinul 490 or 0.05% Uvinul D-50 (Table XI).
D&C Red No. 19: 0.2% Uvinul 400 or 0.2% Uvinul M-40 or 0.05% to 0.1% Uvinul D-50 (Table XII).
D&C Red No. 22: 0.1% to 0.2% Uvinul D-49 or 0.2% Uvinul 490 (Table XIII).

Table III
D&C Violet No. 2

UV Absorber	UV Abs. Conc. (wt %)	Color After *x* Hr Fadeometer Exposure						
		0	8	16	28	57	144	160
	0	dL	—	—	mL	X		
Uvinul 400	0.05	dL	—	—	—	—	mL	vvlL
	0.1	dL	—	—	—	—	—	nc
	0.2	dL	—	—	—	—	—	mL
Uvinul M-40	0.05	dL	—	—	—	mL	X	
	0.1	dL	—	—	—	—	—	m–dL
	0.2	dL	—	—	—	—	—	nc
Uvinul D-49	0.05	dL	—	—	—	—	mL	lL,sp
	0.1	dL	—	—	—	—	—	m–dL,p
	0.2	dL	—	—	—	—	—	m–dL,p
Uvinul 490	0.05	dL	—	—	—	—	mL	vvlL
	0.1	dL	—	—	—	—	—	lPL
	0.2	dL	—	—	—	—	—	l–mL
Uvinul D-50	0.05	dL,Pc	—	—	—	—	mL	m–lL
	0.1	dL,sTc	—	—	—	—	—	nc
	0.2	dL,Tc	—	—	—	—	—	mL,Tc
Uvinul N-35	0.05	dL	—	lL	X			
	0.1	dL	mL	vlL	X			
	0.2	dL	—	mL	X			
Uvinul N-539	0.05	dL	mL	X				
	0.1	dL	mL	X				
	0.2	dL	vlL	—	X			
Uvinul MS-40	0.05	dL	—	—	—	mL	X	
	0.1	dL,vsPc	—	—	mL	X		
	0.2	dL,sPc	—	—	lL	X		

Dye conc.—0.001 wt %. Solvent—90 SDA-40 + 10 H_2O by wt.

KEY TO TABLES III-XVIII

To retain data in compact form, a few readily recognizable letter symbols have been employed to designate colors and modifying values:

B = blue	O = orange	T = tan
G = green	P = pink	X = colorless
L = lavender	R = red	Y = yellow
c = cast or tone	l = light	p = precipitate
d = dark	m = medium	s = slight
f = fluorescence	nc = no change	v = very

When two color abbreviations are used together, the first indicates a tone or cast, and the second the major hue. For example, BG = bluish green (not blue green), or GB = greenish blue.

A dash (—) represents a gradual and progressive change in color from the previous color notation to the next notation.

Table IV
FD&C Blue No. 1

UV Absorber	UV Abs. Conc. (wt %)	Color After x Hr Fadeometer Exposure								
		0	64	94	125	167	181	195	209	219
...	0	B	mB	X						
Uvinul 400	0.05	B	B	—	—	—	—	—	—	X
	0.1	B	—	—	—	—	—	vvlB	X	
	0.2	B	—	—	—	—	—	mB	—	vlB
Uvinul M-40	0.05	B	—	—	—	—	mB	—	X	
	0.1	B	—	—	—	—	—	—	lB	X
	0.2	B	—	—	—	—	—	—	—	mB
Uvinul D-49	0.05	B	—	—	—	1G	X,sp			
	0.1	B	—	—	—	—	—	—	—	sGB,p
	0.2	B	—	—	—	—	—	—	—	nc,p
Uvinul 490	0.05	B	B	—	—	—	—	mG	—	vvlG
	0.1	B	—	—	—	—	—	—	—	BG
	0.2	sGB	—	—	—	—	—	—	—	GB
Uvinul D-50	0.05	B	—	—	—	—	—	—	—	nc
	0.1	sGB	—	—	—	—	—	—	—	nc
	0.2	GB	—	—	—	—	—	—	—	BG
Uvinul N-35	0.05	B	X							
	0.1	B	X							
	0.2	B	X							
Uvinul N-539	0.05	B	vvlB	X						
	0.1	B	X							
	0.2	B	X							
Uvinul MS-40	0.05	B	—	vvlL	X					
	0.1	B	LB	—	X					
	0.2	B	LB	—	X					

Dye conc.—0.001 wt %. Solvent—90 SDA-40 + 10 H_2O by wt.

It should be kept in mind that these performances were obtained under certain specific conditions of dye concentration, solvent system, and source of radiation; under other conditions, absorber concentration and even comparative absorber effectiveness may be different.

2. Certain UV absorbers may sensitize a dye toward ultraviolet radiation rather than protect it. This is illustrated by the substituted acrylonitrile absorbers, Uvinul N-35 and Uvinul N-539. In the case of D&C Violet No. 2, FD&C Blue No. 1, D&C Green No. 5, FD&C Yellow No. 5, D&C Red No. 17, D&C Red No. 19, and D&C Red No. 22, the dye solutions containing no absorber are more resistant to fading than the same solutions plus absorber.

3. UV absorbers having a reactive structure cannot be employed with colorants which can chemically interact with the absorber. This is illustrated by Uvinul MS-40, having a free sulfonic acid group, which reacts with Ext. D&C Green No. 1, D&C Green No. 5, D&C Green No. 8, and D&C Red No. 17 to produce entirely different hues from those of the dyes themselves.

