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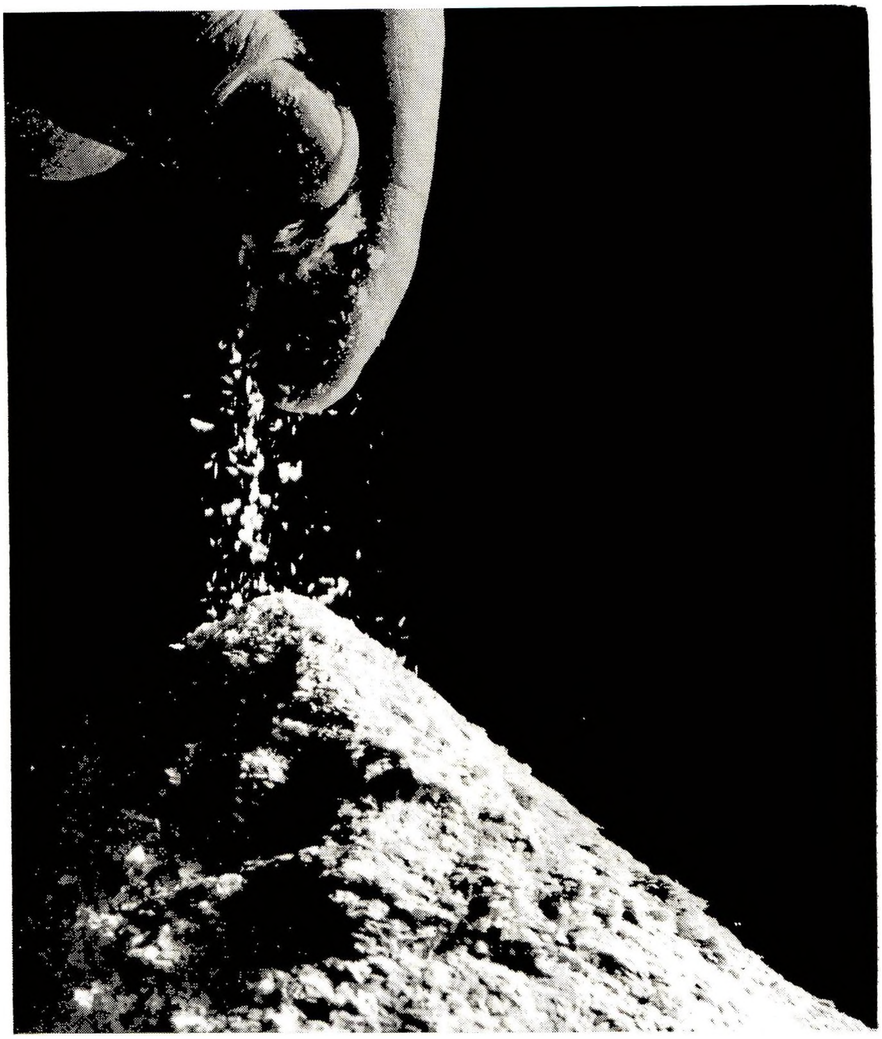

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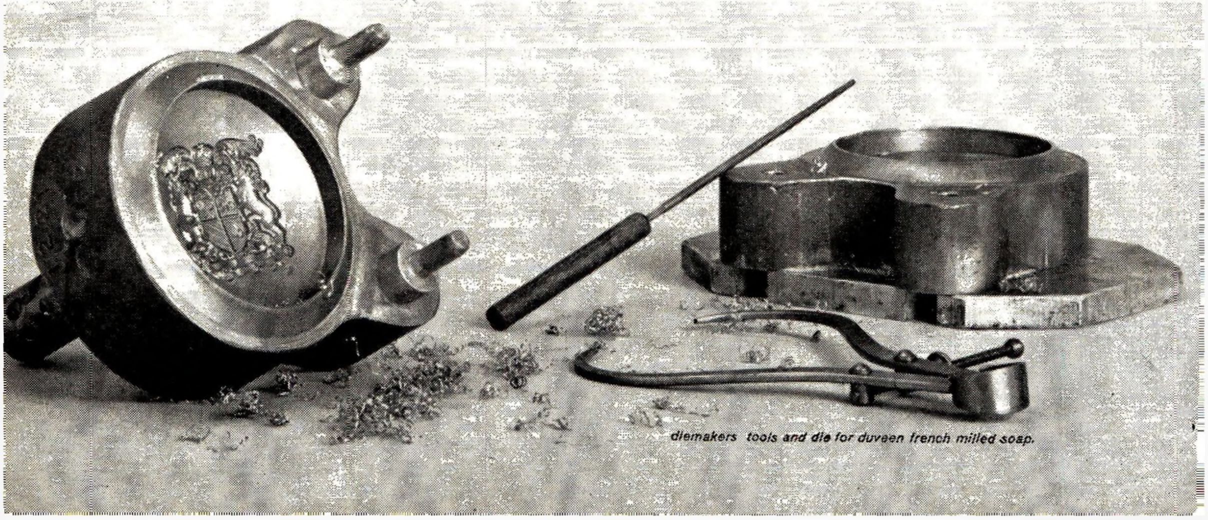

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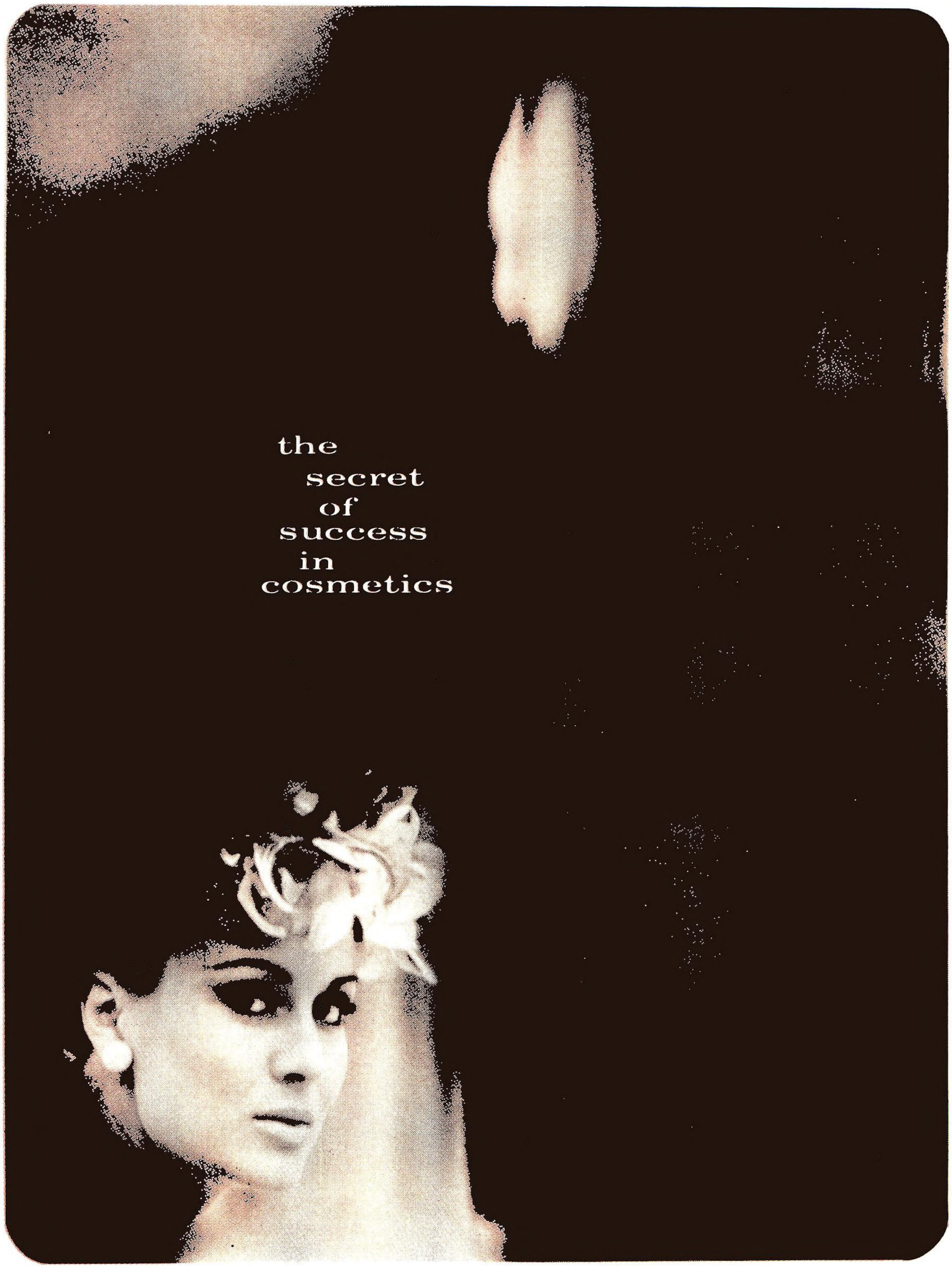
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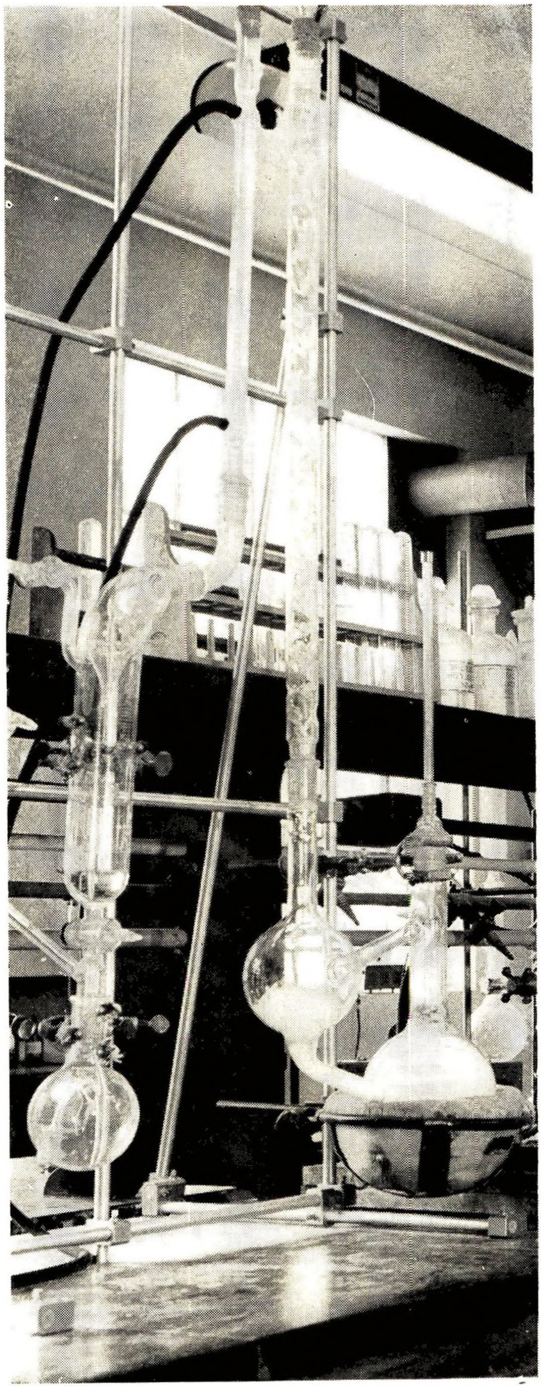

SYNOPSES FOR CARD INDEXES

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

Torsional properties of hair in relation to permanent waving and setting: Herman Bogaty. *Journal of the Society of Cosmetic Chemists* **18,** 575 (Sept. 16, 1967)

Synopsis—Hair on the head frequently exhibits the form of a helical coil. The physics of ideal coils are described; the performance of hair curls in the waving and setting context is qualitatively analogous to the engineering spring theory in respect to the effects of fiber diameter, coil radius, and torsional stiffness of the hair. Torsional properties of waved and unwaved single fibers were studied by two methods and over a wide range of humidities; results are given. Torsional stiffness and mechanical creep of hair are shown to be very sensitive to moisture. Predictions from spring theory are in general agreement with experience with hair, although the complex geometry of a hair coil and the deviation of hair from ideal elastic behavior prevent a quantitative treatment.

Effect of process variables on the stability of some specific emulsions: H. E. Jass. *Journal of the Society of Cosmetic Chemists* **18,** 591 (Sept. 16, 1967)

Synopsis—Three case histories of cosmetic emulsion problems involving rheological and emulsion deterioration with time are described. Despite considerable variation in emulsion type, the three demonstrated similar changes which are traced to changes in the physical state of the crystalline viscosity builders, primarily glyceryl monostearate. It is shown how changes in processing and formulation were able to arrest these changes and stabilize the product. The role of photomicrography in helping to analyze the problem and in predicting the results of experiments is demonstrated.

The effect of pH on the sorption of collagen-derived peptides by hair: S. A. Karjala, A. Karler, and J. E. Williamson. *Journal of the Society of Cosmetic Chemists* **18,** 599 (Sept. 16, 1967)

Synopsis—Sorption of peptides increases very rapidly during the first few minutes to ½ hr of peroxide or thioglycolate treatment, after which sorption is essentially constant for a period, increasing rapidly again as the hair is damaged more extensively. The conclusion is drawn that the first action is on the cuticle, which is readily removed by chemical treatment, and that increased sorption occurs, after removal of the cuticle, only after extensive damage to the cortex. Oxidizing agents cause a maximum sorption of peptide at neutral pH values, while thioglycolate causes maximum sorption at high pH levels. Sorption appears to be an equilibrium phenomenon governed by the pH value of the peptide solution.

Hair coloring with oxidation dye intermediates: Harold H. Tucker. *Journal of the Society of Cosmetic Chemists* **18,** 609 (Sept. 16, 1967)

Synopsis—Data on patents for 33 primary intermediates and 20 color modifiers were collected from the literature. The effect of structure on shade, depth of color, light fastness, and solubility was determined for each product. The effect on color, depth of shade, and light fastness of dyeing mixtures of each of the 20 color modifiers with equimolar quantities of 3 primary intermediates is reported. It is shown that by proper selection of color modifier the shade may be varied, the depth of color greatly increased, the fastness to light increased many fold, and the tendency to turn red on aging decreased.

By using the formation of Bandrowski's base from oxidation of *p*-phenylenediamine as a tool the percentage of conversion to the colored form was shown to be only slightly more than 5% under the conditions normally used for dyeing hair. The effect of various factors on this yield is reported.

The results of using five recently described pyridine derivatives are tabulated and discussed.

A comparison of the bacterial and yeast flora of the human scalp and their effect upon dandruff production: Raymond W. VanderWyk and Karim E. Hechemy. *Journal of the Society of Cosmetic Chemists* **18,** 629 (Sept. 16, 1967)

Synopsis—A half-head experiment was carried out on 10 subjects. Through the application of yeast-inhibiting or bacteria-inhibiting antibiotics to either side of the human scalp, the effect upon dandruff was determined. Samples of dandruff scales (scurf) were removed separately from each side with an Oster HairVac and the weights determined. During a 91-day experiment it was shown that a reduction of the yeast flora was more effective in controlling dandruff than was a reduction in the number of bacteria.

LITERATURE SURVEY*

Analytical

Determination of Soap in Detergents. Heinerth, E., *Tenside*, **4,** 45–47 (1967).

Gas-Chromatographic Methods for the Determination of Aromatic Diamines in Hair Dyes. Pinter, I., and Kramer, M., *Parfum Kosmetik*, **48,** 126–28 (May, 1967).

Uncombined Intermediates in FD&C Blue No. 1. Johnson, R. K., *J. Assoc., Off. Anal. Chem.*, **50,** 526–30 (June, 1967).

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Determination of Terminal Hydroxyl Groups in Polyethyleneoxy Compounds. Han, K. W., *Analyst*, **92,** 316–18 (May, 1967).

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Low Temperature Fluorescence Detection of Organic Compounds on Thin Layer Chromatograms. Chou, J. S. T., and Lawrence, B. M., *J. Chromatog.*, **27,** 279–81 (March, 1967).

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* Prepared by J. H. Kratochvil and H. Feinberg.

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Obituary

Dr. Kenneth L. Russell, consulting chemist who was director of toilet articles research for the Colgate-Palmolive Co. until 1960, died in Montclair, N. J., on May 26, 1967, after a long illness. Born in 1910 in Youngsville, Pa., Dr. Russell graduated from Lebanon Valley College in Annville, Pa. He received his Masters degree in 1934 and his Ph.D. in 1936 from New York University Graduate School in organic chemistry. He was the author of several U. S. patents and their foreign equivalents and published numerous scientific papers. He was a member of the A.C.S., A.A.A.S., A.I.C., N. Y. Academy of Science, Chemists' Club, the S.C.C., and Sigma Xi.

Ken, who leaves his wife, Polly, and a daughter, Ann, at home (a son, James, was killed in an auto accident last October), was president of the Society of Cosmetic Chemists in 1955. He also served the S.C.C. as program chairman in 1950, director in 1953 and a member of the executive committee from 1954–60. Ken's passing is a major loss to the Society, to the cosmetic industry, and to all who were associated with him.

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J. Soc. Cosmetic Chemists, **18**, 575–589 (Sept. 16, 1967)

Torsional Properties of Hair in Relation to Permanent Waving and Setting

HERMAN BOGATY, B.S.*

Presented November 30, 1966, New York City

Synopsis—Hair on the head frequently exhibits the form of a helical coil. The physics of ideal coils are described; the performance of hair curls in the waving and setting context is qualitatively analogous to the engineering spring theory in respect to the effects of fiber diameter, coil radius, and torsional stiffness of the hair. Torsional properties of waved and unwaved single fibers were studied by two methods and over a wide range of humidities; results are given. Torsional stiffness and mechanical creep of hair are shown to be very sensitive to moisture. Predictions from spring theory are in general agreement with experience with hair, although the complex geometry of a hair coil and the deviation of hair from ideal elastic behavior prevent a quantitative treatment.