4. Where borderline solubility of the absorber is involved, exposure to radiation of sufficient duration may cause a decrease in solubility, resulting in precipitation of the absorber. This is demonstrated by Uvinul D-49 which, while initially soluble in the 90/10 SDA-40 ethanol/H_2O solvent at concentrations up to and including 0.2% by weight, tends to precipitate on prolonged exposure to ultraviolet. It is interesting to note that Uvinul 490, which is almost identical to Uvinul D-49 in absorption characteristics and similar in structure, does not exhibit this tendency to precipitate due to better solubility in the solvent medium. Uvinul DS-49 shows the same effect as Uvinul D-49 in the 50/50 SDA-40 ethanol/H_2O system.

Use of UV Absorber in Package

As mentioned earlier, direct incorporation of a UV absorber into a cosmetic product is not the only way in which an absorber may be utilized to protect color. If an absorber is present in an unpigmented coating applied to a clear glass or plastic container or if an absorber is present in the body of a clear plastic container, it can exert a screening action on ultraviolet radiation and, by preventing passage of this

Table V
Ext. D&C Green No. 1

UV Absorber	UV Abs. Conc. (wt %)	Color After x Hr Fadeometer Exposure				
		0	16	28	40	51
	0	vlG	X			
Uvinul 400	0.05	vlG	—	—	X	
	0.1	vlG	—	vvlG	X	
	0.2	vlG	—	vvlG	X	
Uvinul M-40	0.05	vlG	—	—	X	
	0.1	vlG	—	—	—	X
	0.2	vlG	—	—	—	vvlG
Uvinul D-49	0.05	vlG	—	—	—	vvlG
	0.1	vlG	—	—	—	vvlG
	0.2	vlG	—	—	—	lYG,p
Uvinul 490	0.05	vlG	—	—	—	vvlG
	0.1	vlsYG	—	—	—	vvlsYG
	0.2	lYG	—	—	—	vlGY
Uvinul D-50	0.05	vlGY	—	—	—	vvlGY
	0.1	vlsGY	—	—	—	vvlGY
	0.2	lGY	—	—	—	lY
Uvinul N-35	0.05	vlG	—	X		
	0.1	vlG	—	vvlG	X	
	0.2	vlG	—	vvlG	X	
Uvinul N-539	0.05	vlG	—	X		
	0.1	vlG	vvlG	X		
	0.2	vlG	—	vvlG	X	
Uvinul MS-40	0.05	vlPT	Not exposed			
	0.1	lPT				
	0.2	PT				

Dye conc.—0.001 wt %. Solvent—90 SDA-40 + 10 H_2O by wt.

Table VI
D&C Green No. 5

UV Absorber	UV Abs. Conc. (wt %)	Color After *x* Hr Fadeometer Exposure						
		0	8	16	28	40	137	156
...	0	lB	—	—	vvlB	X		
Uvinul 400	0.05	lB	—	—	—	—	—	vlB
	0.1	lB	—	—	—	—	—	nc
	0.2	lB	—	—	—	—	—	vlB
Uvinul M-40	0.05	lB	—	—	—	—	vvlB	X
	0.1	lB	—	—	—	—	—	vlB
	0.2	lB	—	—	—	—	—	vlB
Uvinul D-49	0.05	lB	—	—	—	—	—	vvlB
	0.1	vsGB	—	—	—	—	—	vlGB,p
	0.2	lvsGB	—	—	—	—	—	vvlB,p
Uvinul 490	0.05	vsGB	—	—	—	—	vvlGB	X
	0.1	sGB	—	—	—	—	vlGB	X
	0.2	lsGB	—	—	—	—	—	vlGY
Uvinul D-50	0.05	GB	—	—	—	—	—	nc
	0.1	BG	—	—	—	—	—	vsYG
	0.2	lG	—	—	—	—	—	lsYG
Uvinul N-35	0.05	lB	—	vvlB	X			
	0.1	lB	—	vvlB	X			
	0.2	lB	—	vlB	X			
Uvinul N-539	0.05	lB	vlB	X				
	0.1	lB	—	X				
	0.2	lB	vlB	X				
Uvinul MS-40	0.05	vvlP	Not exposed					
	0.1	vlP						
	0.2	vlP						

Dye conc.—0.001 wt %. Solvent—90 SDA-40 + 10 H_2O by wt.

Table VII
D&C Green No. 8

UV Absorber	UV Abs. Conc. (wt %)	Color After *x* Hr Fadeometer Exposure					
		0	4	8	16	28	160
...	0	YG	vlYG	X			
Uvinul MS-40	0.05	vvlG	Not exposed				
	0.1	X					
	0.2	X					
Uvinul DS-49	0.05	YG	—	vlGY	—	X	
	0.1	mYG	—	—	vlY	—	X
	0.2	lGY	—	—	vlY	—	X

Dye conc.—0.001 wt %. Solvent—H_2O.

radiation through the container, effectively protect the color of the contents. To illustrate, three certified colors, FD&C Blue No. 1, D&C Green No. 8, and FD&C Red No. 3, in the form of 0.001% by weight solutions in distilled water were packaged in 2 oz clear flint glass bottles which had been coated with a 0.5 mil thick film of an unpigmented vinyl-acrylic lacquer* containing various amounts of three

* Stay-Bright vinyl-acrylic lacquer, Crown Coatings Co., Inc., 85 Fifth Ave., Paterson, N. J.

Table VIII
FD&C Yellow No. 5

UV Absorber	UV Abs. Conc. (wt %)	Color After x Hr Fadeometer Exposure											
		0	40	52	64	76	88	100	112	186	211	226	256
...	0	dY	—	—	—	Y	—	vlY	X				
Uvinul 400	0.05	mY	—	—	—	—	—	—	—	lY	X		
	0.1	mY	—	—	—	—	—	—	—	—	lY	X	
	0.2	mY	—	—	—	—	—	—	—	—	vlY	X	
Uvinul M-40	0.05	mY	—	—	—	—	—	—	—	—	lY	X	
	0.1	mY	—	—	—	—	—	—	—	—	—	—	vvlY
	0.2	mY	—	—	—	—	—	—	—	—	—	—	vlY
Uvinul D-49	0.05	mY	—	—	—	—	—	—	—	—	vvlY	X	
	0.1	mY	—	—	—	—	—	—	—	—	—	—	l-mY,p
	0.2	mY	—	—	—	—	—	—	—	—	—	—	nc,p
Uvinul 490	0.05	mY	—	—	—	—	—	—	—	—	vvlY	X	
	0.1	mY	—	—	—	—	—	—	—	—	—	—	l-mY
	0.2	mY	—	—	—	—	—	—	—	—	—	—	nc
Uvinul D-50	0.05	mY	—	—	—	—	—	—	—	—	—	—	mY
	0.1	Y	—	—	—	—	—	—	—	—	—	—	nc
	0.2	Y	—	—	—	—	—	—	—	—	—	—	nc
Uvinul N-35	0.05	mY	—	—	vlY	X							
	0.1	mY	—	—	vlY	X							
	0.2	mY	—	—	—	lY	X						
Uvinul N-539	0.05	mY	—	vlY	X								
	0.1	mY	vlY	X									
	0.2	mY	lY	X									
Uvinul MS-40	0.05	mY	—	—	—	—	—	—	—	—	—	vvlY	X
	0.1	mY	—	—	—	—	—	—	—	—	—	—	vvlY
	0.2	l-mY	—	—	—	—	—	—	—	—	—	—	vvlY

Dye conc.—0.001 wt %. Solvent—90 SDA-40 + 10 H_2O by wt.

Table IX
D&C Yellow No. 8

UV Absorber	UV Abs. Conc. (wt %)	Color After x Hr Fadeometer Exposure					
		0	4	8	16	28	40
...	0	Y,Gf	vlY	X			
Uvinul 400	0.05	mY,Gf	lY	vlY	X		
	0.1	lY,Gf	—	—	vvlY	X	
	0.2	vlY,Gf	—	—	vvlY	—	X
Uvinul M-40	0.05	Y, Gf	—	lY	X		
	0.1	dY,Gf	—	—	vvlY	X	
	0.2	Y,Gf	—	—	lY	—	X
Uvinul D-49	0.05	Y,Gf	—	lY	—	vvlY	X
	0.1	dY,Gf	—	—	—	—	vvlY
	0.2	mY,Gf	—	—	—	—	lY
Uvinul 490	0.05	mY,Gf	—	—	—	—	vvlY
	0.1	mY,Gf	—	—	—	—	vvlY
	0.2	vlY,Gf	—	—	—	—	vvlY
Uvinul D-50	0.05	Y,Gf	—	—	—	—	lY
	0.1	dY,Gf	—	—	—	—	vvlY
	0.2	Y,Gf	—	—	—	—	mY
Uvinul N-35	0.05	Y,Gf	vvlY	X			
	0.1	mY,Gf	lY	—	X		
	0.2	mY,Gf	—	vvlY	X		
Uvinul N-539	0.05	Y,Gf	vvlY	X			
	0.1	dY,Gf	vvlY	X			
	0.2	Y,Gf	—	vvlY	X		
Uvinul MS-40	0.05	vlY,Gf	—	—	—	—	vvlY
	0.1	mY,Gf	—	—	—	—	lY
	0.2	dY,Gf	—	—	—	—	lY

Dye conc.—0.005 wt %. Solvent—90 SDA-40 + 10 H_2O by wt.

Table X
FD&C Red No. 3

UV Absorber	UV Abs. Conc. (wt %)	Color After *x* Hr Fadeometer Exposure					
		0	4	8	16	28	40
...	0	P	lP	X			
Uvinul 400	0.05	P	—	—	vlP	X	
	0.1	P	—	—	—	vvlP	X
	0.2	P	—	—	—	vlP	X
Uvinul M-40	0.05	P	—	—	lP	X	
	0.1	P	—	—	—	vvlP	X
	0.2	P	—	—	—	vlP	X
Uvinul D-49	0.05	P	—	—	—	lP	X
	0.1	P	—	—	—	mP	lP
	0.2	P	—	—	—	—	mP
Uvinul 490	0.05	P	—	—	—	vlP	X
	0.1	P	—	—	—	lP	vlTP
	0.2	P	—	—	—	—	mTP
Uvinul D-50	0.05	P	—	—	—	lTP	vvlT
	0.1	sTP	—	—	—	lP	lPT
	0.2	TP	—	—	—	lTP	lPT
Uvinul N-35	0.05	P	—	vlP	X		
	0.1	P	—	lP	X		
	0.2	P	—	lP	X		
Uvinul N-539	0.05	P	—	vvlP	X		
	0.1	P	—	vlP	X		
	0.2	P	—	lP	X		
Uvinul MS-40	0.05	lTP	—	vvlTP	X		
	0.1	lT	—	vvlT	X		
	0.2	lT	vlT	—	X		

Dye conc.—0.001 wt %. Solvent—90 SDA-40 + 10 H_2O by wt.