INTRODUCTION

A considerable amount of scientific progress has been made in the understanding of hair as a chemical and biological material, and a good deal of this knowledge has been utilized in sound technological developments such as permanent waving. While the chemist has undertaken to study hair waving in terms of chemical reactions, the consumer has practiced it widely because of the desirable alteration in physical properties in producing an effective foundation for setting and styling and for enhancing the physical stability of her style.

This paper presents one means for viewing the physics of some aspects of the waving and setting process. It is intended to suggest that

* The Toni Co., Chicago, Ill. 60654.

Figure 1. Photograph showing detail of hair tresses in the front hair line in a spiral coil arrangement immediately following permanent waving

women's hair frequently assumes a helical coil configuration in the course of its being permanent waved, set, and combed into style. It will be further implied that hair assemblies in helical form can be treated qualitatively in terms of a classical physical model and that predictions of behavior based on this model fit moderately well with the observed behavior. Finally, since consideration of fibers in helical form involve physical properties in torsion, some measurements of the torsional stiffness and creep of single fibers are reported under various test conditions.

Observations of Hair on the Head

Let us first examine the process of wrapping hair on a rod for a permanent-waving treatment. The hair is arrayed with the fibers parallel in the form of a little tress. When it is wound in a cylindrical form around a waving rod bending forces are applied. When the rod is removed at the conclusion of the waving process the tip end of the hair hangs free and the hair tress is converted thereby into a helical coil. This results in the development of shear or torsional forces in the individual fibers. The coil arrangement can very easily be seen by looking at the heads of women just at the completion of the waving procedure. Figure 1 is a photograph of the typical arrangement of women's hair just after removal of the rods in a permanent-waving process. The helical coils and spiral arrangement of the groups of fibers are very evident. Spiral coils like these in permanent waved hair are also seen in naturally curly and wavy hair. Coils of varying degrees of regu-

Figure 2. Photograph of a hair style produced by setting the waved hair in the front hair line on rollers with water and drying. The detail illustrates the helical arrangement of the style.

larity can often be observed by wetting out single fibers of naturally wavy hair and floating them freely on the surface of water in a large container.

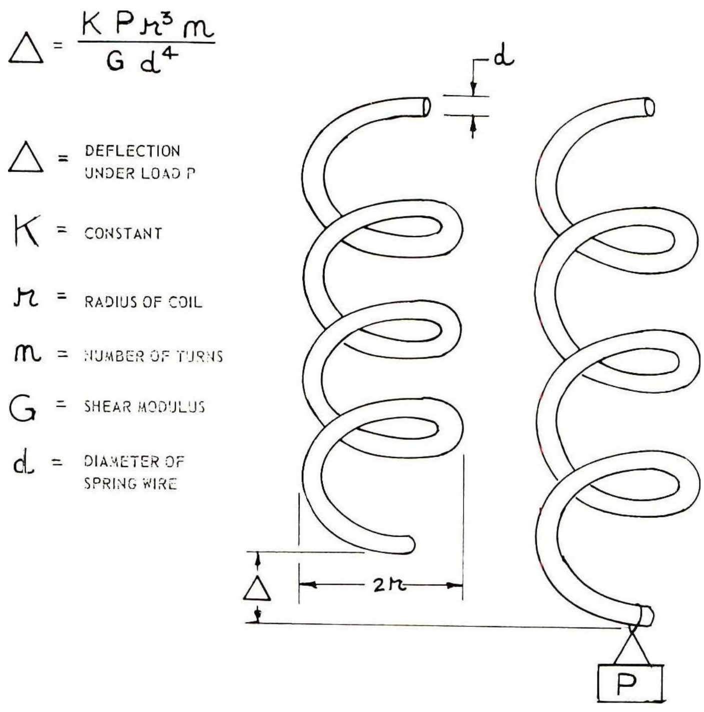
A similar situation is obtained when one looks at hair just after removal of setting or styling rollers, or after the hair tresses have been set into pin curls and combed out. Here, also, one typically finds the helical coil arrangements, as shown in Fig. 2. These photographs illustrate the tendency to coil formation of hair tresses in setting, as in certain style configurations desired by some consumers.

This evidence permits us to assert, therefore, that in several of the very common operations women employ in dealing with their hair it is usual to find the fibers arranged in the form of helices. It is now proposed to discuss the behavior of typical helical tresses by examining the characteristics of a mechanical spring for which a good deal of the theory has been developed.

A Mechanical Spring Model and Fiber Torsion

Classical physics has treated the mechanical behavior of springs (1, 2). The deflection or extension of a helical spring coil under axial loading is generally given by the following equation:

$$\Delta = \frac{KPr^3n}{Gd^4} \tag{1}$$



A MECHANICAL SPRING MODEL SHOWING THE VARIABLES INVOLVED IN THE EXTENSION OF A COIL UNDER LOAD.

Figure 3

where:

Δ = deflection
K = proportionality constant
P = axial load
r = radius of the spring
n = number of coils
G = shear or torsional modulus
d = diameter of the wire composing the spring

The sketch shown in Fig. 3 illustrates the key variables. It is important to emphasize the conditions under which this theoretical relationship holds: The spring is one of large spring index, i.e., the diameter of the spring is large compared with the diameter of the wire of which the spring is made; the deflection or extension under load is assumed to be small; the pitch angle is small, i.e., the spring is relatively flat; and the spring material exhibits completely elastic behavior, i.e., no creep takes place under the loading conditions described. However most fibers do exhibit creep when they are subjected to stress, the deformation observed continues to increase with time. The treatment by the simple spring theory is limited to the extent that hair fibers exhibit viscous mechanical properties and depart from ideal elastic behavior.

While it is intended to consider the properties of "springs" made of hair, it was thought useful first to examine the characteristics of the spring material—the hair fiber. It was, therefore, decided to study the mechanical properties of hair in torsion to obtain some measurements of the usual elastic constants (torsion modulus) and some information as to the creep behavior. Since moisture and permanent waving are important in cosmetic practice the effects due to these were also investigated.

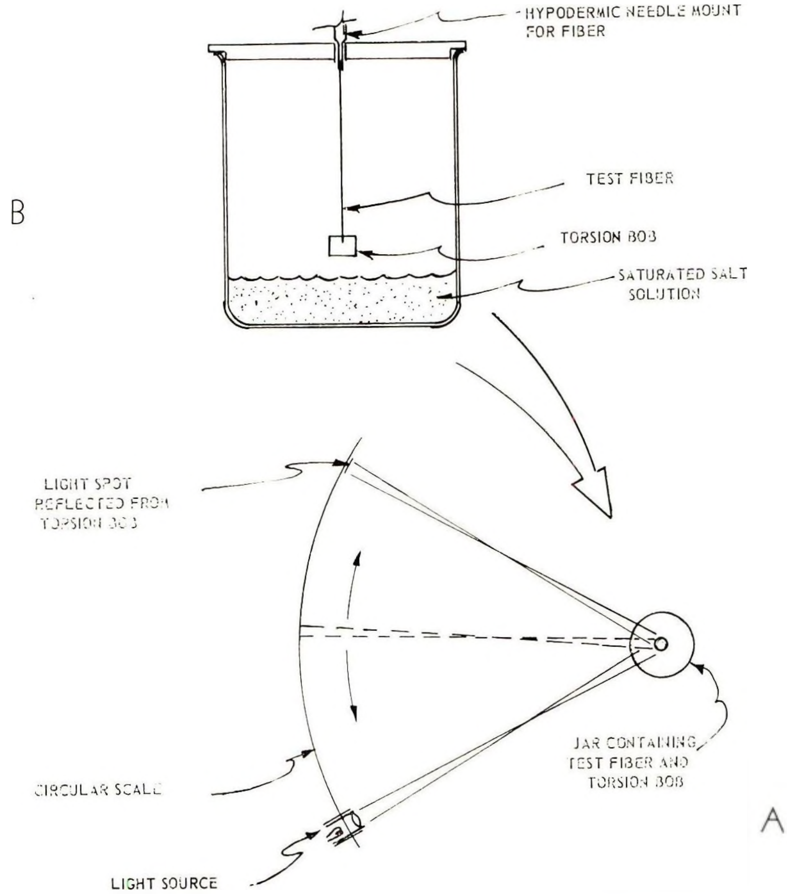
Work was undertaken to measure the physical properties of hair in torsion using two different methods. The first technique will be referred to as the torsion pendulum method. It will not be described in detail since the method has been used by a number of workers in studies of textile fibers (3–5). In brief, the test hair is utilized to suspend a small bob which can be set into free rotational oscillation. By measuring the period of oscillation (T), the fiber length (l), and diameter (d), and by calculating the moment of inertia (I) of the bob (from its weight and shape), it is easy to compute the fiber torsion modulus:

$$G = \frac{128\ \pi\ I\ l}{T^2 d^4} \qquad (2)$$

The measurements were made in a constant temperature room at 21° ± 1°C, the fibers being suspended in glass jars over saturated solutions of different salts. Equilibration of the fiber with the constant humidity atmosphere in the jars was allowed to take place for at least two days.

It was also possible to make observations useful in assessing the tendency of the fiber to flow or creep under the influence of torsional strain. Lochner (6), using textile fibers, showed that the damping or the decrease in amplitude of successive oscillations of the torsion pendulum is related to the internal viscosity of the fiber. He used a parameter called the logarithmic decrement (S) which is the natural logarithm of the ratio of the amplitude of successive swings (a_1, a_2, $a_3 \ldots a_n$) of the torsion bob:

$$S = \frac{2.3}{n} \log_{10} \frac{a_1}{a_n} \qquad (3)$$



SCHEMATIC DIAGRAM OF APPARATUS USED FOR TORSION MEASUREMENTS BY PENDULUM METHOD. A – PLAN VIEW OF ARRANGEMENT OF JAR CONTAINING TEST FIBER, TORSION BOB, OPTICAL LENSES AND SCALE. B – ENLARGED VIEW OF FIBER AND TORSION BOB.

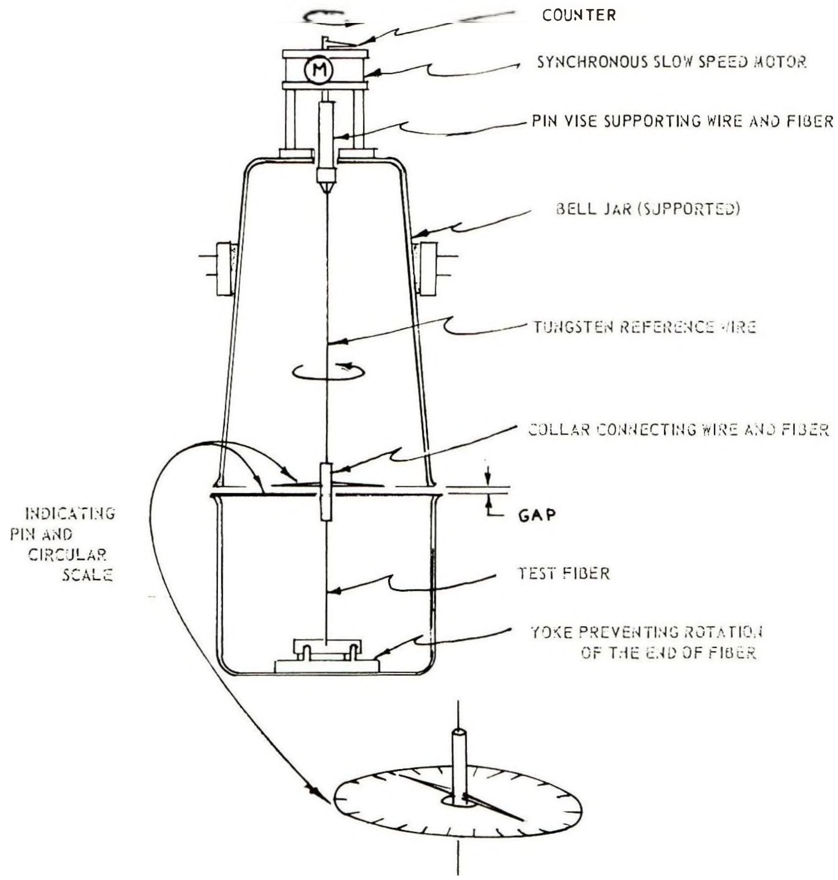
Figure 4

The sense of the meaning of S can be seen by asserting that for fibers which are highly elastic by nature any rotational oscillation induced will continue for a long time with only very small decay in amplitude, any change being produced largely by the frictional resistance of the air on the bob. Conversely, in the case of fibers of low elasticity, the mechanical work stored in the fiber with a swing of the bob in one direction will not be entirely recoverable on the reverse oscillation. Thus, fibers which show appreciable damping are said to creep or to have high internal viscosity and will exhibit large decreases in the amplitude of successive swings in a torsion pendulum experiment; this will result in large values of S, the logarithmic decrement.

Measurement of S is relatively simple. Torsion bobs were made of discs of sheet metal with a highly reflective chrome-plated surface. A light beam focused on the torsion bob through the glass jar placed centrally with respect to a semicircular scale about 60 cm away (Fig. 4). Reading of the light spot on the scale was simple and determined the amplitude of any oscillation. In practice, the amplitude of the first and tenth swing was determined for the calculation of S and the time period (T) for the ten swings measured with a stopwatch for the calculation of G.

It was also desired to measure fiber properties in torsion in the wet state, as is frequently done in fiber tensile measurements. The pendulum method is not suitable for wet testing; accordingly, a new procedure was selected—the direct twist method, based on the principles of a technique described by Morton and Permanyer (7). In brief, the method used consists in mounting a test fiber in series with a reference wire made of an elastic substance such as steel, quartz, or tungsten, the last being employed in the present case. As shown in Fig. 5, the fiber is prevented from rotating at the bottom, while twist can be inserted into the wire at the top with a slow speed motor rotating at 1–4 rpm as desired. An indicating pointer is present on the lightweight piece connecting the wire and fiber. In operation, switching the motor on inserts twist into the wire-fiber assembly, the total twist being noted on the counter attached to the motor. The pointer at the bottom of the wire (the top of the fiber) is followed and represents the twist in the fiber. By difference, the twist in the wire is obtained; since the wire is elastic, the twist in it corresponds to a known shear stress which is the same in the reference wire and in the fiber being tested. The stress may be computed using the constants from the literature or from measurements of torsion modulus of the wire made by an independent (pendulum) method. The fiber may be equilibrated at any given atmosphere or may be immersed in water or any other liquid during the measurement.

Results of measurement of fibers exposed to a wide range of moisture conditions are shown in Table I. Reported is the torsional stiffness of replicate fibers from four different samples of authentic hair in the unwaved state. Most striking is the response of the fibers to moisture. As the humidity increases the value of the torsional modulus decreases substantially. The observed effect of moisture is considerably larger than in the case of tensile measurements: the tensile modulus decreases by only a factor of two in going from 65% RH to water wet fibers.



SKETCH OF APPARATUS USED FOR TORSION MEASUREMENTS BY THE DIRECT TWIST METHOD. SMALL SKETCH SHOWS DETAIL OF COLLAR WITH INDICATING PIN PASSING THROUGH CIRCULAR-MEASURING SCALE.

Figure 5

Table I

Torsion Modulus of Unwaved Hair at Various Moisture Conditions

Hair Lot No.	Torsion Modulus, 10^{10} dynes/cm^2 41% RH	58% RH	65% RH	81% RH	93% RH	In Water
405	1.13	0.98	0.83	0.65	0.39	0.20
404	1.13	1.01	0.91	0.71	0.45	0.21
403	1.22	1.12	0.94	0.77	0.47	0.24
402	1.27	1.11	0.89	0.79	0.38	0.22
Mean	1.19	1.06	0.89	0.73	0.42	0.22

All measurements were made at 21 ± 1°C. The results for fibers tested at 65% RH and immersed in water were obtained by the direct twist method, all other results by the pendulum method.

Table II

Creep Properties of Unwaved Hair under Torsion at Various Moisture Conditions

Hair Lot No.	Logarithmic Decrement				Creep in 5 Minutes at a Constant Couple of 3.1 dyne-cm, Turns per cm Length[a]	
	41% RH	58% RH	81% RH	93% RH	65% RH	In Water
405	0.13	0.13	0.19	0.26	0.01	0.08
404	0.12	0.13	0.16	0.22	0.01	0.08
403	0.11	0.12	0.17	0.24	0.01	0.08
402	0.13	0.14	0.21	0.29	0.01	0.08
Mean	0.12	0.13	0.18	0.25	0.01	0.08

All measurements were made at 21 ± 1°C. The results for fibers tested at 65% RH and immersed in water (creep) were obtained by the direct twist method, all other results (logarithmic decrement) by the pendulum method.

[a] A couple of 3.1 dyne-cm produces a fiber twist in a typical hair of about 0.5 turn per cm at 65% RH and about 3–4 turns per cm in a wet fiber.

The data for the individual hair lots do not differ greatly; no morphological or chemical basis for the observed small differences could be found.

The creep behavior of unwaved hair is reported in Table II in terms of the fiber flow parameters obtained from the two torsion methods employed. Again, the plasticizing effect of moisture is noted. The logarithmic decrement as measured in the pendulum method increases sharply in going from 41 to 93% RH, and the creep measured directly is greater by almost an order of magnitude in going from 65% RH to water-immersion conditions.

In examining the data in Tables I and II, it is easy to see why wet hair is easier to set than dry, why it conforms well to the imposed configuration in the wet state and why it holds this configuration on drying. Wetting the hair reduces the stiffness greatly, so that it may readily be wrapped around a styling rod or the finger for pin curling. Being held in the wrapped form, the induced torsional stress decays rather quickly, and on drying the set is "frozen" in. The dry fiber is restored to its initial physical state of relatively high stiffness. The tendency for creep is also comparatively low in the dry fiber, and so long as the ambient humidity remains low the set configuration resists deformation.

The effect of a typical permanent waving treatment is seen in the data of Table III. The torsion moduli are similar to those in Table I in

Table III

Torsion Modulus of Waved Hair[a] at Various Moisture Conditions

Hair Lot No.	Torsion Modulus, 10^{10} dynes/cm^2 41% RH	58% RH	65% RH	81% RH	93% RH	In Water
405	1.16	1.05	0.96	0.68	0.37	0.14
404	1.27	1.13	1.09	0.80	0.44	0.17
403	1.34	1.23	0.99	0.81	0.39	0.12
402	1.24	1.11	0.91	0.76	0.40	0.13
Mean	1.25	1.13	0.99	0.76	0.40	0.14

All measurements were made at 21 ± 1°C. The results for fibers tested at 65% RH and immersed in water were obtained by the direct twist method, all other results by the pendulum method.

[a] Permanent waving process corresponded to standard type of commercial treatment except that process time was extended to 90 minutes.

Table IV

Creep Properties of Waved Hair[a] under Torsion at Various Moisture Conditions

Hair Lot No.	Creep in 5 Minutes at a Constant Couple of 3.1 dyne-cm, Turns per cm Length[b] 65% RH	In Water
405	0.01	0.10
404	0.01	0.10
403	0.01	0.12
402	0.01	0.09
Mean	0.01	0.10

All measurements were made at 21 ± 1°C. The results for fibers tested at 65% RH and immersed in water (creep) were obtained by the direct twist method.

[a] Permanent waving process corresponded to standard type of commercial treatment except that process time was extended to 90 minutes.

[b] A couple of 3.1 dyne-cm produces a fiber twist in a typical hair of about 0.5 turn per cm at 65% RH and about 3–4 turns per cm in a wet fiber.

that moisture acts to decrease them. Most interesting, however, is the finding that waved hair on the average tends to exhibit greater stiffness at low humidities. The effect of permanent waving in increasing the torsional stiffness is seen in most, but not all, samples; hair lot 402 is an example of a case in which the permanent waving treatment produced no significant alteration in the "dry" torsional properties.

The damping capacities of the hair given by the logarithmic decrement are, within experimental error, similar in the waved and unwaved fibers and are not reported here. The creep properties of the waved hair obtained by the direct twist method are shown in Table IV. The application of the chemical waving treatment does not seem to alter the flow properties appreciably at low humidities, the creep being low in any event. In the wet state, however, the permanent-waved hair is even more plastic and less stiff than before treatment.

These results may explain the value of permanent waving in the hair setting process. The fibers assume the set configuration more easily in the wet state, and the ease of deformation is further enhanced with wet waved hair. The hair flows more easily under the configurational strain, especially when waved. Drying to normal low humidities restores the fiber stiffness and elasticity to higher levels; with hair containing a permanent wave, the torsional stiffness offers at least equal, and often greater, resistance to deformation than unwaved hair.

The Behavior of Hair Tresses as Coils

The previous section started with consideration of the behavior of an ideal elastic spring and showed that the hair fiber is not an ideally elastic substance. For this reason, at least, application of the simple theory cannot be expected to hold in a quantitative way. It may, nonetheless, be useful to examine equation 1 and the information on the creep behavior of hair in a qualitative sense and to consider the extension of hair tresses in coil form under gravitational loading in a variety of circumstances.

From equation 1, one would expect a hair coil to become more easily deformed under load as the torsional stiffness (G) decreased. One important way in which the torsion modulus of human hair can be altered is by change in the ambient humidity. As the data presented indicate, a hair fiber at 40% RH is about three times as stiff in torsion as at 90% RH; thus increasing the humidity decreases the shear modulus markedly. Additionally, the hair fiber shows substantially more creep at higher moisture contents. It would be expected that hair coils exposed in more humid atmospheres, therefore, would extend to a greater degree under stress or under gravitational forces than those similarly exposed under drier conditions. This conclusion is no great surprise to any woman who knows from extensive experience that her hair set is poorer and tends to be lost in damp weather.

It might also be expected that imposition of the set and ready coil formation in the setting operation would be favored by lower torsion modulus, i.e., at higher moisture content, since the fibers can be deformed more easily. Creep of the fibers in the moist state also favors

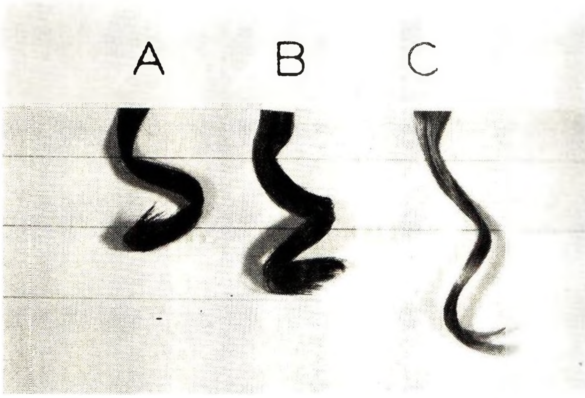


Figure 6. The effect of fiber diameter on hair coil length. Hair tresses made of fibers averaging 70, 55 and 42 μ in diameter from left to right, respectively. Tresses were set in pin curls averaging 16 mm in diameter with water, dried, and then suspended at 65% R.H., and photographed at one hour.

formation of a set. These facts are also consistent with experience which suggests that better setting of the hair is obtained in the moist rather than in the dry state. Of course, after the set is imparted in the moist state, drying restores the fiber to the stiffer condition and the set to the more stable form.

The spring equations also predict that the extension of the spring should increase as a power of the coil radius. Thus, for maximum set holding, small, tight pin curls or the smallest diameter rollers consistent with the demands of the hair style would be indicated. Since hair with a permanent wave treatment is easier to wrap in conformity to a given diameter, such set curls will often have a smaller diameter than those of straight hair, and this effect would favor resistance to extension and greater permanence of set.

A final deduction from the spring theory concerns the relationship of the extension of the spring to the fourth power of hair diameter—the finer the hair the easier it will be to extend the spring. It appears to be a well-accepted generalization of the hair art that fine hair shows very poor set holding in agreement with the theory. Figure 6 shows some hair coils produced by setting tresses of identical length using hair from heads of differing hair fineness. The coils were set in pin curls of similar diameter and after drying were hung in a chamber at constant humidity of 65%. The photograph illustrates very plainly the extended coil of fine hair compared to the shorter, tighter helices for the coarse fibers. These results may be attributable not only to fiber diameter and

Table V

The Effects of Fiber Diameter on Torsional Properties of Hair Fibers by Direct Twist Method

	Hair Lot S403		Hair Lot PF	
	Fine	Coarse	Fine	Coarse
Cross section, cm^2 $\times$ 10^{-6}	31	48	24	56
Torsion modulus, dyne/cm^2 $\times$ 10^{10}				
At 65% RH	0.96	1.01	...	...
Immersed in water	0.22	0.25	0.26	0.24
Creep at a couple of 3.1 dyne-cm in 5 minutes, turns/cm				
At 65% RH	0.025	0.01	...	...
Immersed in water	0.11	0.06	0.12	0.05

to possible effects of torsional stiffness but to creep as a function of diameter. Some relevant data are shown in Table V.

In the previous single fiber results the test fibers were sorted out so that hairs of similar diameter were used for measurement. In the present case fibers from the same head but differing in cross section were employed. The data show no real differences in modulus between coarse and fine fibers of the same lots. It should be recalled, however, that the modulus describes the property of a unit volume of substance; a fine hair presents less material to resist stress and is therefore more easily deformable than a coarse fiber of the same modulus.

The tendency for creep also seems to be influenced by fiber fineness. The precision of the results at 65% RH is not very high so that it is uncertain whether fine fibers really creep more under these conditions. Under moist conditions, however, the creep rate for fine fibers is clearly greater than for coarse, as shown in Table V. The lower intrinsic stiffness and the tendency for greater creep would be consistent with the poorer retention of set of fine hair. This appears to be the situation in practice with fine adult or children's hair.

Discussion and Conclusion

The presentation above has emphasized the existence and behavior of helical coils. From this one is led to attempt analysis of setting and styling behavior in terms of classical theory of mechanical springs. While the theory holds for ideal materials and circumstances the departure from ideality does not appear to rule out the qualitative relations that the theory suggests.

One of the implications of the spring theory is that torsional forces are important in the behavior of hair coils. Measurement of the torsional properties of hair reveals the great influence of moisture in softening the fiber and in increasing the torsional creep. Permanent waving appears to enhance these effects of water on hair and, surprisingly, to increase in many cases the stiffness of the hair at low humidities. All of these findings are consistent with the behavior of hair in setting and styling on the head.

The observation of mechanical creep in hair under torsional stress indicates that the fiber is not truly elastic and rules out strict application of the simple spring theory. Indeed, it is certain that loss of the set configuration in practice involves creep phenomena to a greater extent than elastic properties.

Because of the point of view adopted in this paper, considerable emphasis has been placed on torsional forces. Yet, it must be acknowledged that other types of mechanical forces, e.g., bending, come into play in reality and could explain some of the phenomena about as well. For example, the helical spring theory described above requires the deflection under load to be small. As the deflection becomes large, equation 1 must be altered to:

$$\Delta = K'Pr^2L\left(\frac{\cos^2 \alpha}{GI_p} + \frac{\sin^2 \alpha}{EI}\right) \qquad (4)$$

in which α is the pitch angle, E is the bending modulus, I is the moment of inertia about a diameter or about the center (subscript p) and L is the length of wire composing the spring.

Thus, the theoretical treatment suggests that as the coil gets longer and the pitch angle greater, bending forces contribute to the deformability to an increasing extent. Hair coils are of relatively large pitch angle, and, as they relax, the angle increases further. Presumably also, creep in bending takes place so that for complete understanding the viscous as well as elastic properties in bending need elucidation.

Another obvious departure from the simple view is that hair tress coils are not composed of single "wire" but consist of an array of approximately parallel single fiber springs. There is a substantial contribution to the mechanics of the system of frictional forces between the individual fibers in the coil between different groups of fibers in the same spring and among adjacent tresses of a finished coiffure.

It is concluded that torsional forces are involved in waving and setting of hair on the head. New data have been presented on torsional properties of waved and unwaved hair fibers exposed to a variety of moisture conditions. Classical physical theory of springs provides a useful viewpoint for considering hair behavior since helical coil tresses are often found in both waving and setting. Predictions from the theory are in general agreement with the result of experience, although deviations from ideal elastic properties and from simple systems make quantitative comparisons impossible.

ACKNOWLEDGMENT

A number of ideas and techniques for dealing with the torsional properties of hair arose from discussion with Dr. Lyman Fourt.

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S. C. C.

Annual Scientific Meeting

Dec. 6, 1967

The Americana Hotel

New York, N. Y.

J. Soc. Cosmetic Chemists, **18**, 591–598 (Sept. 16, 1967)

Effect of Process Variables on the Stability of Some Specific Emulsions

H. E. JASS, Ph.D.*

Presented before the New York Chapter, January, 1966, New York City

Synopsis—Three case histories of cosmetic emulsion problems involving rheological and emulsion deterioration with time are described. Despite considerable variation in emulsion type, the three demonstrated similar changes which are traced to changes in the physical state of the crystalline viscosity builders, primarily glyceryl monostearate. It is shown how changes in processing and formulation were able to arrest these changes and stabilize the product. The role of photomicrography in helping to analyze the problem and in predicting the results of experiments is demonstrated.

Introduction

The literature on emulsion theory, technology, and stability prediction is probably the most extensive portion of the cosmetic chemist's library. Yet, no other problem facing the chemist today poses as much mystery or demands an empirical approach as does emulsion formulation. Admittedly, the contributions of the many researchers in this area have been extremely valuable. They have advanced knowledge in this area to a considerable degree, affording the formulator a greatly superior springboard for his leap into the unknown. However, despite their noteworthy efforts, a cosmetic chemist, even after careful scientific preparation, still must adopt an optimistic attitude and must devote considerable time to testing to confirm his product's stability.

Despite the large background of intuitive knowledge possessed by experienced and skilled chemists, publication has been scanty, to

* Carter Products Div., Carter-Wallace, Inc., Cranbury, N. J. 08512.

the disadvantage of all. Despite the reluctance of scientists to publish data of unplanned and unorganized observations, this is a field in which such pragmatic information on usually complex systems can be valuable, especially in supplementing basic research on simple emulsions such as exemplified by the recent paper by Sherman (1). As an example of such information, this paper presents a trio of case histories out of the daily effort under the pressure caused by the usual urgency of the cosmetic marketing situation.

Case Histories

Many varieties of emulsions have two types of emulsifier systems working in conjunction: the primary system, either anionic, cationic, or nonionic, which serves to emulsify by interfacial action, and a secondary system, consisting of agents which act as stabilizers due to viscosity building or gelling action on one or more components of the emulsion system. Among the latter are such crystalline materials as glyceryl monostearate, cetyl alcohol, and beeswax, this last one being a combination of both an anionic primary emulsifier and a gelling agent. It is with the use of these materials, whose value has made them generally used but whose crystalline properties pose special stability problems, that this discussion is concerned.

All photomicrographs included in this paper are Polaroid photographs taken from 35 mm Agfachrome color slides. The latter were made on a Zeiss Universal Microscope using polarized light at a 165× magnification. Where a scale is shown on the picture, each division corresponds to 6.5 μ.

Water-in-Oil Cream

The first case concerns a water-in-oil cream emulsion, utilizing a beeswax-borax emulsifier system. Despite a good gross stability record in the laboratory, the pilot-plant-processed product demonstrated an alarming tendency to develop a grainy texture after a few months of storage, which was quite variable in its extent from batch to batch. The product was processed in the plant in the usual manner, the final emulsion being milled in an Eppenbach Colloid Mill* at a narrow setting after cooling to slightly above room temperature and then further cooled to room temperature.

Figure 1 is a photomicrograph of the finished cream when just a few days old. The occasional large agglomerates and a wide range of ir-

* Gifford-Wood Co., Hudson, N. Y. 12534.

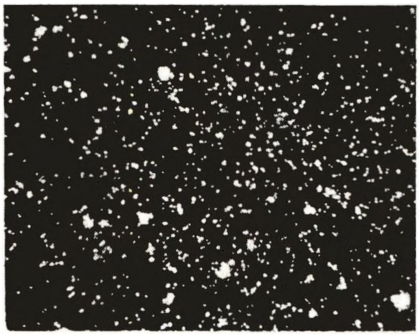

Figure 1. Water-in-oil cream emulsion, freshly made. Polarized light, 165×

Figure 2. Water-in-oil emulsion, one year old. Polarized light, 165×

Figure 3. Water-in-oil emulsion, one year old. Left half: Votator-processed cream; right half: traditionally processed (see text). Polarized light, 165×

Figure 4. Oil-in-water antiperspirant cream, freshly made. Polarized light, 165×

Figure 5. Oil-in-water antiperspirant cream, two weeks old. Polarized light, 165×

Figure 6. Oil-in-water antiperspirant cream, three months old. Polarized light, 165×

regular particle sizes superimposed on a rather uniform basic emulsion should be noted. Figure 2 shows the material after about one year of storage, although this condition does not change significantly after the first 3–4 months' storage. Growth of the solid agglomerates, especially the large cluster in the top center of the figure, is observed.

It was eventually noted that variability in granule size was related to the length of the cooling period *after* milling. Also, the granules were crystalline and attained their maximum growth in a few months. Their composition by infrared spectrophotometric analysis roughly approximated beeswax. It was also found that the cream did not become grainy on long-term storage if microscopic examination, one week after manufacture, did not reveal clumps over about 10–20 μ in diameter.

Based on these facts, rapid cooling was employed to reduce the size of the crystalline particles. Cooling was accomplished by use of the Chemetron Votator®* with the results shown in Fig. 3. This is a split photomicrograph: the right half shows an extreme example of a cream made by the original method, the agglomerates having grown to the size of palpable grains; the other half shows a Votator-processed batch which reflects this improved microscopic appearance in its good macroscopic quality. Both creams were over one year old when photographed.

Guessing at the underlying process, one might suggest that the beeswax, in addition to functioning at the interface of oil and water as a soap-type emulsifier, stabilized the emulsion by increasing the viscosity of the continuous phase. However, due to its limited solubility a portion crystallized out during the cooling process. If the cooling is slow enough, a smaller number of crystals form, the larger ones growing at the expense of the small ones.

Under the influence of sudden cooling, a large number of small seeds crystallize out, and under conditions of low mobility and limited residual insoluble material, there is limited growth of the original crystals. This may be analogous to crystallization techniques in old wet-method inorganic analysis or in purification of organic materials by crystallization.

Antiperspirant Cream

The second case concerns a somewhat similar situation involving an oil-in-water antiperspirant cream. The primary system was a combination of nonionic emulsifiers with a high HLB number using glyceryl monostearate (GMS) as stabilizer and thickener. The cream was processed in a routine manner without homogenization.

* Votator Division, Chemetron Corp., 2820 West Broadway, Louisville, Ky.