Table XI
D&C Red No. 17

UV Absorber	UV Abs Conc. (wt %)	Color After *x* Hr Fadeometer Exposure								
		0	49	63	87	103	130	143	157	181
...	0	R	—	—	—	X				
Uvinul 400	0.05	R	—	—	—	—	lP	—	X	
	0.1	R	—	—	—	—	P	—	X	
	0.2	R	—	—	—	—	—	—	—	vlP
Uvinul M-40	0.05	R	—	—	—	—	lR	—	vvlP	X
	0.1	R	—	—	—	—	—	—	P	X
	0.2	R	—	—	—	—	—	—	—	mR
Uvinul D-49	0.05	R	—	—	—	—	—	—	—	mR,p
	0.1	R	—	—	—	—	—	—	—	nc,p
	0.2	R	—	—	—	—	—	—	—	nc,p
Uvinul 490	0.05	R	—	—	—	—	—	—	—	mR
	0.1	R	—	—	—	—	—	—	—	nc
	0.2	R	—	—	—	—	—	—	—	nc
Uvinul D-50	0.05	R	—	—	—	—	—	—	—	nc
	0.1	vsOR	—	—	—	—	—	—	—	nc
	0.2	sOR	—	—	—	—	—	—	—	nc
Uvinul N-35	0.05	R	X							
	0.1	R	X							
	0.2	R	lY	X						
Uvinul N-539	0.05	R	X							
	0.1	R	X							
	0.2	R	X							
Uvinul MS-40	0.05	R	—	—	lP	X				
	0.1	R	—	P	—	X				
	0.2	R	—	—	vlP	X				

Dye conc.—0.001 wt %. Solvent—90 SDA-40 + 10 H_2O by wt.

Table XII
D&C Red No. 19

UV Absorber	UV Abs. Conc. (wt %)	Color After *x* Hr Fadeometer Exposure						
		0	117	134	158	183	326	513
...	0	dP,Yf	—	—	—	P,Yf	X	
Uvinul 400	0.05	dP,Yf	—	—	—	—	—	lP,Of
	0.1	dP,Yf	—	—	—	—	—	lP,Yf
	0.2	dP,Yf	—	—	—	—	—	nc
Uvinul M-40	0.05	dP,Yf	—	—	—	—	—	P,Of
	0.1	dP,Yf	—	—	—	—	—	lP,Yf
	0.2	dP,Yf	—	—	—	—	—	nc
Uvinul D-49	0.05	dP,Yf	—	—	—	—	—	O,Pf,p
	0.1	dP,Yf	—	—	—	—	—	lR,Yf,p
	0.2	dP,Yf	—	—	—	—	—	lR,Yf,p
Uvinul 490	0.05	dP,Yf	—	—	—	—	—	O,Pf
	0.1	dP,Yf	—	—	—	—	—	lR,Yf
	0.2	dP,Yf	—	—	—	—	—	lR,Yf,p
Uvinul D-50	0.05	dP,Yf	—	—	—	—	—	nc
	0.1	dP,Yf	—	—	—	—	—	nc
	0.2	dP,Yf	—	—	—	—	—	lR,Yf
Uvinul N-35	0.05	dP,Yf	vvlP	X				
	0.1	dP,Yf	—	vvlP	X			
	0.2	dP,Yf	—	—	—	P,Yf	X	
Uvinul N-539	0.05	dP,Yf	vvlP	X				
	0.1	dP,Yf	—	vvlP	X			
	0.2	dP,Yf	—	—	vvlP	X		
Uvinul MS-40	0.05	dLP,Yf	—	—	—	—	—	lO,sf
	0.1	dLP,Yf	—	—	—	—	—	vlP,Yf
	0.2	dLP,Yf	—	—	—	—	—	lP,Yf

Dye conc.—0.001 wt %. Solvent—90 SDA-40 + 10 H_2O by wt.

Table XIII
D&C Red No. 22

UV Absorber	UV Abs. Conc. (wt %)	Color After *x* Hr Fadeometer Exposure				
		0	8	16	28	40
...	0	P,Yf	—	—	vvlP	X
Uvinul 400	0.05	P,Yf	—	—	vvlP	X
	0.1	P,Yf	—	—	lP,Yf	X
	0.2	P,Yf	—	—	—	vlP,Yf
Uvinul M-40	0.05	P,Yf	—	—	vvlP	X
	0.1	P,Yf	—	—	vlP,Yf	X
	0.2	P,Yf	—	—	—	vlP,Yf
Uvinul D-49	0.05	P,Yf	—	—	—	lP,Yf
	0.1	P,Yf	—	—	—	nc
	0.2	P,Yf	—	—	—	nc
Uvinul 490	0.05	P,Yf	—	—	—	lP,Yf
	0.1	P,Yf	—	—	—	mP,Yf
	0.2	P,Yf	—	—	—	nc
Uvinul D-50	0.05	P,Yf	—	—	—	mP,Yf
	0.1	sOP,Yf	—	—	—	vsOP,Yf
	0.2	OP,Yf	—	—	—	mOP,Yf
Uvinul N-35	0.05	P,Yf	LP,Yf	X		
	0.1	P,Yf	LP,Yf	X		
	0.2	P,Yf	—	vvlPL	X	
Uvinul N-539	0.05	P,Yf	lLP,Yf	X		
	0.1	P,Yf	LP,Yf	X		
	0.2	P,Yf	mP,Yf	X		
Uvinul MS-40	0.05	vvlT	X			
	0.1	vvlT	X			
	0.2	vlT	X			

Dye conc.—0.001 wt %. Solvent—90 SDA-40 + 10 H_2O by wt.