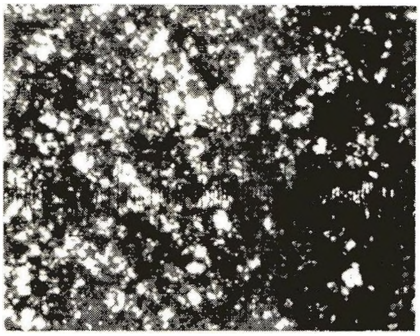

Figure 7. Oil-in-water antiperspirant cream, six months old. Polarized light, 165×

Figure 8. Oil-in-water antiperspirant cream, filled one day after manufacturing. Photomicrograph taken 11 days after filling. Polarized light, 165×

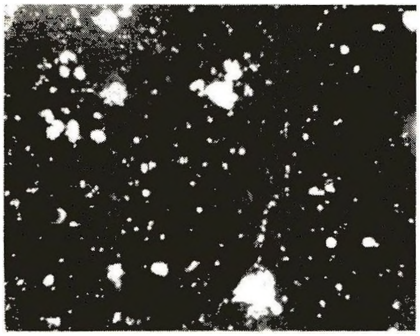

Figure 9. Oil-in-water antiperspirant cream, filled two days after manufacturing. Photomicrograph taken six months after filling. Polarized light, 165×

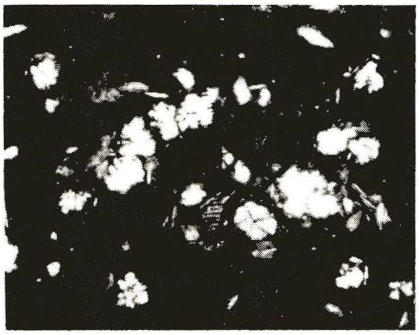

Figure 10. Oil-in-water lotion, bulk emulsion prior to packaging. Polarized light, 165×

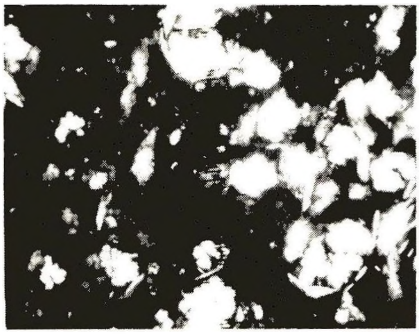

Figure 11. Oil-in-water lotion, five days old. Polarized light, 165×

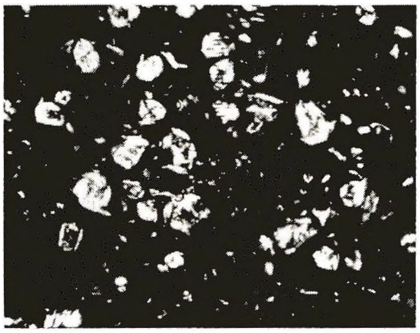

Figure 12. Oil-in-water lotion, one year old. Polarized light, 165×

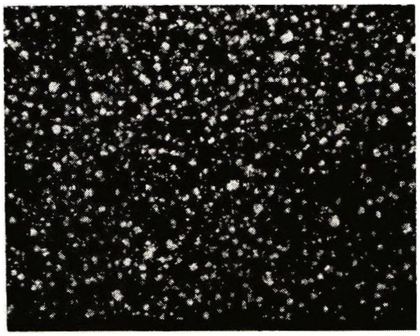

Figure 13. Oil-in-water lotion, freshly made. Polarized light, 165×

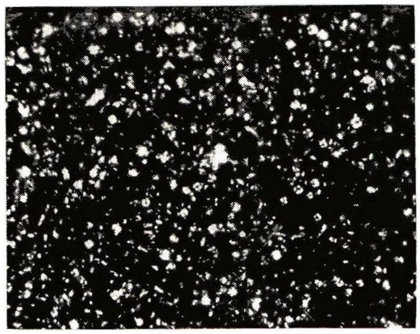

Figure 14. Oil-in-water lotion, one month old. Polarized light, 165×

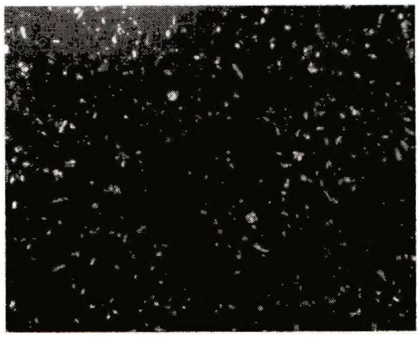

Figure 15. Oil-in-water emulsion, six months old. Polarized light, 165×

Figure 4 shows the appearance of the freshly made emulsion, the average particle of dispersed phase being about 6μ. When the batch was filled the next day, it gradually set to a firm smooth cream with the microscopic appearance shown in Figs. 5 through 7, which illustrate the change in emulsion character with time. Despite some crystal formation and growth, microscopic changes for such a long period are small. The macroscopic stability is also good. However, when the bulk cream is stored for one day before filling, it is softer; the crystals are larger and suspiciously like GMS (Fig. 8). If this bulk cream is held two days before filling it is still softer than the previous one. Figure 9 shows its microscopic appearance after six months.

Here, the mechanism is less clear. One possible explanation is that crystallization of material, probably GMS, proceeds slowly and for a fairly long time. The cream takes a rather fragile set which manifests itself over a 72 to 96-hour period. If filled early in this setting period, stabilization occurs by gelation of the interface by GMS. If disturbed after this initial setting period, the interfacial film is less structured, allowing migration of dispersed GMS into the continuous phase at an accelerated rate with subsequent loss of the stabilizing effect of the gelled structure.

Antiperspirant Lotion

The third example is an antiperspirant emulsion. This one is a rather viscous oil-in-water lotion. The viscosity builder and stabilizer consisted mainly of cetyl alcohol and a purified, high-melting glyceryl monostearate. The product was made in a Gifford-Wood Agi-Mixer.*

Figure 10 shows the appearance of the freshly prepared bulk and Fig. 11 the 5-day old packaged material. The viscosity at this point is about 3000 cps. It is quite apparent that crystal growth is already considerably advanced. Figure 12 depicts a batch that is one year old. The large clumps or "rosettes," mainly disintegrated by now, appear to be GMS, and the rods may be cetyl alcohol. At this point the emulsion tends to separate slightly, and the viscosity has dropped to less than 500 cps.

Attempts to improve this formula by process changes did not appear likely to succeed or to be economical. It did seem logical to attempt to retain the valuable viscosity-building characteristics of GMS and cetyl alcohol while impeding their tendency to crystallize. This was attempted through use of a lower-melting, less crystalline GMS, made from a "triple-pressed" stearic acid, and inclusion of other materials in the oil phase to act as plasticizers or improve solvency. Figures 13 through 15 illustrate the results. Figure 13 shows the fresh bulk product with an average particle size of about 10–13 μ. After one month, some glyceryl monostearate rosette formation has occurred, as shown in Fig. 14, but growth is slow, viscosity stationary, and prognosis for shelf life appears to be good. Figure 15, a photomicrograph taken after six months, confirms the anticipated stability. The macroscopic stability, with respect to viscosity and visual characteristics, is also satisfactory.

Concluding Comments

In the foregoing examples, considerable additional information concerning stability tests, viscosity measurement, and analytical data were collected but were omitted from this report in the interest of clarity.

* Gifford-Wood Co., Hudson, N. Y. 12534.

However, these data were helpful in analyzing the problems and arriving at solutions.

The points of importance are that solubility and crystallization characteristics of the viscosity builders and stabilizers were predominantly influential in the long-range stability of the product. Where these characteristics offered problems, they were amenable to correction by process changes or modification by other agents in a logical manner.

It should also be noted that photomicrography was particularly helpful in clarifying the process of stability breakdown and predicting the eventual fate of the emulsion.

Acknowledgment

Thanks are due to Joseph Miglietta for the preparation of the photomicrographs used in this work.

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The Effect of pH on the Sorption of Collagen-Derived Peptides by Hair

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

Presented November 30, 1966, New York City

Synopsis—Sorption of peptides increases very rapidly during the first few minutes to one-half hour of peroxide or thioglycolate treatment, after which sorption is essentially constant for a period, increasing rapidly again as the hair is damaged more extensively. The conclusion is drawn that the first action is on the cuticle which is readily removed by chemical treatment, and that increased sorption occurs after removal of the cuticle, only after extensive damage to the cortex. Oxidizing agents cause a maximum sorption of peptide at neutral pH values, while thioglycolate causes maximum sorption at high pH levels. Sorption appears to be an equilibrium phenomenon governed by the pH value of the peptide solution.

Introduction

A procedure for the objective evaluation of sorption of peptides to human hair was described in a previous publication (1). The method is based on the fact that collagens and peptides derived from collagen or gelatin contain hydroxyproline which is not present in keratin or in any of the other common proteins which at one time or another have been suggested in cosmetic formulations. The presence of hydroxyproline in hydrolyzed samples of hair after immersion in collagen-derived peptide solution and rinsing is definite proof of sorption of the peptide on the hair.

This analytical method used is applicable only to collagen and to peptides derived from collagen. Different procedures, based on the use of radioactive peptides or some dye-binding procedure, would have to be

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used for peptides other than those from collagen. The method is sensitive, and analytical differences arise primarily from the high variability of the hair itself.

In a further study of the parameters affecting sorption (2), it was shown that, in general, protein sorption is rapid for the first fifteen minutes of treatment of virgin or bleached hair; thereafter the sorption increases more slowly over a one-hour period. Peptide sorption is increased markedly by two one-hour bleach periods, while a third one-hour bleach has relatively little effect. Within the concentration range of 5–20% of peptide there is relatively little difference in the amount of peptide sorbed. Weight increases of the hair strands demonstrated that there was considerable water sorption along with peptide sorption.

Some preliminary investigations which have been made relative to the binding and elution of dyes at high and low pH levels led to the present study on the effect of pH on peptide sorption by human hair.

A few rather limited studies have been made on the effect of pH on several aspects of hair treatment. Heilingötter (3) studied the effect of thioglycolate solutions on the swelling of hair in the pH range 7.0 to 9.8, and Freytag (4) extended this type of study to bleached hair as well as virgin hair over the pH range 3 to 10. Swelling was found to increase with increase in pH and was greater for bleached hair than for virgin hair.

Laden and Finkelstein (5), using dye solutions, showed that the rate and extent of sorption could be modified by changing the pH of the system from which sorption occurs: An acid pH induces a positive charge on keratin favoring the uptake of anionic materials, whereas a basic pH value favors the sorption of cationic materials.

Methods and Results

The hair used in all of the tests was dark brown DeMeo Blue String* virgin human hair. It was shampooed in a nonionic detergent (Triton X-100†) at 1% concentration, after which the hair was rinsed thoroughly in distilled water and dried. For the bleach treatments, 100 mg tresses of the shampooed hair were immersed for varying periods of time in 6% hydrogen peroxide, prepared by treating 50 parts of 6% H_2O_2 with 1 part of concentrated ammonium hydroxide.

* DeMeo Company, 135 Fifth Ave., New York, N. Y. 10010.
† A product of Rohm and Haas, Philadelphia, Pa.

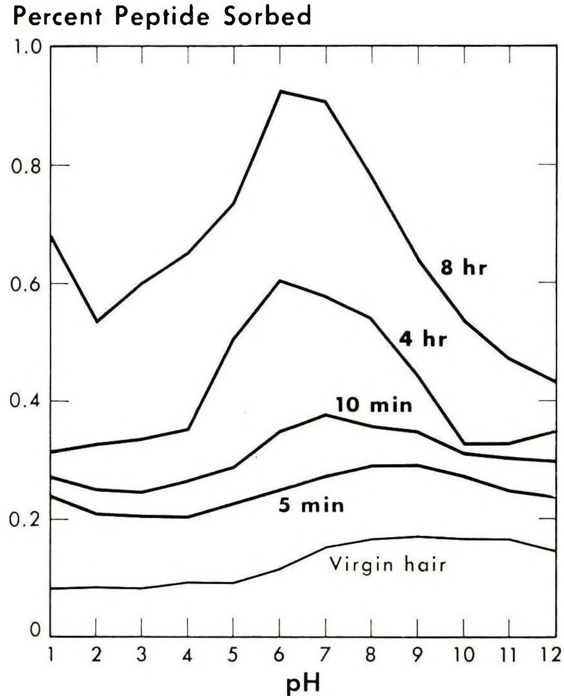

Figure 1. Sorption of peptides from solutions of different pH values by peroxide-damaged hair. (The curves are identified by the time the hair was bleached)

Cold wave treatments were carried out in 5% ammonium thioglycolate at pH 9.3; for neutralization 3% sodium bromate was used for a period of five minutes.

In all cases, at the completion of a given treatment or combination of treatments, the samples were rinsed in running tap water for two to three minutes, blotted, dried, and finally immersed in 5% peptide* solutions which had been adjusted by the addition of dilute HCl or NaOH to specific pH values from pH 1 to 12. The strands were kept in the peptide solution for 15 minutes, after which they were rinsed by immersion in distilled water for twenty-five minutes, blotted, and dried. The sorbed peptide was measured by means of the hydroxyproline analysis. The treatment period of fifteen minutes was chosen since it has been shown (2) that there is rapid sorption of peptide in fifteen minutes, followed by a much slower sorption rate up to a period of

* Wilson & Co., Inc., Substantive Proteins WSP-X250.

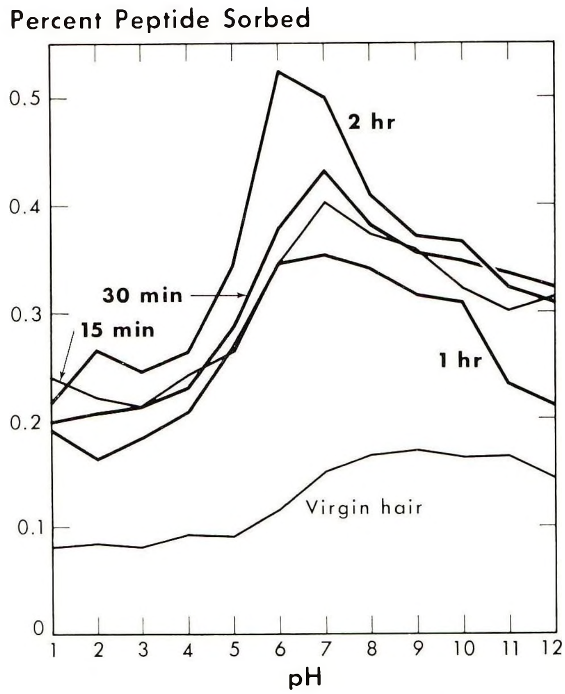

Figure 2. Sorption of peptides from solutions of different pH values by peroxide-damaged hair. (The curves are identified by the time the hair was bleached)

one hour. In some instances in which treatment at pH values of 1 to 4 did not appear to show differences, the strands were treated with peptide solutions from pH 4 to 12.

Effect of Bleaching on Peptide Sorption at Various pH Levels

The curves in Fig. 1 demonstrate the shift in the pH of maximum peptide sorption with extent of bleaching. The curve for unbleached virgin hair shows little peptide sorption from solutions at pH 1 to 5, after which a gradual increase occurs to a maximum at pH 8 to 11 with a slight drop at pH 12. After a five minute bleach period, the maximum appears at pH 8–10; and after ten minutes of bleaching, the maximum drops to 7 and remains at pH 6–7 thereafter, even after bleaching periods of sixteen hours.

Sorption increases considerably after only five to ten minutes of bleaching, but for somewhat longer periods of time (fifteen to thirty minutes) there is very little further increase in peptide sorption, as shown on Fig. 2. After one hour of bleaching an actual decrease in

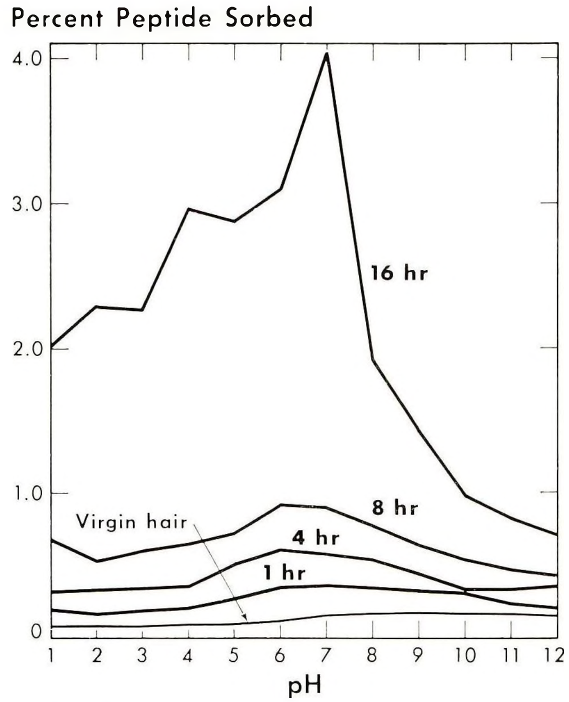

Figure 3. Sorption of peptides from solutions of different pH values by peroxide-damaged hair. (The curves are identified by the time the hair was bleached)

the sorption maximum is noted. Still longer bleaching periods (two hours or more) again cause the sorption maximum to increase to higher levels, as shown in Fig. 3 which shows a larger scale graph covering bleaching periods, from one to sixteen hours.

A similar anomalous effect was noted, for a different time period, in the case of virgin hair strands treated with ammonium thioglycolate, as will be described later. It is in all probability due to differences in susceptibility to oxidation as well as differences in sorption capacity between the cuticle and cortex of the hair. A short bleaching period may be sufficient to soften the cuticle and open up a large surface area as the scales loosen. Once the cuticle has been penetrated or removed, action on the more compact cortex begins, although it appears to be considerably more resistant to attack than is the cuticle layer. However, once the cortex has been extensively degraded, sorption of peptide increases to a very high value.

Figure 4 summarizes the results of an experiment on the removal of peptide, sorbed on hair at pH 6 by buffers at other pH levels. A group

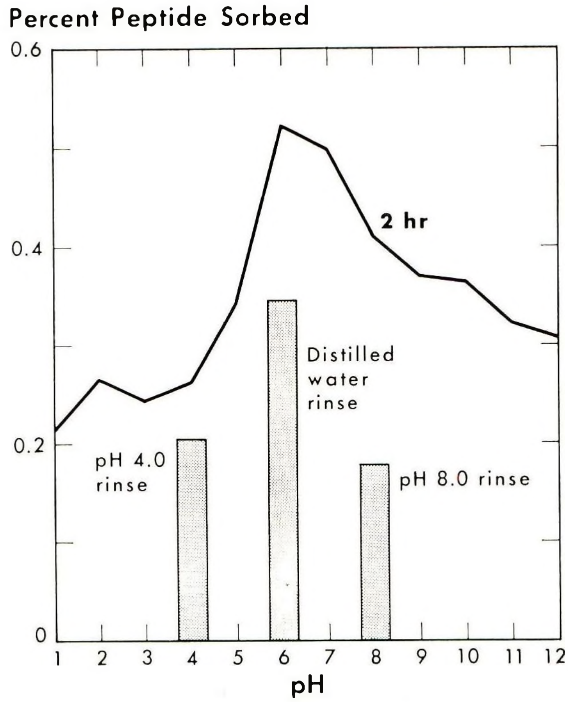

Figure 4. Elution of peptides sorbed at pH 6 on peroxide-damaged hair by buffers of differing pH

of nine samples of hair, in which the strands were formed into coils for ease of handling and weighing, approximately 100 mg each which had been subjected to a two-hour bleach treatment, was placed in 5% peptide adjusted to pH 6. After fifteen minutes, the coils were removed; three were rinsed for twenty-five minutes in distilled water at pH 6, three were rinsed in citrate-phosphate buffer at pH 4, and the last three in a similar buffer mixture at pH 8. The bar graphs showing the residual peptide in the hair after rinsing and the curve originally obtained for the sorption of peptides by hair strands treated with 5% peptide at the various pH levels are included in the figure.