Table XIV
Uvinul DS-49

Certified Color	UV Abs. Conc. (wt %)	Color After *x* Hr Fadeometer Exposure											
		0	8	28	40	51	132	156	181	219	256	326	513
D&C Violet No. 2	0	dL	—	—	—	—	mL	vlL,sp					
	0.05	dL	—	—	—	—	—	l–mL,p					
	0.1	dL	—	—	—	—	—	mL,p					
	0.2	lB (dye ppts.)	BL	PL	—	—	—	mPL,p					
FD&C Blue No. 1	0	B	—	—	—	—	—	—	—	mB			
	0.05	B	—	—	—	—	—	—	—	B,sp			
	0.1	sGB	—	—	—	—	—	—	—	B,p			
	0.2	GB	—	—	—	—	—	—	—	B,p			
Ext. D&C Green No. 1	0	vlG	—	vvlG	X								
	0.05	vlYG	—	—	—	vvlYG,sp							
	0.1	vlYG	—	—	—	nc, p							
	0.2	GY	—	—	—	lGY,p							
D&C Green No. 5	0	lB	—	—	—	—	—	nc					
	0.05	lGB	—	—	—	—	—	nc					
	0.1	lBG	—	—	—	—	—	lB					
	0.2	lYG	—	—	—	—	—	lB,p					
FD&C Yellow No. 5	0	dY	—	—	—	—	—	—	—	—	Y		
	0.05	dY	—	—	—	—	—	—	—	—	Y		
	0.1	dY	—	—	—	—	—	—	—	—	Y,p		
	0.2	dY	—	—	—	—	—	—	—	—	Y,p		
D&C Yellow No. 8	0	dY,Gf	—	Y,Gf	lY,Gf								
	0.05	dY,Gf	—	—	Y,Gf								
	0.1	dY,Gf	—	—	Y,p,Gf								
	0.2	dY,Gf	—	—	nc,p								
FD&C Red No. 3	0	P	—	vvlP	X								
	0.05	P	—	—	vlP								
	0.1	PO	—	—	lP								
	0.2	PO	—	—	lP								

D&C Red No. 17	0	P	—	—	—	—	—	—	dP				
	0.05	lOT	P	—	—	—	—	—	dP,Rp				
	0.1	OT	—	P	—	—	—	—	—	—	—	P,Rp	
	0.2	dOT	—	—	—	P	—	—	P,Rp				
D&C Red No. 19	0	dP,Yf	—	—	—	—	—	—	—	—	—	vlP,Yf	lYG
	0.05	dP,Yf	—	—	—	—	—	—	—	—	—	—	nc,p
	0.1	dP,Yf	—	—	—	—	—	—	—	—	—	—	nc,p
	0.2	dTP,Yf	—	—	—	—	—	—	—	—	—	—	dP,p,Yf
D&C Red No. 22	0	lP,Yf	—	—	nc								
	0.05	sOP,Gf	—	—	nc,sp								
	0.1	OP,Gf	—	—	nc,p								
	0.2	PO,Gf	10P,Gf	—	10P,Gf,p								

Dye conc.—0.001 wt % (except D. & C. Yellow No. 8—0.005 wt %). Solvent—50 SDA-40 + 50 H_2O by wt.

Table XV
Bottle Coatings Containing UV Absorbers

UV Absorber in Coating	UV Abs. Conc. (pph on Solids)	Color After *x* Hr Fadeometer Exposure											
		0	133	159	175	192	210	241	253	346	360	395	501
...	0	dB	lL	lY	X								
Uvinul 400	3	dB	—	—	—	—	—	mB	X				
	5	dB	—	—	—	—	—	—	—	mB,Lt	L	X	
	10	dB	—	—	—	—	—	—	—	—	—	X	
Uvinul 490	3	dB	—	—	—	—	—	—	—	—	—	—	nc
	5	dB	—	—	—	—	—	—	—	—	—	—	nc
	10	dB	—	—	—	—	—	—	—	—	—	—	nc
Uvinul N-35	3	dB	—	—	mB	X							
	5	dB	—	—	—	vvlB	X						
	10	dB	—	—	vvlB	X							

Dye—FD&C Blue No. 1. Dye conc.—0.001% by wt in H_2O.

different UV absorbers. The filled bottles were then exposed in an Atlas Model FDA-R single carbon arc Fadeometer operating at a 145°F black panel temperature until significant changes in color were observed. The absorbers employed were Uvinul 400, Uvinul 490, and Uvinul N-35 at 3.0, 5.0, and 10.0% by weight based on coating solids. The coating was selected on the basis of its known excellent resistance

Table XVI
Bottle Coatings Containing UV Absorbers

UV Absorber in Coating	UV Abs. Conc. (pph on Solids)	Color After x Hr Fadeometer Exposure					
		0	12	23	40	52	69
...	0	dP	lT	Y	lY		
Uvinul 400	3	dP	lP	Y	lY		
	5	dP	lP	Y	lY		
	10	dP	l–mP	Y	lY		
Uvinul 490	3	dP	—	lP	—	vlT	lY
	5	dP	—	l–mP	—	vlP	vlT
	10	dP	—	mP	—	lP	vlP
Uvinul N-35	3	dP	lPT	Y	lY		
	5	dP	lPT	Y	lY		
	10	dP	lPT	Y	lY		

Dye—PFD&C Red No. 3. Dye conc.—0.001% by wt in H_2O.

Table XVII
Bottle Coatings Containing UV Absorbers

UV Absorber in Coating	UV Abs. Conc. (pph on Solids)	Color After x Hr Fadeometer Exposure					
		0	12	23	40	52	69
...	0	YG,f	lGY,f	Y	—	vlY	X
Uvinul 400	3	YG,f	lGY,f	Y	—	vlY	X
	5	YG,f	lGY,f	Y	—	vlY	X
	10	YG,f	—	vlGY,f	lY	—	vlY
Uvinul 490	3	YG,f	—	—	vlGY	vvlGY	lY
	5	YG,f	—	—	—	vlGY,f	vvl,GY
	10	YG,f	—	—	—	—	lGY,f
Uvinul N-35	3	YG,f	lGY,f	Y	—	vlY	X
	5	YG,f	lGY,f	Y	—	vlY	X
	10	YG,f	lGY,f	Y	—	vlY	X

Dye—D&C Green No. 8. Dye conc.—0.001% by wt in H_2O.

to ultraviolet radiation and its transparency to ultraviolet between 290 and 400 mμ. Table XV, XVI, and XVII show the results of testing. From these tables it can be seen that incorporating a UV absorber into the bottle coating protects the three dye solutions from color fading As with the method in which the absorber is present in the dye solution, the degree of protection is dependent upon the particular dye employed, the absorber used, and the concentration of the absorber. Uvinul

490, a near UV absorber, gives the best results with all three colors; Uvinul 400 is second best; Uvinul N-35, absorbing farthest down the ultraviolet spectrum, is poorest.

Summary and Discussion

Having demonstrated the general utility of UV absorbers in protecting cosmetic colors, the question arises as to which method of employment is best. Actually it is better to consider both methods as different possible approaches to achieve the same end. Dependent on the particular set of circumstances, one method may be the only satisfactory means and, even if either method will work, other factors than performance, such as cost, may determine selection. Keeping this in mind, the following example of comparative performance in one specific instance is cited. Individual 2 oz clear flint glass bottles were given single coats (0.5 mil dry film thickness) of vinyl-acrylic lacquer containing 3.0, 5.0, and 10.0 pph by weight based on lacquer solids of Uvinul M-40, Uvinul D-49, and Uvinul N-35. Ten pph was taken as an absorber concentration approaching the upper practical limits for use in a coating. The bottles were filled with a 0.001% by weight solution of FD&C Red No. 3 colorant in 90/10 SDA-40 ethanol plus water. Into uncoated bottles of the same type were placed samples of the same dye solution containing 0.2% by weight of Uvinul M-40, Uvinul D-49, and Uvinul N-35, respectively. A concentration of 0.2% of absorber was known to be the maximum level of Uvinul D-49 employable without producing serious initial discoloration of the dye solution. These specimens, together with controls consisting of unmodified dye solution in uncoated bottles, were exposed simultaneously to natural sunlight outdoors until significant visual changes in appearance had occurred. The results given in Table XVIII show that, under the conditions of this particular experiment, Uvinul M-40 and Uvinul D-49 afford better protection when incorporated into the dye solution while Uvinul N-35, due to its sensitizing action on the dye, is better when used in the bottle coating. The results with respect to Uvinul M-40 and Uvinul D-49 are not surprising when it is realized that the actual weight of absorber present in the dye solution contained in the 2 oz bottle employed in the test is approximately four times greater than the weight of absorber present in the 0.5 ml thick coating applied over the entire outer surface of the same bottle. The difference in degree of protection, offered by the two methods could be narrowed by increasing the weight of absorber in the coating either through higher

Table XVIII
UV Absorbers in Bottle Coating *vs.* UV Absorbers in Dye Solution

UV Absorber	UV Abs. Conc. in coating (pph on Solids)	Abs. Conc. in Dye Soln. (wt %)	Color After *x* Hr Natural Sunlight Exposure					
			0	2	3	4	5	8
Uvinul M-40	3	—	dP	—	—	vvlP		
Uvinul M-40	5	—	dP	—	—	vvlP		
Uvinul M-40	10	—	dP	—	—	vlP		
Uvinul M-40	—	0.2	dP	—	—	P	—	lP
—	0	0	dP	P	lP	vvlP	X	
Uvinul D-49	3	—	dP	—	—	lP	—	lP
Uvinul D-49	5	—	dP	—	—	lP	—	lP
Uvinul D-49	10	—	dP	—	—	lP	—	lP
Uvinul D-49	—	0.2	dP,sOc	—	—	P,sOc	—	mP,Oc
—	0	0	dP	P	lP	vvlP	X	
Uvinul N-35	3	—	dP	—	—	vvlP		
Uvinul N-35	5	—	dP	—	—	vvlP		
Uvinul N-35	10	—	dP	—	—	vlP		
Uvinul N-35	—	0.2	dP	lP	vvlP	X		
	0	0	dP	P	lP	vvlP	X	

Dye—FD&C Red No. 3. Dye conc.—0.001% by wt in 90 SDA-40 + 10 H_2O.

absorber concentration or by applying a thicker film; however, there are obvious practical and economic limitations to both approaches.