Each of the coils presumably sorbed an equivalent amount of peptide from the 5% peptide solution at pH 6. However, rinsing of the coils with water left more peptide sorbed to the hair than rinsing with buffers at pH 4 or 8. Modification of the ionic character of the hair as well as that of the peptide itself shift, the sorption equilibrium to a pattern similar to that of the original sorption curve.

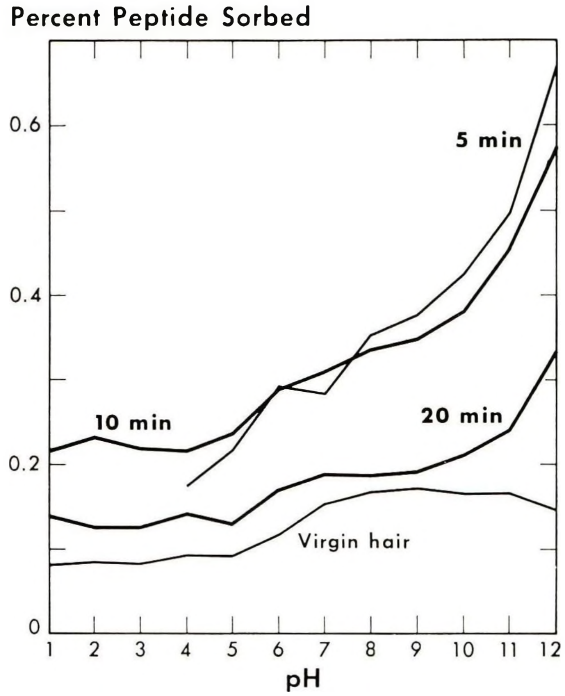

Figure 5. Sorption of peptides from solutions of different pH values by thioglycolate-damaged hair. (The curves are identified by the time the hair was reduced)

Effect of Ammonium Thioglycolate on Peptide Sorption at Various pH Levels

The curves in Figs. 5 and 6 show the effect of treatment of the hair coils with ammonium thioglycolate, followed by rinsing and treatment in 5% solutions of peptides at various pH levels. Figure 5 shows the curves for the five, ten, and twenty minute thioglycolate treatments. Peptide sorption remains at a relatively low value to pH 4–5 and then increases rapidly. It is remarkable that maximum absorption over most of the range is observed with hair treated for the shortest time (five minutes) with ammonium thioglycolate. After a treatment time of ten minutes, sorption decreases slightly and is sharply reduced after twenty minutes. At this stage, with the exception of a slight divergence above pH 10, the hair behaves very much like virgin hair.

Treatment of the hair for one hour or more with ammonium thioglycolate again changes the character of the curves. Sorption begins to increase with a longer time period of treatment following the absorp-

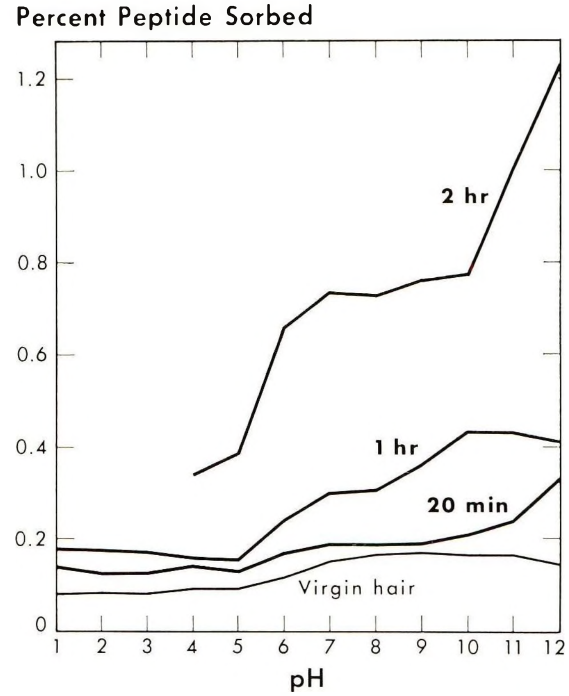

Figure 6. Sorption of peptides from solutions of different pH values by thioglycolate-damaged hair. (The curves are identified by the time the hair was reduced)

tion minimum observed after twenty minutes of reduction. This is shown in Fig. 6, which includes the twenty minute curve again for reference. The peptide is sorbed more readily at the lower pH values of 5 to 9, and sorption increases very rapidly after two hours' treatment in ammonium thioglycolate at pH values from 10 to 12.

A suggested explanation for the results is that only a short period of treatment with thioglycolate is necessary to open up the cuticle and increase the protein area for sorption of the peptide. The cuticle is rapidly separated from the hair strands, and in 20 minutes it has apparently been removed almost completely. The cortex then reacts but here the action is much slower, so that after one hour of treatment the sorption over the entire pH range has not increased markedly above that obtained after twenty minutes of treatment. It is only after additional treatment that the great increase in peptide sorption occurs.

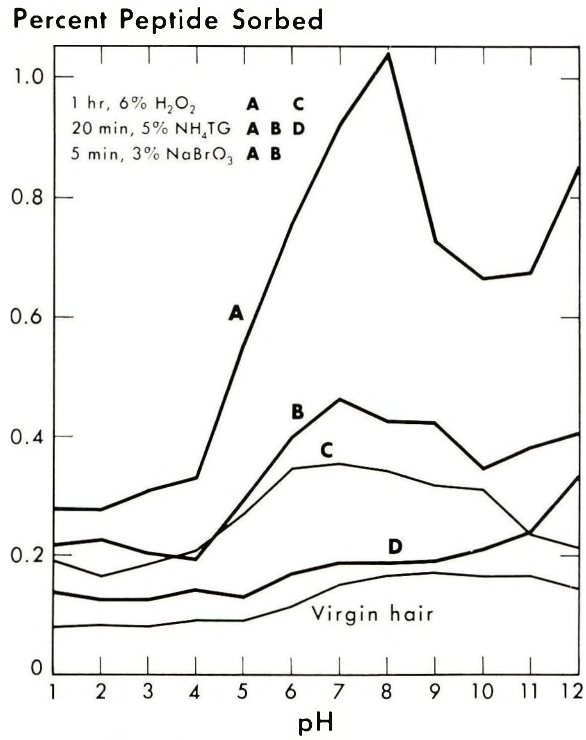

Figure 7. Sorption of peptides from solutions of different pH values by hair subjected to various types of treatment. (In curve A the hair has been bleached with H_2O_2, treated with thioglycolate, and neutralized with bromate. In Curve B the unbleached hair has been treated with thioglycolate and neutralized with bromate. Curve C shows the effect of H_2O_2 alone and Curve D the effect of thioglycolate alone.)

Effect of Sodium Bromate and Combined Treatments on Peptide Sorptivity

Figure 7 shows the effect of sodium bromate when used after ammonium thioglycolate. The curves for the one-hour treatment with hydrogen peroxide and for the twenty-minute treatment with ammonium thioglycolate are shown again for comparative purposes. Treatment with bromate for five minutes after a twenty minute thioglycolate treatment causes the sorption maximum to shift to pH 7; the curve, at pH 11 and 12, appears quite similar to that obtained with peroxide alone. Treatment of the hair for one hour in hydrogen peroxide followed by twenty minutes in ammonium thioglycolate and five minutes in sodium bromate results in a high sorption peak at pH 7–8.

Summary and Conclusion

In the case of both hydrogen peroxide and ammonium thioglycolate, rapid changes in sorption occur in the first five to ten minutes. There is little change in sorption for the next thirty minutes to one hour of treatment with either reagent. After one hour of hydrogen peroxide treatment, peptide sorption becomes progressively greater with increase in time. This apparently is true also in the case of ammonium thioglycolate treatment.

Oxidizing agents, such as hydrogen peroxide used in bleaching, or sodium bromate used to neutralize ammonium thioglycolate, have relatively little effect in increasing peptide sorption at the highest pH levels but cause sharp increases in sorption at neutral pH values. The use of ammonium thioglycolate alone has less effect on promoting sorption at neutral pH values than at the higher pH levels.

It is concluded that the cuticle is destroyed rapidly by the reagents used, with the swelling and opening up of the cuticle being responsible for the rapid uptake of peptide at this stage. Further chemical treatment removes the cuticle, leaving a cortex which is considerably more resistant to chemical action. Sharply increased peptide sorption occurs only after the oxidation or thioglycolate treatments have damaged the hair extensively.

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Hair Coloring with Oxidation Dye Intermediates

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Synopsis—Data on patents for 33 primary intermediates and 20 color modifiers were collected from the literature. The effect of structure on shade, depth of color, light fastness, and solubility was determined for each product. The effect on color, depth of shade, and light fastness of dyeing mixtures of each of the 20 color modifiers with equimolar quantities of 3 primary intermediates is reported. It is shown that by proper selection of color modifier the shade may be varied, the depth of color greatly increased, the fastness to light increased many fold, and the tendency to turn red on aging decreased.

By using the formation of Bandrowski's base from oxidation of *p*-phenylenediamine as a tool the percentage of conversion to the colored form was shown to be only slightly more than 5% under the conditions normally used for dyeing hair. The effect of various factors on this yield is reported.

The results of using five recently described pyridine derivatives are tabulated and discussed.

Introduction

Oxidation dye intermediates account for a major share of the hair dye market today. These dyes differ from the usual textile dyes in that, with the exception of the nitro dyes, they are colorless or nearly colorless products which form dyes upon oxidation. According to Heald (1), the intermediates, because of their small size, are able to penetrate into the hair fiber where they undergo oxidation. This converts them into dyes which, because of their increased size, are trapped in the fiber. In other words, during the use of the oxidation dye intermediates, dye manufacturing occurs within the hair fiber.

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Wilmsmann (2) has demonstrated that there exists a critical molecular size which is important for the penetration of hair. He showed that, under conditions used in hair dyeing, globular molecules having a diameter of more than 6 A are prevented from penetrating into the hair cortex by a barrier near the hair surface. The intermediates used in oxidative hair dyeing vary in diameter from 4.7 A for *p*-phenylenediamine to 5.6 A for *p*-aminodiphenylamine, well under this critical molecular size. Although the first patent for the use of *p*-phenylenediamine in dyeing hair was granted to Erdmann (3) in 1883, the commercial development of this class of dyes took place largely in the fur industry.

Kass (4) has classified oxidation hair dyes as: *i*, primary intermediates which yield colors on oxidation; *ii*, color couplers or modifiers which do not form dyes on oxidation but do produce color changes when used with primary intermediates; and *iii*, nitro derivatives which do not depend upon oxidation for the production of color but are limited to shades of yellow, red, and orange. In this work the primary intermediates have been divided into derivatives of *p*-phenylenediamine, *o*-phenylenediamine, *p*-aminophenol, *o*-aminophenol, and diphenylamines; and the color modifiers into derivatives of *m*-phenylenediamine, *m*-aminophenol, hydroxyphenols, and naphthols. The nitro compounds are included in the classification corresponding to their structure. An attempt has been made to include all of the important intermediates used for oxidative hair dyeing along with pertinent data, some of which were collected from the literature and the balance determined in this laboratory.

Methods and Results

In order to determine standard practice in this country, ten commercially available black oxidation dye solutions, products of the recognized leaders in this field, were purchased. All of them were solutions of low viscosity which thickened upon the addition of the oxidizing agent. For nine of these products the user was directed to add an equal quantity of 6% hydrogen peroxide just prior to application. Directions for the tenth product called for the addition of a solid material from a packet which contained both the oxidizing agent and a thickening agent. According to the directions furnished by the manufacturers, the dyeing times varied from five minutes to forty-five minutes. The pH of these products, after the addition of the oxidizing agent, varied from 9.5 to 10.2, with an average of 9.7. It has therefore been concluded that, in this country, it is common practice in oxidation hair dyeing to use a pH of 9.7 and hydrogen peroxide at a concentration of 3% as applied to the hair.

In the tables data are listed for each intermediate on patents, fadeometer readings, solubility, and color produced. Patent information was obtained from the patent literature, from publications by Forster and Soyka (5) and Austin (6), and the Color Index (7). Additional data on toxicity may be found by consulting Heilingötter (8). All fastness-to-light tests were run on a standard fadeometer. Most of the solubilities in water were determined by dissolving a weighed excess of the intermediate in deionized water at 35°C, adjusting the pH to 9.7 ±0.2 by the dropwise addition of ammonium hydroxide, and bringing the total volume to 100 cc. After the temperature had fallen to 25°C, the solution was filtered through a Gooch crucible and the solubility determined by difference. In a few cases where the solubility given in the literature far exceeded that used in hair dyeing this figure was used in the tables but always with the temperature recorded beside the solubility figure. In all cases the purest intermediates available were used.

All dyeings were performed by immersion for forty-five minutes at room temperature, using natural white hair at a hair/liquor ratio of 1 to 50. For the primary intermediates, with the exception of the diphenylamine derivatives, 0.025 *M* solutions of each dye were used. With the diphenylamine derivatives dye concentrations of 0.005 *M* were used because of their limited solubility and intense coloring power. For the mixtures of color modifiers and primary intermediates the concentration of each was 0.01 *M*. In addition to the intermediates the solutions contained deionized water, 10% isopropyl alcohol, hydrogen peroxide at a concentration of 3% and sufficient ammonium hydroxide to adjust the pH to 9.7 ± 0.2 after the addition of the peroxide. After immersion for forty-five minutes the hair was rinsed in running water and dried.

Dyeing with Primary Intermediates

The effect of constitution on color, depth of shade, solubility, and light fastness of *p*-phenylenediamine derivatives is shown in Table I. Table II summarizes the results with *o*-phenylenediamine and its derivatives. The results with *p*-aminophenol and its derivatives are given in Table III.

It was expected that the addition of an amino-group in the ortho-position of *p*-aminophenol would increase the depth of shade, as was the case with *p*-phenylenediamine. However, the opposite effect was ob-

Table I
Para-Phenylenediamine Derivatives

Compound	Patent	Color on Hair[a]	Depth of Shade (Darkest to Lightest)	Solubility at pH 9.7 (g/100 ml)	Fades After (in hours)
p-Phenylenediamine	F.P. 158,558	Black with red cast	3	4.27	6
p-Toluylenediamine sulfate	G.P. 47,349	Medium brown	6	11.9	6
Chloro-*p*-phenylene diamine sulfate	U.S.P. 1,434,449	Red brown	5	7.75	38
Nitro-*p*-phenylene diamine	G.P. 211,567	Dark red	...	0.23	30
1,2,4-Triaminobenzene dihydrochloride	G.P. 514,003	Deep black	1	9.78	30
p-Aminodimethylaniline	G.P. 47,349	Oxford grey	4	1.97	8
p-Aminodiphenylamine	G.P. 92,006	Blue black	2	0.10	24
p-Aminoacetanilide	...	No color	7	...	...

[a] Derivative used at a concentration of 0.025 moles/l.

Table II
Ortho-Phenylenediamine Derivatives

Compound	Patent	Color on Hair[a]	Depth of Shade (Darkest to Lightest)	Solubility at pH 9.7 (g/100 ml)	Fades After (in hours)
o-Phenylenediamine	G.P. 213,581	Yellow	4	3.56	4
3,4-Toluylenediamine	G.P. 213,581	Golden brown	2	2.49	6
o-Toluylenediamine	G.P. 213,581	Golden grey brown	1	2.29	10
4-Chloro-*o*-phenylene diamine	U.S.P. 1,536,725	Brown gold	3	0.91	6
4-Nitro-*o*-phenylene diamine	G.P. 190,622	Red orange	...	0.03	42
5-Chloro, 3-nitro *o*-phenylenediamine	...	Orange	...	0.03	14

[a] Derivative used at a concentration of 0.025 moles/l.

Table III
Para-Aminophenol Derivatives

Compound	Patent	Color on Hair[a]	Depth of Shade (Darkest to Lightest)	Solubility at pH 9.7 (g/100 ml)	Fades After (in hours)
p-Aminophenol	G.P. 51,073	Golden brown	2	0.63	12
4-Amino-2-methyl phenol sulfate	G.P. 80,814	Red brown	1	1.17	14
4-Amino-3-methyl phenol	G.P. 80,814	Light grey brown	5	0.43	10
4-Amino-2-nitro phenol	U.S.P. 1,466,747	Red brown	3	2.97	10
2,4-Diaminophenol hydrochloride (amidol)	G.P. 80,814	Light red brown	4	7.46	2
p-Methylamino phenol sulfate (metol)	G.P. 80,814	No color	6	5.58	...

[a] Derivative used at a concentration of 0.025 moles/l.

Table IV
Ortho-Aminophenol Derivatives

Compound	Patent	Color on Hair[a]	Depth of Shade (Darkest to Lightest)	Solubility at pH 9.7 (g/100 ml)	Fades After (in hours)
o-Aminophenol	G.P. 103,505	Golden orange	3	0.95	2
4-Chloro-2-amino phenol	G.P. 103,505	Grey yellow	5	1.19	10
4-Nitro-2-amino phenol	G.P. 103,505	Golden brown	6	3.47	10
5-Nitro-2-amino phenol	U.S.P. 1,416,646	Bright yellow	4	0.99	4
4,6-dinitro-2-amino-phenol	G.P. 103,505	Dark orange	1	$0.13^{25°C.}$	12
6-Chloro-4-nitro-2-aminophenol hydrochloride	...	Dark orange	2	1.49	28

[a] Derivative used at a concentration of 0.025 moles/l.

Table V
Diphenylamine Derivatives

Compound	Patent	Color on Hair[a]	Depth of Shade (Darkest to Lightest)	Solubility at pH 9.7 (g/100 ml)	Fades After (in hours)
4-Aminodiphenylamine	G.P. 92,006	Brown black	1	0.10	15
2,4-Diaminodiphenyl amine	B.P. 270,075	Brown	3	0.15	7
4,4′-Diaminodiphenyl-amine sulfate	G.P. 98,431	Red brown	2	0.65	10
2-Aminodiphenylamine	G.P. 162,625	Grey red	4	0.07	6
3-Methyl-4-amino-4′-hydroxydiphenyl-amine	G.P. 209,121	Very little color	6	0.09	2
4-Methoxy-4′-amino-diphenylamine sulfate	G.P. 257,763	Light ash	5	1.06	4
4-Hydroxydiphenyl-amine	G.P. 162,625	No color	8	0.15	...
3-Hydroxydiphenyl-amine	G.P. 286,337	No color	7	0.16	...

[a] Derivative used a concentration of 0.005 moles/l.

tained under the conditions used in these dyeing experiments. It seemed possible that the reason that 2,4-diaminophenol hydrochloride did not produce a darker color than *p*-aminophenol might be due to oxidative destruction of the molecule because of the high concentration of hydrogen peroxide used in the dyeing. In order to check this the dyeings of these two intermediates were repeated with the hydrogen peroxide concentration reduced from 3.0% to 0.3%. Under these conditions the color produced by *p*-aminophenol matched that of the original dyeing but that produced by 2,4-diaminophenol hydrochloride was many times darker and redder than the original color. It can therefore be concluded that 2,4-diaminophenol hydrochloride (amidol) is not satisfactory for use under the conditions generally used for oxidative hair dyeing.

The results for *o*-aminophenol and its derivatives are given in Table IV, and those for the diphenylamine derivatives are shown in Table V.

Dyeing with Color Modifiers

The color modifiers were dyed alone on natural white hair from 0.025 *M* solutions and from equimolar (0.01 *M* each) mixed with solutions

Table VI

Meta-Phenylenediamine Derivatives Alone and with *p*-Aminodiphenylamine

Compound	Alone: Patent	Alone: Solubility at pH 9.7 (g/100 ml)	Alone: Color on Hair (from 0.025 *M* Solution)	Mixed Solution with P.A.D.A.: Color on Hair[a]	Mixed Solution with P.A.D.A.: Fades After (in hours)
m-Phenylenediamine	G.P. 255,858	42.8	Very light grey	Blue black	12
Chloro-*m*-phenylene diamine	G.P. 255,858	1.19	Very light red grey brown	Grey black	22
Nitro-*m*-phenylene diamine	G.P. 255,858	1.71	Bright yellow	Golden brown	28
m-Toluylenediamine	G.P. 255,858	4.00	Very light yellow brown	Blue black	24
2,4-Diaminoanisol sulfate	G.P. 228,245	14.7	Light grey brown	Black	18
4-Methoxy-6-methyl-*m*-phenylenediamine	G.P. 230,630	1.10	Medium grey brown	Black	16
1,3,5-Triaminobenzenetrihydrochloride	...	8.63	No color	Dark brown	12
2,4,6-Triamino toluene trihydrochloride	...	13.4	No color	Grey brown	20
p-Aminodiphenylamine (alone)	...	...	...	Brown black	14

[a] Solutions were 0.01 *M* in both components.

with *p*-phenylenediamine (P.P.D.) *p*-aminodiphenylamine (P.A.D.A.), or *p*-aminophenol (P.A.P.). The properties of eight *m*-phenylene diamine derivatives dyed alone and mixed with P.A.D.A. are given in Table VI. With the exception of nitro-*m*-phenylenediamine the colors given with *m*-phenylenediamine derivatives, when dyed alone, were so light that no fadeometer tests were run. Hair dyed with nitro-*m*-phenylenediamine faded after an exposure of two hours.

The results of dyeing hair with equimolar quantities of *m*-phenylenediamine derivatives mixed with P.P.D. or P.A.P. are given in Table VII. It is apparent that *m*-phenylenediamine, *m*-toluylenediamine, 2,4,-diaminoanisol sulfate and 4-methoxy-6-methyl-*m*-phenylenediamine all were effective in giving a blue-black color when mixed with P.P.D. which was many times darker and showed a tenfold increase in light fastness compared with that of *p*-phenylenediamine alone. This illustrates the

Table VII

Meta-phenylenediamine Derivatives Mixed with *p*-Phenylenediamine or *p*-Aminophenol

Compound	Mixed Solution with P.P.D. Color on Hair[a]	Mixed Solution with P.P.D. Fades After (in hours)	Mixed Solution with P.A.P. Color on Hair[a]	Mixed Solution with P.A.P. Fades After (in hours)
m-Phenylenediamine	Blue black	42	Red with a grey cast	2
Chloro-*m*-phenylene diamine	Black with a red cast	20	Light grey	6
Nitro-*m*-phenylene diamine	Yellow brown	20	Bright yellow	2
m-Toluylenediamine	Black with a purple cast	50	Dark red	16
2,4-Diaminoanisol sulphate	Black	50	Orange red	8
4-Methoxy-6-methyl-*m*-phenylene-diamine	Black	46	Orange red	4
1,3,5-Triaminobenzene trihydrochloride	Red brown	14	Light grey brown	18
2,4,6-Triaminotoluene trihydrochloride	Grey brown	22	Light golden brown	6
p-Phenylenediamine (alone)	Dark brown	4	...	...
p-Aminophenol (alone)	...	...	Light golden brown	4

[a] Solutions were 0.01 *M* in both components.

Table VIII

Meta-Aminophenol Derivatives Alone and with *p*-Aminodiphenylamine

Compound	Alone: Patent	Alone: Solubility at pH 9.7 (g/100 ml)	Alone: Color on Hair (from 0.025 *M* Solution)	Mixed Solution with P.A.D.A.: Color on Hair[a]	Mixed Solution with P.A.D.A.: Fades After (in hours)
m-Aminophenol	G.P. 210,643	3.85	No color	Blue black	28
3,5-Diaminophenol hydrochloride	...	3.57	No color	Red brown black	28
Diethyl-*m*-amino-phenol	U.S.P. 3,216,899	0.20	Very light grey brown	Dark red brown	5
p-Amino-*o*-cresol (4-amino-2-hydroxy-1-methylbenzene)	U.S.P. 3,210,252	0.65	Golden blonde	Dark grey purple	8
p-Aminodiphenyl-amine (alone)	...	...	...	Brown black	14

[a] Solutions were 0.01 *M* in both components.

Table IX

Meta-Aminophenol Derivatives Mixed with *p*-Phenylenediamine or *p*-Aminophenol

	Mixed Solution with P.P.D.		Mixed Solution with P.A.P.	
Compound	Color on Hair[a]	Fades After (in hours)	Color on Hair[a]	Fades After (in hours)
m-Aminophenol	Dark purple grey	8	Medium red brown	16
3,5-Diaminophenol hydrochloride	Red brown	4	Grey brown	14
Diethyl-*m*-aminophenol	Olive brown	5	Green brown	7
p-Amino-*o*-cresol	Dark red with blue cast	18	Bright orange	18
p-Phenylenediamine (alone)	Dark brown	4	...	...
p-Aminophenol (alone)	...	...	Light golden brown	4

[a] Solutions were 0.01 *M* in both components.

importance of these color modifiers in increasing the depth of shade, changing the color, and increasing the fastness to light.

It is apparent that *m*-phenylenediamine, *m*-toluylenediamine, 2,4-diaminoanisol sulfate, and 4-methoxy-6-methyl-*m*-phenylene diamine are all equally effective in producing a deep blue shade of comparable light fastness. The tendency of hair dyed with oxidation colors to turn red on aging has long been a deep concern of the hair colorist. As evidenced by references in the patent literature (9, 10) this tendency is accelerated by the application of acid rinses or contact of the hair with acid perspiration. Fadeometer readings are a measure of the fading of colors due to the exposure to light. However, it is doubtful if such determinations measure the reaction of colors to aging. Dyeings that had been made in December, 1952, using mixtures of P.P.D. and each of the four meta-compounds listed above, were found in our files. These had been stored in the absence of light and out of contact with acid fumes. Records showed that originally they were all blue-black colors of comparable depth of shade, with light fastness ratings varying from forty-two to fifty hours. Examination of these dyeings after thirteen and one-half years revealed that the one made with 2,4-diaminoanisol sulfate was still black, while that made with *m*-phenylenediamine was slightly red and those made with *m*-toluylenediamine and 4-methoxy-6-methyl-*m*-phenylenediamine were very red. This indicates the need for additional tests for the control of hair dye formulations. Such tests

Table X
Phenolic Compounds Mixed with *p*-Aminophenol

Compound	Patent	Solubility at pH 9.7 (g/100 ml)	Color on Hair[a]	Fades After (in hours)
Hydroquinone	G.P. 51,073	$5.9^{15°C}$	Blond	6
Resorcinol	G.P. 162,625	$58.4^{20°C}$	Grey blond	14
Pyrocatechol	G.P. 276,761	$31.2^{20°C}$	Red brown	12
Chlororesorcinol	G.P. 276,761	29.9	Green blond	8
Pyrogallol	G.P. 104,622	$62.5^{25°C}$	Light golden brown	12
α-Naphthol	G.P. 162,625	0.26	Red	6
1,5-Dihydroxynaphthalene	G.P. 51,073	0.27	Red	6
2,7-Dihydroxynaphthalene	G.P. 367,680	0.84	Yellow blond	2
p-Aminophenol (alone)	...	...	Light golden brown	4

[a] Solutions were 0.01 *M* with regard to both the phenolic and P.A.P.

might consist of spectrophotometric or photographic records of freshly dyed samples compared with the same samples after definite periods of aging.

In Table VIII the results obtained with *m*-aminophenol derivatives dyed alone and mixed with equimolar quantities of P.A.D.A. are given. With the exception of *p*-amino-*o*-cresol the colors given with *m*-aminophenol derivatives, when dyed alone, were so light that no fadeometer tests were run. Hair dyed with *p*-amino-*o*-cresol faded after an exposure of seven hours.

The results of dyeing hair with equimolar quantities of *m*-aminophenol derivatives mixed with P.P.D. and P.A.P. are given in Table IX.

In Table X the results obtained with phenolic compounds mixed with equimolar quantities of P.A.P. are given. None of these phenolic compounds gave any color when used alone.

The results of dyeing hair with equimolar quantities of phenolic compounds mixed with P.P.D. are given in Table XI. Included in this table are the results of phase diagrams taken from the International Critical Tables (11). These are relevant since fusions of P.P.D. and phenolic compounds are often used in dyeing hair. This shows, for example, that, when mixtures of P.P.D. and resorcinol are melted together, a compound is formed and that the composition of this new compound is 1 mole of P.P.D. for each mole of resorcinol. Judged by light fastness alone it would appear that, for mixing with P.P.D, resorcinol is the most

Table XI
Phenolic Compounds Mixed with *p*-Phenylenediamine

Compound	% Phenolic (in Fusion Compound)	Mole Ratio of Phenolic to P.P.D. in Fusion Compound	Color on Hair[a]	Depth of Shade (Darkest to Lightest)	Fades After (in hours)
Hydroquinone	75.5 and 50.4	3 to 1 and 1 to 1	Light grey brown	4	4
Resorcinol	49.5	1 to 1	Golden brown	6	14
Pyrocatechol	60.4	3 to 2	Grey brown	5	12
Chlororesorcinol	...	...	Yellow brown	7	10
Pyrogallol	69.9 and 53.8	2 to 1 and 1 to 1	Grey brown	8	4
α-Naphthol	72.7	2 to 1	Purple black	1	10
1,5-Dihydroxynaphthalene	...	...	Grey purple	2	10
2,7-Dihydroxynaphthalene	74.8	2 to 1	Grey brown	3	2
p-Phenylenediamine (alone)	...	...	Dark brown	...	4

[a] Solutions were 0.01 *M* with regard to both the phenolic and P.P.D.

effective compound to use, followed by pyrocatechol and chlororesorcinol. However, examination of dyeings that had been in files for over thirteen years showed that the tendency to turn red on ageing increased in this order: chlororesorcinol (the least), resorcinol, pyrogallol, hydroquinone, pyrocatechol, and P.P.D. alone (the most). It appears that more attention to chlororesorcinol might be fruitful.

All of the dyeings discussed thus far were made by immersion, while the application to heads must be made by brushing. However, it was felt that conditions could be much better controlled and the conclusions drawn more valid with dyeings made by immersion rather than by brushing. In order to make direct comparisons of the depth of shade obtained by brush and dip dyeing a base solution was prepared, as described by Cook (12). Natural white hair was dyed using the mixture shown in Table XII, in which the concentration of P.P.D. was varied from 0.11% to 0.66% for the brush application. It was concluded that in order to obtain the same depth of shade with a brush application (in the presence of surface active agents) as with dipping, it would be necessary to use approximately four times the concentration of dye used in the dip application.

Table XII

Compositions Used for Company Immersion and Brush Dyeing

Immersion Dyeing[a]		Brush Dyeing[a]
0.11%	*p*-Phenylene diamine	Varied
0.20%	Sodium sulfite	0.20%
10.00%	Isopropyl alcohol	5.00%
40.00%	Deionized water	14.00%
...	Cook's base concentrate[b]	26.00%
...	Ammonium hydroxide	5.00%
50.00%	Hydrogen peroxide (20 volume)	50.00%
9.7	pH adjusted to	9.7

[a] Hair was dyed for 30 minutes at room temperature.

[b] Cook's Base Concentrate:

Propylene glycol	100 g
Cetyl alcohol	20 g
Oleic acid	300 g
Polyoxyethylene sorbitan monoleate	100 g

Table XIII

Pyridine Derivatives Alone and Mixed with *p*-Phenylenediamine and *p*-Aminophenol

	Alone		Mixed Solution with P.P.D.		Mixed Solution with P.A.P.	
Compound	Color on Hair[a]	Fades After (in hours)	Color on Hair[b]	Fades After (in hours)	Color on Hair[b]	Fades After (in hours)
2,3-Diaminopyridine	Very light blond	3	Dark grey brown	3	Blond	6
2,5-Diaminopyridine hydrochloride	Medium red orange	6	Dark red brown	4	Red orange	5
2,6-Diaminopyridine	Very light green blond	1	Black	2	Green grey	1
3,4-Diaminopyridine	Very light orange	5	Dark brown	3	Light blonde	5
2,6-Dihydroxypyridine hydrochloride	Very light grey	1	Dark brown	3	Red blonde	9
p-Phenylenediamine (alone)	...	...	Dark brown	4	...	...
p-Aminophenol (alone)	...	...	...	...	Light golden brown	4

[a] Derivative used at concentration of 0.025 moles/l.

[b] Solutions were 0.01 *M* in both components.

Dyeing with Pyridine Derivatives

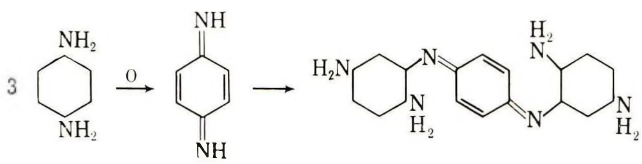
Recently Lange (10, 13, 14) reported on a series of oxidation hair dyes based on pyridine derivatives. Advantages were claimed for their use both alone and in conjunction with the well-known benzene derivatives. One of these products, 2,6-diaminopyridine, has been used in this country as a drabber for several years (15). Dyeings were made with five of these pyridine derivatives (in 0.025 *M* solutions) using the same method as previously used for the benzene derivatives, except that the concentration of hydrogen peroxide, as applied to the hair, was 1.8%, as suggested by Lange in his patent. All of the pyridine derivatives were purchased except 2,5-diaminopyridine hydrochloride, which was prepared according to Tschitschibabin and Kirsanow (16) by the reduction of 2-amino-5-nitropyridine.

The results of dyeing the pyridine derivatives alone and mixed with P.P.D. and P.A.P. are given in Table XIII. In addition to those shown in this table two other mixtures were dyed. A mixture of 0.01 *M* solutions of 2,5-diaminopyridine hydrochloride and 2,6-diaminopyridine gave a light ash blond shade which faded after one hour exposure. A light brown shade with a red cast, which faded after one hour, was produced using a mixture of 2,5-diaminopyridine hydrochloride and 2,6-dihydroxypyridine. Based on the results of tests with the five pyridine derivatives considered in this paper, it seems unlikely that they will replace the benzene derivatives for dyeing hair. The factors which contribute to this conclusion are their low tinctorial power, their poor fastness to light alone and in mixtures, the difficulty in obtaining these products, and their high cost.

Factors Influencing the Oxidation of *p*-Phenylenediamine

The question has often arisen as to how much oxidation of the intermediates to their colored forms is obtained under the conditions used in dyeing hair. Fortunately, there is a relatively simple experimental procedure that can be used for studying the effect of certain variables on the amount of this oxidation during the dyeing process. This is based upon the oxidation of P.P.D., which was first investigated by Bandrowski (17) in 1894 and Erdmann (18) in 1904. This reaction is pictured in Fig. 1. Several workers (17–19) favor structure I for Bandrowski's base, others (20, 21) favor structure II, while Austin (22) states that the structure has not been definitely established. However, all agree that Bandrowski's base is the principal and first stable product formed by the oxidation of

P.P.D. under conditions used for dyeing hair and furs. Heiduschka and Goldstein (23) were able to account for 93.8% of the originally used P.P.D. by determining Bandrowski's base and unchanged P.P.D. in the reaction mixture. Bandrowski's base can be treated as a solvent-soluble dye and used to dye hair a dark grey shade, or an aqueous suspension can be used to dye wool a fast blue-grey shade at boiling temperature. However, it is generally agreed that an azine, formed by the further oxidation of Bandrowski's base, is the final coloring material. However, Cox (24) has shown that this azine is even more insoluble in water than Bandrowski's base. It would therefore be included with Bandrowski's base when using an analytical method based on the formation of material insoluble in water. It is evident that the amount of Bandrowski's base or insoluble material formed can be used as a measure of the efficiency of the dyeing operation.