In summary, it has been demonstrated that UV absorbers will protect many of the certified colors used in cosmetic products against light induced fading. In general, near-UV absorbers are more effective in this respect than absorbers exhibiting peak absorbance farther down the ultraviolet spectrum, although exceptions do exist. The relative performance of nine different UV absorbers used in conjunction with eleven certified colors has been shown. Finally, the two methods of employing UV absorbers to protect the colors of cosmetic products have been described and their advantages and disadvantages pointed out.

Acknowledgments

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Book Reviews

TECHNIQUES FOR EFFICIENT RESEARCH, edited by Lewis E. Lloyd, Chemical Publishing Co., Inc., New York, 1966. 210 pages, indexed. Price $8.50.

This book is described by the author as a "do-it-yourself" manual for self improvement in the selection of problems and in solving them. The examples are taken largely from the chemical industry, but the principles are intended for broad application to all types of problems.

The introduction, Chapter 1, presents (a) total expenditures for research and development in the United States for the past forty years, (b) sources of funds and (c) numbers of research personnel in industrial laboratories. The need for efficient research is thus made evident.

Chapters 2, 3, 4 and 5 are concerned primarily with problem solving—the researcher's responsibility. A method of solving problems, creative thinking, the reporting of results of research, and training the researcher are considered.

Management's problems and responsibility are presented in Chapters 6 to 11, inclusive. The subject matter covered includes selecting the problem, selecting the researcher, organization of the research, morale and motivation, communication and equipment for research. Each chapter includes selected references which cover in more detail the specific topic involved.

This book, written concisely and avoiding obscure phraseology, is not pedantic nor academic. It is a highly readable, personalized and practical presentation emphasizing the need to go beyond the statement of objectives in research to a consideration of how to attain the objectives. For research or management neophytes, the book is well worth reading. For experienced scientists or management, it should be a stimulating review of the principles involved in attaining efficient research.—SOL D. GERSHON—Lever Bros. Research Center.

TOXICITY AND METABOLISM OF INDUSTRIAL SOLVENTS by Ethel Browning, Elsevier Publishing Company, New York, 1965. 739 pages, indexed. Price $32.50.

This edition, in the author's words, "does not represent a third edition of the former book. It is a completely new appraisal of the present position

of the principal industrial solvents now in use." Compared to the last edition, it is twice as large, indicating the tremendous number of newer compounds in everyday industrial use and the increase in the toxicologist's knowledge of the dangers of these compounds.

Each chapter describes the activities of a group of closely related and structurally similar compounds. For each individual chemical a standard format is followed which concisely describes all available (to the author) knowledge of its activity, both physical and biological. The headings of each section, biochemistry and toxicology, indicate the main theme of the work. Under biochemistry there are methods and references; the methods described are those for quantitatively estimating the content of the material under discussion in air as well as in body fluids. The metabolism of each compound is also described, both in animals and in man.

As is to be expected, the larger portion of each description is to be found under the heading of toxicology. Here the acute and chronic activity of each compound is given, and human response to intoxication is noted. This portion of each description is fully documented, including a complete group of references at the end of each chapter.

The format of the book is clear and concise and can be used to check quickly the current extent of our knowledge of the toxic reaction resulting from exposure to the most commonly used industrial solvents. It is a valuable reference, well executed, and has a place in the library of those responsible for the area of industrial hygiene in research and manufacturing.—I. LEVENSTEIN—Leberco Laboratories.

COMPREHENSIVE BIOCHEMISTRY, VOLUME 16, HYDROLYTIC REACTIONS COBAMIDE AND BIOTIN COENZYMES, edited by Marcel Florkin and Elmer H. Stotz, Elsevier Publishing Co., Amsterdam, London, New York. 1966. 267 pages, indexed. Price $14.

For those interested in hydrolytic enzymes this volume will not only serve as an up-to-date review of the field but also as an excellent reference source.

The first two chapters concern the cholinesterase, esterase, lipase and phosphatase enzymes. The material is covered so that the enzymes in each class are briefly reviewed, along with their properties and the hydrolytic reactions they catalyze. Emphasis is also placed on discussions of the reactive sites in several of the enzymes and their mechanism of action.

The major chapter in this volume deals with the structure and mechanism of action of proteolytic enzymes. In this review (covering some 90 pages with over 350 references) the author attempts to discuss in detail only one or two of the proteases from each of the major classifications rather than review the large number of individual proteases that have been

described in the literature. The current state of knowledge with regard to the amino acid sequence of several proteases is given. This is related in detail to the present theories concerning the active sites in the protein and the mechanism of action of proteases. The rapidly expanding field of relating the catalytic action of enzymes to modern organic chemical reaction mechanism is also ably covered.

The second part of this volume contains a brief chapter on the cobamide coenzymes which covers the structure, general properties, and biological reactions involving the B_{12} coenzymes.

Also included in this volume is an excellent chapter reviewing the carboxylase enzymes and the role of biotin as a carbon dioxide carrier in these enzyme systems.—K. LADEN—Gillette Medical Research Institute.