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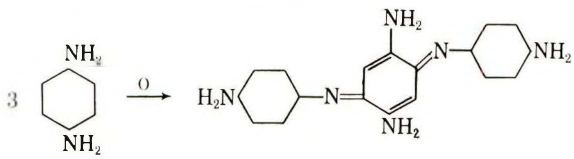

II

Figure 1. Proposed structures for Bandrowski's base

Heiduschka and Goldstein (23) studied the oxidation of P.P.D. and the effect of various factors on the yield of Bandrowski's base and the amount of P.P.D. left unchanged in the bath. However, they used one mole of hydrogen peroxide for each mole of P.P.D and a treatment time of twenty-four hours, which is vastly different from the conditions used for coloring hair. They showed that the yields of Bandrowski's base were at best only about 30% and that, even in the presence of excess peroxide, some 50% of the P.P.D. remained unchanged. Cox (24) showed that after dyeing copper mordanted fur for twenty-four hours about 15% P.P.D. remained in the unoxidized state. These conditions, too, differ greatly from those used in dyeing hair. On the other hand, a

Table XIV

Effect of Time of Treatment on the Yield of Bandrowski's Base

Time	Average Yield of B.'s Base[a]
5 minutes	1.04
15 minutes	1.63
30 minutes	3.00
45 minutes	5.29
1 hour	7.11
2 hours	12.2
4 hours	17.8
96 hours	57.8

[a] Solutions were 0.1 *M* in P.P.D. and contained 3% H_2O_2. PH = 9.7 ± 0.2; T = 25° ± 2C. The numerical values are based on the averages of two determinations and are expressed as % of the original P.P.D.

Table XV

Effect of Concentration of P.P.D. on the Yield of Bandrowski's Base

Concentration of P.P.D. (*M*)	Average Yield of B.'s Base[a]
0.2	5.12
0.1	5.93
0.05	4.96
0.025	4.59

[a] Solutions contained 3% H_2O_2—pH = 9.7 ± 0.2; T = 25° ± 2°C. The numerical values are based on the averages of two determinations after 45 min. of treatment and are expressed as per cent of the original P.P.D.

statement appeared in a recent publication (25) that by using excess peroxide complete oxidation of hair dye intermediates to the final pigment form is achieved.

Experiments were designed to simulate conditions used for dyeing hair in this country. The concentration of P.P.D. chosen was 0.10 *M*, which approximates the maximum amount used for dyeing hair, and the concentration of hydrogen peroxide was 3%. The pH of the solution was adjusted with ammonium hydroxide to 9.7 ± 0.2 after the addition of the peroxide. The solution was made up to a final volume of 100 ml with deionized water. After the stated time at 25°C ± 2°C, the solution was filtered through a Gooch crucible of medium porosity, the precipitate washed with 50 ml of deionized water and dried at 105°C. It was determined that a correction factor of 0.0029 g should be added to the weight of the precipitate in order to correct for the solubility of Bandrowski's base in the solution and wash water. For each experiment one of the conditions given above was varied while the rest remained constant.

Table XVI

Effect of Concentration of Hydrogen Peroxide on the Yield of Bandrowski's Base

Concentration of Hydrogen Peroxide (%)	Average Yield of B.'s Base[a]
4.5	8.86
3.0	5.93
1.5	4.88
0.75	3.28
0.375	2.26

Theory: 1 mole of para phenylenediamine plus 1 mole of hydrogen peroxide −0.34%.
Fur dyeing: −0.49%.

[a] Solutions were 0.1 *M* in P.P.D. pH = 9.7 ± 0.2; T = 25 ± 2°C. The numerical values are based on the averages of two determinations after 45 min. of treatment and are expressed as % of the original P.P.D.

Commercial products currently on the market have recommended dyeing times of from five to forty-five minutes. In Table XIV the results are given for an experiment in which the dyeing time was varied from five minutes to ninety-six hours. Natural white hair was dyed in another portion of each solution. All of these samples were dyed black except the one that had been treated for only five minutes, which was brown. These results confirm the fact that, under the conditions used, the oxidation of P.P.D. is a slow reaction. After forty-five minutes, which is the maximum time usually recommended for dyeing hair, only slightly more than 5% of the P.P.D. had been converted to Bandrowski's base. Even after ninety-six hours less than 60% conversion had been achieved.

In the next experiment the concentration of P.P.D. was varied from 0.025 to 0.20 *M*, with all other conditions remaining constant. The results, given in Table XV, indicate that the percentage yield of Bandrowski's base does not vary appreciably in the concentration range studied. Natural white hair was dyed, as in the previous experiment. All of the dyeings were black except the one at 0.025 *M*, which was brown. Heiduschka and Goldstein (23) found that, under the conditions used, the percentage yield increased with increase in concentration.

Next, the concentration of hydrogen peroxide was varied from 0.375 to 4.5%, with all other conditions remaining constant. The results are shown in Table XVI. Natural white hair was dyed, as in the previous experiments, and all of the dyeings were black.

It has long been known that, in addition to the oxidation of the intermediate, another function of the hydrogen peroxide is to bleach and soften the hair. In fact, Lange (13) states that each new hair dyeing method that does not permit the simultaneous bleaching of melanin is hopelessly at a disadvantage when compared with the oxidative hair dyeing methods of today. In this experiment equivalent solutions were prepared except that the P.P.D. was eliminated. Natural dark brown hair was treated in these solutions in order to determine the amount of bleaching achieved. The color, as expected, became progressively lighter as the concentration of hydrogen peroxide was increased, with practically no bleaching occurring when the concentration was only 0.375%. It was found that the percentage yield of Bandrowski's base increased as the concentration of hydrogen peroxide was increased. However, under these conditions—at a concentration of 4.5% hydrogen peroxide, which is the most that can be used without substantial damage to the hair—the yield was only 8.86%. Heiduschka and Goldstein (23) also found that the yield of Bandrowski's base increased with increase in the concentration of hydrogen peroxide.

It is interesting to note that, in the fur trade, the concentration of hydrogen peroxide is based upon the concentration of dye. The rule is that, in dyeing without a mordant, 15 ml of 3% hydrogen peroxide is used for each gram of dye. Since a 1.08% solution of P.P.D. was used in this experiment, this would mean that for each 100 ml of solution 16.2 ml of 3% hydrogen peroxide or a concentration of about 0.5% would be required. On the theory that one mole of hydrogen peroxide is required for each mole of P.P.D., as used by Heiduschka and Goldstein (23), the theoretical concentration of hydrogen peroxide would be 0.34%. Since the concentration of P.P.D. used in this experiment is approximately the maximum amount used in dyeing hair, it is evident that when the concentration of hydrogen peroxide in the solution is 3% the amount used is almost nine times that required by theory and almost six times the amount that would be used in accordance with fur trade practice. The above facts suggest that a critical study on hair and heads, especially for dark shades, using hydrogen peroxide at concentrations less than 3% might be fruitful.

In the next experiment the effect of pH, after the addition of the peroxide, on the yield of Bandrowski's base was determined. The results are shown in Table XVII. All of the dyeings on natural white hair were black. Substantial bleaching of the natural dark brown hair was obtained in the pH range 9.3 to 10.0, with much less bleaching at pH 7.0 and 5.7. A maximum yield of Bandrowski's base of 6.52% was obtained at a pH of 9.8, with the yield decreasing slightly at higher pH values and substantially at lower pH's to a low of 0.59% at pH 5.7.

Table XVII
Effect of pH on the yield of Bandrowski's Base

Final pH	Average Yield of B.'s Base[a]
10.0	5.54
9.9	5.87
9.8	6.52
9.6	6.11
9.3	4.75
7.0	2.26
5.7	0.59

[a] Solutions were 0.1 *M* in P.P.D. and contained 3% H_2O_2. T = 25 ± 2°C. The numerical values are based on the averages of two determinations after 45 min. of treatment and are expressed as % of the original P.P.D.

Table XVIII
Effect of Temperature on the Yield of Bandrowski's Base

Temperature (°C)	Average Yield of B.'s Base[a]	Melting Point (°C)
25	5.03	236
35	9.83	236
50	18.9	237

[a] Solutions were 0.1 *M* in P.P.D. and contained 3% H_2O_2. pH = 9.7 ± 0.2. The numerical values are based on the averages of two determination after 45 min. of treatment and are expressed as per cent of the original P.P.D.

In the next experiment the effect of temperature on the yield of Bandrowski's base was studied, and the results are shown in Table XVIII. The yield of Bandrowski's base is substantially increased by an increase in temperature between 25°C and 50°C. In fact, the yield was almost doubled by a 10-degree rise in temperature and increased almost four fold by a 25-degree rise. There was no decrease in the purity of the product, as determined by melting points. Heiduschka and Goldstein (23) also obtained an increase in yield with an increase in temperature.

What is the significance of these experiments involving Bandrowski's base? It is apparent that at the end of the normal dyeing time a large percentage of P.P.D. has not been converted to Bandrowski's base. In fact, Heiduschka and Goldstein (23) showed that a very large percentage of the P.P.D. remained unchanged in the bath at the end of the dyeing time. Since P.P.D. is readily soluble in water, a thorough washing and rinsing after dyeing is of the utmost importance in order to reduce the chance of toxic reactions. Even though it is not desirable to have an instantaneous conversion of P.P.D. to Bandrowski's base, because of the desirability of having the small P.P.D. molecule penetrate into the cortex of the fiber before it is changed into the larger Bandrowski's base, an efficiency of 5 to 10% for the dyeing operation is certainly less than desired. This procedure can be used as an experimental method for studying practical ways for improving the yield of colored procucts.

The formation of Bandrowski's base has also been used to determine what happens when P.P.D., and resorcinol are used together. By using 0.10 M P.P.D. alone a yield of 5.03% Bandrowski's base was obtained. However, when the solution was 0.10 M in both P.P.D. and resorcinol, there was no visual evidence of a precipitate; but an insoluble residue of 0.10%, based on the concentration of P.P.D., was obtained. It is evident that the presence of resorcinol prevented the formation of Bandrowski's base. This agrees with the results obtained by Cox (26).

Summary

A survey of oxidation hair coloring has been presented along with data and suggestions that should be useful to those working in this field. Included are 33 primary intermediates and 20 color modifiers of the benzene-naphthalene series and the 5 main members of the recently announced pyridine series. The important effect of the color modifiers on fading and color has been demonstrated, and areas and possible methods for additional fruitful research in improving oxidation hair coloring have been suggested.

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A Comparison of the Bacterial and Yeast Flora of the Human Scalp and Their Effect Upon Dandruff Production

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Synopsis—A half-head experiment was carried out on ten subjects. Through the application of yeast-inhibiting or bacteria-inhibiting antibiotics to either side of the human scalp, the effect upon dandruff was determined. Samples of dandruff scales (scurf) were removed separately from each side with an Oster HairVac and the weights determined. During a 91-day experiment it was shown that a reduction of the yeast flora was more effective in controlling dandruff than was a reduction in the number of bacteria.

Introduction

Previous studies (1–8) have indicated that the microbial flora of the scalp is a mixed one, comprising at least 25 species of bacteria, 15 species of yeasts, and 31 species of molds.

While our knowledge of the identity of scalp microorganisms has increased, a causal relationship of individual representatives or groups of microorganisms to the problem of dandruff has not been established. VanderWyk (9), using a quantitative gravimetric method for removing and measuring the amount of human dandruff production, showed

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that an almost complete elimination of the microbial flora lessened the severity of dandruff by 31% in seven out of nine subjects studied.

It is the purpose of this investigation to determine whether the bacterial flora or the yeast flora has the greater influence upon scurf production. Included among the yeasts is *Pityrosporum ovale*, normally found in 80% of human scalps and considered by some to be dandruff-associated. It should be possible to control the nature of the scalp microbial flora by applying selectively acting antibiotics or mixtures of them to either side of the human scalp. Tetracycline* was used to control the bacteria and nystatin† to control yeasts. A mixture was applied when it was desired to suppress the entire microbial flora. Using the method of VanderWyk (9), scurf samples were removed with an Oster HairVac from both sides of the scalp prior to and during treatment. Quantitative comparisons based upon the weight of the samples indicated the severity of dandruff on both sides.

Method

Ten subjects were selected at random without consideration of their scalp condition. Each subject was given detailed instructions to follow throughout the entire experimental period. He was permitted to shampoo his head once with any nonmedicated product of his own choice one week before the start of the testing. Thereafter shampooing and swimming in chlorinated pools were not permitted.

Sampling Periods

The entire experiment lasted for 98 days and was divided into six sampling periods. Samples of scurf were removed and weighed on Monday, Wednesday, and Friday of each week.

Pre-sampling Period: (7 days). During this time any special treatment of the scalp was discontinued, and each subject was permitted to apply only tap water to his scalp. No scurf samples were removed.

Pre-treatment Period: (12 days). During this time the tap water treatment was continued, and samples of scurf were removed from both sides of the scalp three times weekly. This period established "normal" scurf values for each subject.

Treatment Period A: (26 days). Each subject was given two prep-

* Tetracycline was supplied as Achromycin® by Lederle Laboratories, a Div. of American Cyanamid Co., Pearl River, N. Y.

† Nystatin was supplied as Mycostatin® by E. R. Squibb & Sons, N. Y.

arations, one to be applied on the right and the other to the left side of his scalp. One-half ounce of each was massaged into the appropriate side three times a day instead of the tap water which had been used during the pre-treatment period. The formulas for the two preparations are:

Prep. LS-A (left side)		*Prep. RS-A (right side)*	
Tetracycline	2.0 g	Tetracycline	2.0 g
Susp. *P. ovale*	1.0 ml	Nystatin	500,000 units
Tap water	1000 ml	Tap water	1000 ml

The saline suspension of *P. ovale* organisms was obtained by isolating this yeast from the scalp of one of the subjects and was equal in density to that of a No. 5 MacFarland nephelometer tube. The mixture of antibiotics applied on the right side of the scalp is inhibitory to both bacteria and yeasts, while Prep. LS-A used on the left side is inhibitory only to bacteria.

During this period scurf samples were removed from both sides three times each week.

Treatment Period B: (26 days). During this time the treatment on the right side of the scalp remained the same as in Period A. The formula for Prep. LS-B applied on the left side was:

Prep. LS-B (left side)	
Nystatin	500,000 units
Bacterial susp.	1 ml
Tap water	1000 ml

The bacterial suspension was prepared before the start of the experiment. Approximately 5 mg of scurf from each subject was placed in 50 ml of thioglycolate broth. After incubation, the suspension of mixed bacterial flora was adjusted with saline to a turbidity equal to that of a No. 5 MacFarland nephelometer tube. Prep. LS-B allows the bacterial flora to flourish in large numbers and at the same time inhibits the growth of *P. ovale* and other yeasts. Scurf samples were removed from both sides 3 times each week.

Treatment Period C: (14 days). During this time the treatment on the right side of the scalp remained the same as before. Antibiotic treatment on the left was omitted entirely, and the preparation applied consisted of a mixture of suspensions of scurf bacteria and *P. ovale* prepared as previously described. The usual samples were removed three times weekly.

Treatment Period D: (13 days). The treatment for both sides was the same. It consisted of the application of a mixture of suspensions of scurf bacteria and *P. ovale.*

Method of Removing Scurf Samples

Scurf was removed from the scalp with the aid of the Oster HairVac Model 215.* It is supplied with disposable plastic heads which can be sterilized by chemical means. Samples were obtained by passing the apparatus over each half of the scalp 12 times in such a manner as to obtain a uniform collection each time. Three passes through the scalp were made beginning at the right (or left) of the median line and proceeding from temple to nape of neck. Each pass covered a different area of the scalp moving to the right (or left), with the final pass just grazing the top of the ear. The entire procedure was repeated four times for each half. Each subject was permitted to collect his own scurf. Samples were prepared for microbiological examination under sterile conditions.

Treatment of Scurf Samples

The weights of all samples were recorded. Smears were made, stained with Loeffler's methylene blue and examined microscopically for the presence of *P. ovale* and other yeast forms. An evaluation of each sample was made on the basis of the average number of yeast cells counted in 10 immersion oil objective fields. The effect of nystatin in suppressing the numbers of *P. ovale* could thus be determined. Bacterial plate counts were made using Trypticase Soy agar (B.B.L.). The weighed scurf samples were placed in flasks containing 100 ml of sterile saline. After shaking for 10 minutes, 1 ml aliquot portions were plated out. Bacteria counts were computed as number of organisms per mg of scurf sample.

Results

Scurf Evaluation. Table I shows the average scurf sample weights for all subjects in each sampling period. Except for two subjects (3 and 5) the weights from opposite sides of the scalp during the pre-treatment period were very similar. The average weight from eight subjects was 33.7 mg from the left side and 34.5 from the right, a variation of only 2.3%. Subjects 3 and 5 both parted their hair on the left side,

* John Oster Manufacturing Co., Milwaukee, Wis.

Table I
The Average Weights of Scurf Samples for All Subjects in Mg

Subject	Pre-treatment Period	Treatment Period A	Treatment Period B	Treatment Period C	Treatment Period D
			Left Side		
1	67.9	77.0	43.9	28.1	39.0
2	35.0	37.0	37.7	25.7	25.9
3	40.8	37.9	30.1	19.2	13.9
4	20.2	19.0	14.0	14.5	...[a]
5	32.0	49.0	62.5	47.5	60.5
6	39.1	48.8	24.7	19.5	18.8
7	47.2	55.4	39.5	43.0	32.6
8	26.0	30.3	28.0	27.3	23.3
9	25.3	43.5	21.1	12.1	11.1
10	76.3	56.4	39.8	41.2	31.1
Ave.	41.0	45.4	34.1	27.8	29.8
			Right Side		
1	71.4	21.6	11.8	10.6	8.2
2	32.4	24.9	19.9	14.9	17.3
3	62.4	30.6	14.0	14.5	15.4
4	19.5	19.7	12.1	14.3	...[a]
5	46.8	48.8	47.8	34.9	44.3
6	43.0	31.9	13.5	15.1	9.8
7	51.8	44.6	37.7	34.1	25.7
8	25.8	32.1	26.0	25.4	22.6
9	29.7	33.4	15.2	11.9	14.1
10	71.7	35.9	20.8	24.9	16.7
Ave.	45.4	32.3	21.9	20.6	20.3

[a] Not done.

probably accounting for greater right side values. Table II shows the average percentage increase or decrease in scurf weights during each of the four treatment periods. These are computed from results obtained during the pre-treatment period. Figure 1 shows a comparison of the average weights from all subjects.