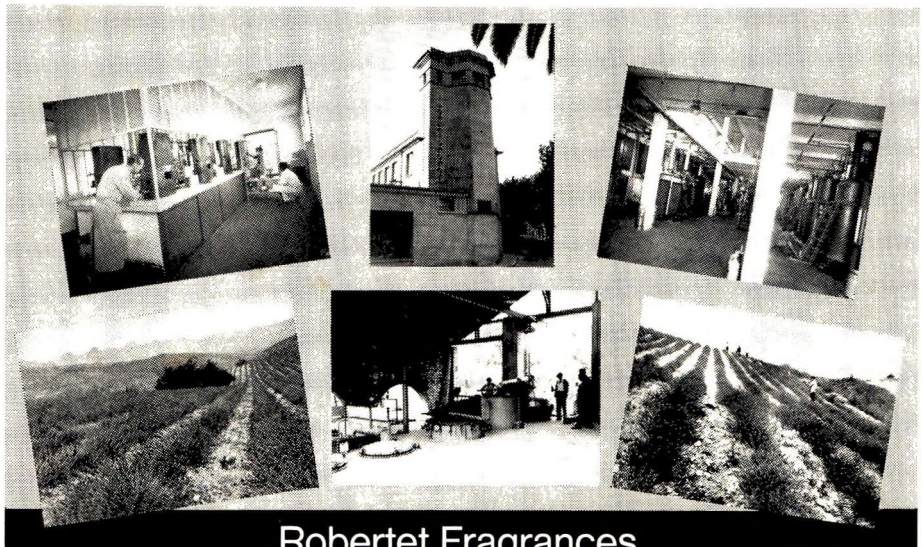
ADVANCES IN CHROMATOGRAPHY—VOLUME I, edited by J. Calvin Giddings and Roy A. Keller, Marcel Dekker Inc., New York. 392 pages, illustrated and indexed. Price $14.50.

This book has been designated, according to the introduction, as Volume 1 of a comprehensive review of the field of chromatography. Research in this field has grown at such a rapid pace that it is nearly impossible for an individual chemist to follow effectively all the original research papers being published. Most of the other reviews available are outdated or cover only a small aspect of the field of chromatography. The need for a comprehensive up-to-date review is obvious and judging from the first volume, this series will effectively perform that function.

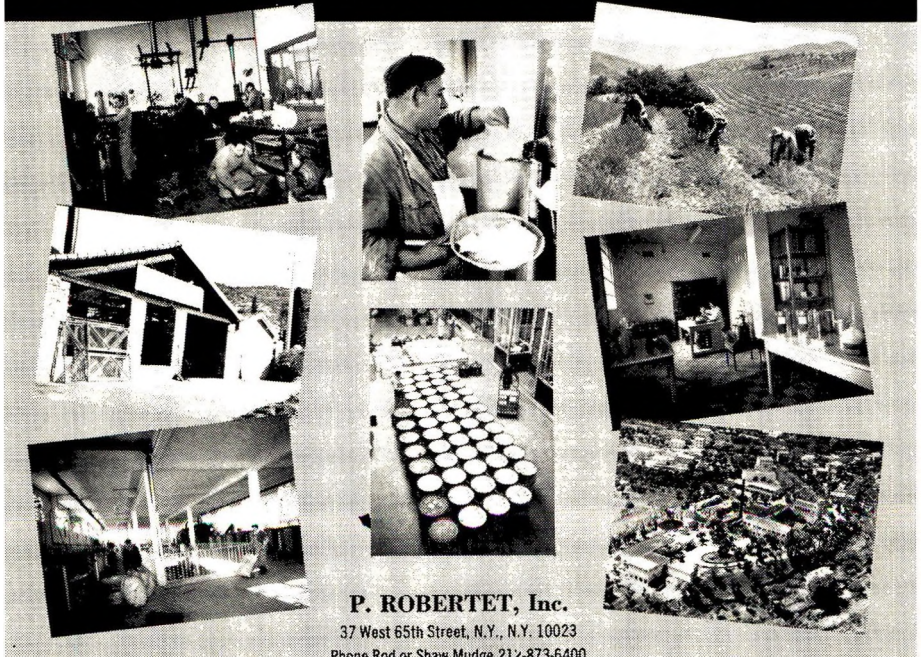
The book is divided into two parts: General Chromatography and Gas Chromatography. The first section includes chapters on thin layer, paper, and ion-exchange chromatography. The second section, of approximately equal length, is devoted entirely to the subject of gas chromatography. This part covers research in steroid analysis, use of capillary columns, lightly loaded columns, and many of the most recent advances in gas chromatography.

The section on the teaching of chromatography and electrophoresis is unique. While it is not directly applicable to the interest of most readers, it should be an invaluable aid to the teacher of chemistry. The information contained in the chapters on the Kovats Retention Index System and Inorganic Gas Chromatography are probably less familiar to most readers than many of the other subjects covered. The treatment of these two areas is excellent and appears to be of particular value.

The book is well organized and clearly written. It contains excellent theoretical treatments of the various fields of chromatography and provides an excellent bibliography for practical applications. These volumes should serve as an invaluable reference work for any researcher who has an interest in the field of chromatography.—R. SUFFIS—The Mennen Company.



Robertet Fragrances
are also backed up by this kind of a commitment



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