Microbial Evaluation. Figures 2 and 3 represent bacterial plate counts and *P. ovale* slide counts respectively. During the pre-treatment period bacteria counts on both sides of the scalp averaged 50,000/mg. During Period A when both sides were treated with tetracycline, counts were reduced to an average low of 200/mg. Values for both sides were similar and in no instance was a sample of scurf obtained which was entirely free of bacteria.

During Period B when a suspension of bacteria was applied to the left side the counts varied considerably. The highest count recorded was

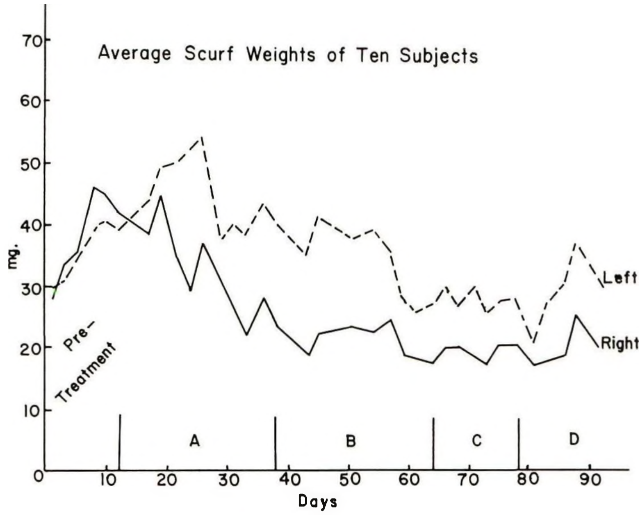

Figure 1. Average scurf weights in mg of all subjects

Table II

The Average Percentage Variation in Scurf Weights During Each of the Treatment Periods from those of the Pre-Treatment Period

Subject	Treatment Period A	Treatment Period B	Treatment Period C	Treatment Period D
		Left Side		
1	+13.4	−23.5	−58.5	−42.5
2	+5.7	+7.7	−26.6	−26.0
3	−7.1	−26.2	−52.9	−60.6
4	−5.9	−30.6	−28.2	...[a]
5	+53.1	+95.3	+48.2	+89.0
6	+24.8	−36.8	−50.0	−51.9
7	+17.3	−16.3	−8.9	−30.9
8	+16.5	+7.6	+5.0	−10.4
9	+41.9	−34.1	−62.2	−65.3
10	−26.0	−47.8	−46.0	−58.5
Ave.	+9.1	−16.8	−33.2	−28.4
		Right Side		
1	−69.7	−84.4	−85.2	−89.3
2	−23.3	−38.7	−54.1	−46.7
3	−51.1	−77.6	−76.9	−75.4
4	+1.0	−37.9	−26.7	...[a]
5	+4.2	+2.1	−25.4	−5.3
6	−25.8	−68.6	−64.8	−77.2
7	−13.8	−27.2	−34.1	−50.4
8	+24.4	+0.8	−1.6	−12.4
9	+11.1	−35.8	−70.0	−61.8
10	−49.9	−70.9	−65.2	−76.7
Ave.	−30.0	−52.6	−55.4	−56.4

[a] Not done.

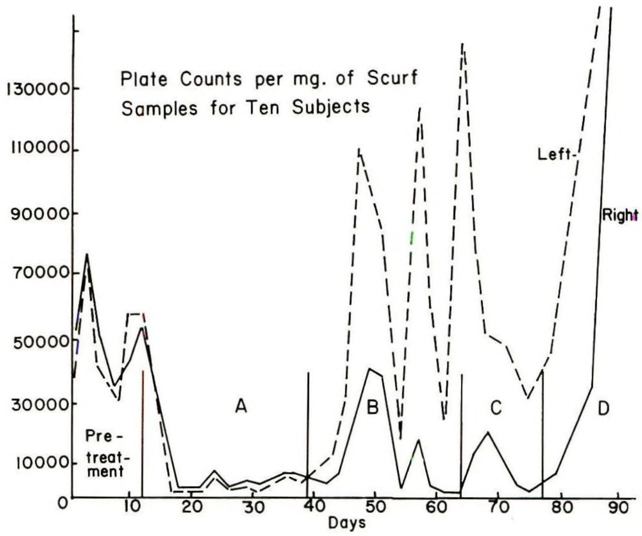

Figure 2. Average bacterial plate counts per mg of scurf sample for all subjects

145,000/mg. The counts on the left were much higher than on the right. During Period D, with the cessation of anti-microbial treatment and the application of a suspension of mixed bacteria, the counts quickly rose on both sides, averaging 200,000/mg.

The average *P. ovale* count during the pre-treatment period was the same for both sides (17 per immersion oil objective field). During Period A there was a decrease in *P. ovale* counts on the right side in nine subjects. The left side counts of all subjects showed an increase during this time. The average count was 13 per field on the right and 47 per field on the left. Although the actual reduction in *P. ovale* counts on the right side might not seem to be significant, it is possible that some organisms were picked up by the HairVac as a carry-over from the left. A microscopical comparison of scurf from both sides was made. Preparations from the left side showed a greater number of organisms embedded in the scurf particles than from the right side.

During Period B when both sides were treated with nystatin the average number of *P. ovale* cells in nine subjects was seven per field for both sides. One subject had high counts throughout the entire experiment. Periods C and D showed very high counts, as might be expected in the absence of any nystatin application. Despite continuous nystatin treatment on the right side for most of the experiment it was very unusual to find a scurf sample completely negative for *P. ovale*.

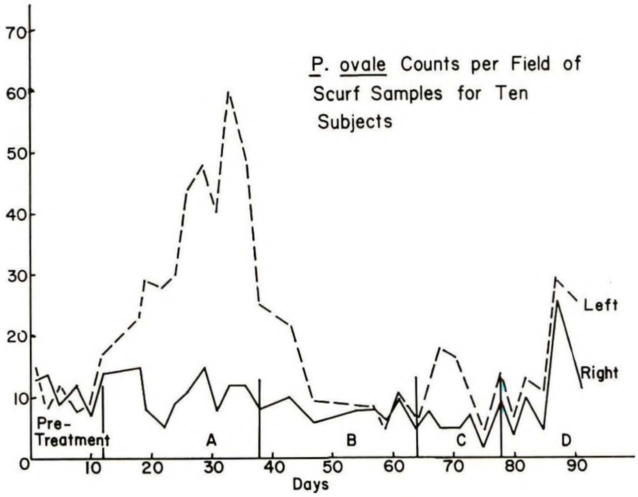

Figure 3. Average *P. ovale* slide counts per immersion oil objective field for all subjects

Discussion

Except during the last 13 days of the experiment, treatment on the right side consisted of a mixture of tetracycline and nystatin, having activity against bacteria and yeasts. Results for the first 66 days support the previous findings of VanderWyk (9). He had shown that elimination of the entire microbial flora from the scalp reduced scurf production in seven of nine subjects by 31%. In the present half-head experiment after a similar period a significant reduction was seen in nine of ten subjects. The average reduction for all subjects was 56.4%. The range in nine subjects was between 25.4 and 85.2%.

During Period A (26 days) when the entire microbial flora on the right side was controlled by a mixture of two antibiotics, scurf reduction occurred in six subjects. The average reduction for ten subjects was 30%. In contrast, the left side, treated with a mixture of *P. ovale* suspension and tetracycline, showed an increase of 9.1% in seven subjects.

The interpretation of these differences is that the yeast scalp flora (including *P. ovale*) plays a greater role in dandruff production than does a mixed bacterial flora. To test this idea further, treatment on the left side was changed for the next 26 days to control the yeast flora and to allow the bacterial flora to flourish. In addition, a mixed bacterial suspension was applied to the left side. Treatment on the right side continued as before. At the end of this period, scurf production on the left side was reduced in seven of ten subjects. The average reduction was 16.8% from pre-treatment levels. On the right side scurf production continued to lessen, averaging 52.6% in all subjects. This represented an increased reduction of 22% over Period A.

During Period C (14 days) treatment on the right side continued as before, but antibiotic treatment on the left side was omitted entirely. A mixture of *P. ovale* cells and bacteria was applied daily. The right side showed a definite leveling off in scurf production with only a 3% decrease from Period B. Previous studies (9) had shown that threshold levels were established for different individuals and that it was impossible to lower scurf production below certain levels by eliminating the microbial flora. A reduction was also seen on the left side (19% from Period B) despite the application of a microbial flora. Two explanations can be offered for this. The first is that the residual effect of nystatin treatment was carried over into Period C and prevented the establishment of a substantial yeast flora. The second is that the mixture of antibiotics applied on the right side exerted a similar suppression effect due to a possible carry over from right to left side. Microbiological studies of the scurf from both sides (Figs. 1 and 2) showed no significant increase in the microbial flora during this time.

For this reason all antibiotic treatment was stopped, and a mixed microbial flora was applied to the entire scalp. After 14 days (Period D) when the experiment had to be terminated, it was apparent that scurf production was beginning to increase, particularly on the left side (Fig. 1). This period was too short to show definitely how soon scurf values would return to pre-treatment levels. VanderWyk (9) observed that under similar conditions a lag period of about 21 days passed before a significant rise in scurf production was evident.

Observations on Individual Subjects. Variations in results were noted among several individuals taking part in the experiment. Of the ten subjects six showed a pattern of scurf production previously described. Two subjects (4 and 8) had very low pre-treatment scurf values of 20.2 mg and 26.0 mg per sample respectively on the left side. Neither subject showed any visible dandruff problem, and their scurf production did not appear to be significantly affected by antibiotic treatment. One subject (5) showed little or no change in scurf production on the right side during the first 66 days despite the continuous use of nystatin. On the left side, however, there was an increase of 95%. Microscopic studies of the scurf indicated an increase in *P. ovale* counts during all four treatment periods on both sides. During Period B the average counts were 60 per field on the right and 65 per field on the left side. A nystatin resistant organism was indicated. Confirmation of this was made when a culture of *P. ovale* was isolated from the scalp and subjected to sensitivity studies. Only one subject (10) showed any significant decrease in scurf production on the left side during Period A. The reduction was 26%. This same subject showed a reduction of 49.9% on the right side which was treated with nystatin.

Summary and Conclusions

1. A half-head experiment was carried out on ten subjects in which the application of a mixture of tetracycline and nystatin to the right side of the human scalp resulted in a reduction of 56.4% in dandruff production after 66 days of treatment.

2. The left side of the scalp was treated with tetracycline for 26 days and then with nystatin for 26 days. The effect of these separate treatments upon dandruff production was compared with the effect of the combined treatment on the right side. Tetracycline was used to control the bacterial flora, nystatin to control yeasts (including *P. ovale*) and a mixture to control the entire flora.

3. Treatment with a tetracycline-nystatin combination on the right side during the first 26 days resulted in a 30% reduction in dandruff in six subjects. During the same period a 9.1% increase in dandruff was seen on the left side when the bacterial flora was suppressed with tetracycline but the yeast flora was encouraged to flourish.

4. During an additional 26 day period, a tetracycline-nystatin combination treatment on the right side resulted in a 52.6% reduction in scurf production in eight subjects. During this same period when the left side was treated with nystatin instead of tetracycline scurf production was reduced by 16.8% from pre-treatment levels in seven subjects.

5. These results indicate that the presence of a yeast flora in the scalp, principally *P. ovale*, has a greater influence upon dandruff production than does a bacterial flora in the majority of individuals studied. Eight subjects showed scurf productions which were lower when the scalp was treated with nystatin than when treated with tetracycline. The final results also showed that for best control of dandruff the entire microbial flora should be suppressed.

6. There were variable results among individuals. Two subjects with low pre-treatment scurf values and no obvious dandruff problems

did not respond with a significant reduction in scurf production. Another subject harbored a nystatin resistant *P. ovale* in his scalp. As a result scurf production on the left side increased by 89% after 79 days.

7. It was not possible under the conditions of the treatment to produce microbial-free scalps in any subject.

8. The results clearly demonstrated the beneficial effect of antimicrobial agents in the control of dandruff. The use of agents having broad spectrum activity, particularly against yeasts is important. This work suggests further studies in the use of long-acting, substantive, penetrating creams and dressings. Such an approach, combined with periodic use of medicated shampoos, seems to offer the best solution to the dandruff problem.

(Received November 30, 1966)

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Book Reviews

PLASTICS, by J. Harry Du Bois and Frederick W. John. Reinhold Publishing Corporation, New York. 1967. 342 pages, illustrated and indexed. Price $11.

This book can be barely recognized as the fourth edition of a work last revised in 1945. Developments during this rapid growth period of the plastics industry have required a virtually complete rewriting of the earlier edition. This edition provides a broad treatment of plastics materials and processing with emphasis on the engineering aspects.

Following an interesting presentation of the history of the industry since early in the last century there are concise descriptions of each of the various commercial plastics. The advantages of both thermosetting and thermoplastic materials are described as well as their principal and unique applications.

The remainder of the book is principally concerned with processing methods and material properties in so far as they are related to processing. Extensive treatment is given to extrusion, injection, and compression molding techniques including several detailed diagrams of the processing machinery. Other precedures such as vacuum coating and blow molding are also outlined, but in less detail. Considerable discussion of a rational for material choice from both end-use and processing viewpoints is also included.

The book is well illustrated with more than a hundred photographs as well as many line drawings, graphs, and diagrams. It is clearly written and would be useful to the cosmetic chemist generally concerned with packaging and processing problems. —John D. Galligan—Gillette Research Institute.

NONIONIC SURFACTANTS, edited by Martin J. Schick. Marcel Dekker, Inc., New York, N. Y. 1967. 1085 pages, illustrated and indexed. Price $43.50.

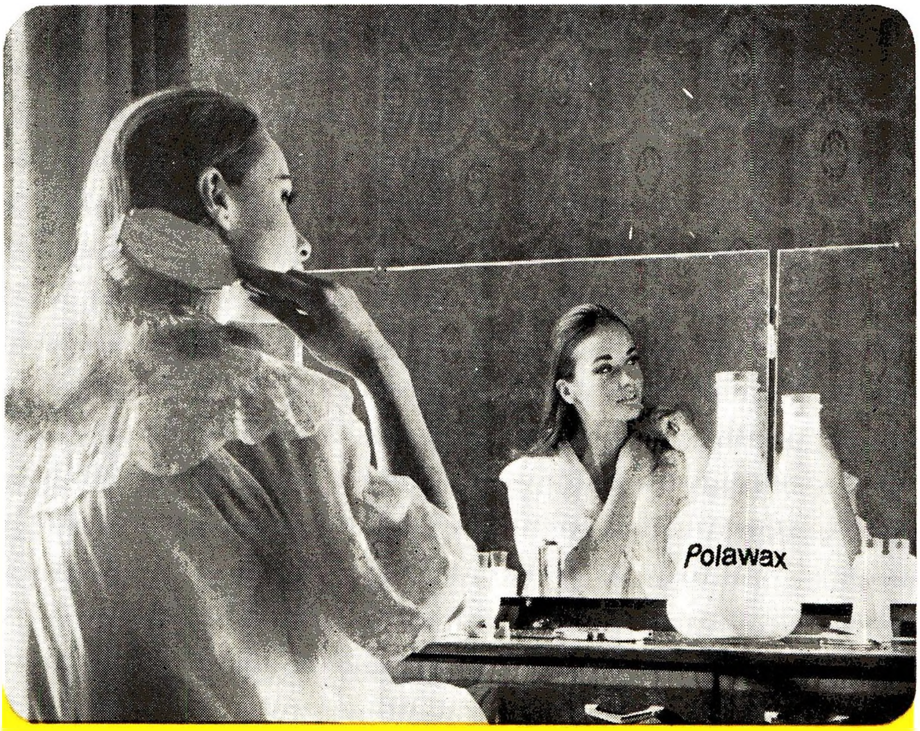
This volume is the first one in a series entitled Surfactant Science Series. It is a collection of papers covering the subject of nonionic detergents. This book is massive and comprehensive and includes 28 chapters by more than 30 contributors. The book is divided into four parts. The largest portion is devoted to Organic Chemistry but includes also comments on the practical applications of the many chemical entities discussed. The remaining three parts are concerned with Physical Chemistry, Analytical Chemistry, and Biology of Nonionic Surfactants.

Any review of a book covering such a wide variety of highly specialized fields is difficult and perforce becomes very personal and subjective. To this reviewer the chapters on Mechanism of Ethylene Oxide Condensation (Shachat and Greenwald), Solubilization (Nagakawa), and Thermodynamics of Micelle Formation (Hall and Pethica) were the most interesting. Admittedly, the chemist concerned primarily with application problems may find other sections of greater interest; still, answers to the more fundamental problems should be most helpful whenever the utility of various nonionic wetting agents is the ultimate concern.

Unfortunately, the large number of authors makes for occasional repetition; however, the editor is probably justified in presenting chapters which can be read without need for referral to other chapters. The major objection to the book is its size. Much of the material in the first 400 pages is reminiscent of the catalogues published by companies engaged in the distribution of surfactants. Much space and effort could have been saved by referring the interested reader to these readily available sources of practical information. Additional space could have been saved by reducing the size of the figures and paying closer attention to their arrangement.

Only a few of the chapters are provided with summarizing paragraphs; this, in turn, makes it rather difficult to gain a clear picture of the scope of each chapter except by scanning the chapter index. The alphabetical index comprises almost 50 two-column pages but is still inadequate to make the material within this volume readily accessible. It is unfortunate that authors, at times, emphasize some aspects of the activity of nonionic surfactants while neglecting aspects which are of practical importance. For example, this book allots considerable space to the rather meager antimicrobial activity of nonionic surfactants but refers only in passing to the interference by nonionic surfactants with the activity of many commonly used preservatives. Many contributors to this volume are employed by commercial organizations, and the emphasis on the favorable qualities of nonionic surfactants can be readily understood.

In summary, this book is not intended for casual reading or for browsing. It is, instead, a comprehensive reference to the science and technology of nonionic surfactants. Despite some minor flaws, the primary objective of this book, "to provide the neophyte research worker with an introduction and the advanced reader with critical reviews," has been admirably met.—M. M. Rieger—Warner-Lambert Research Institute.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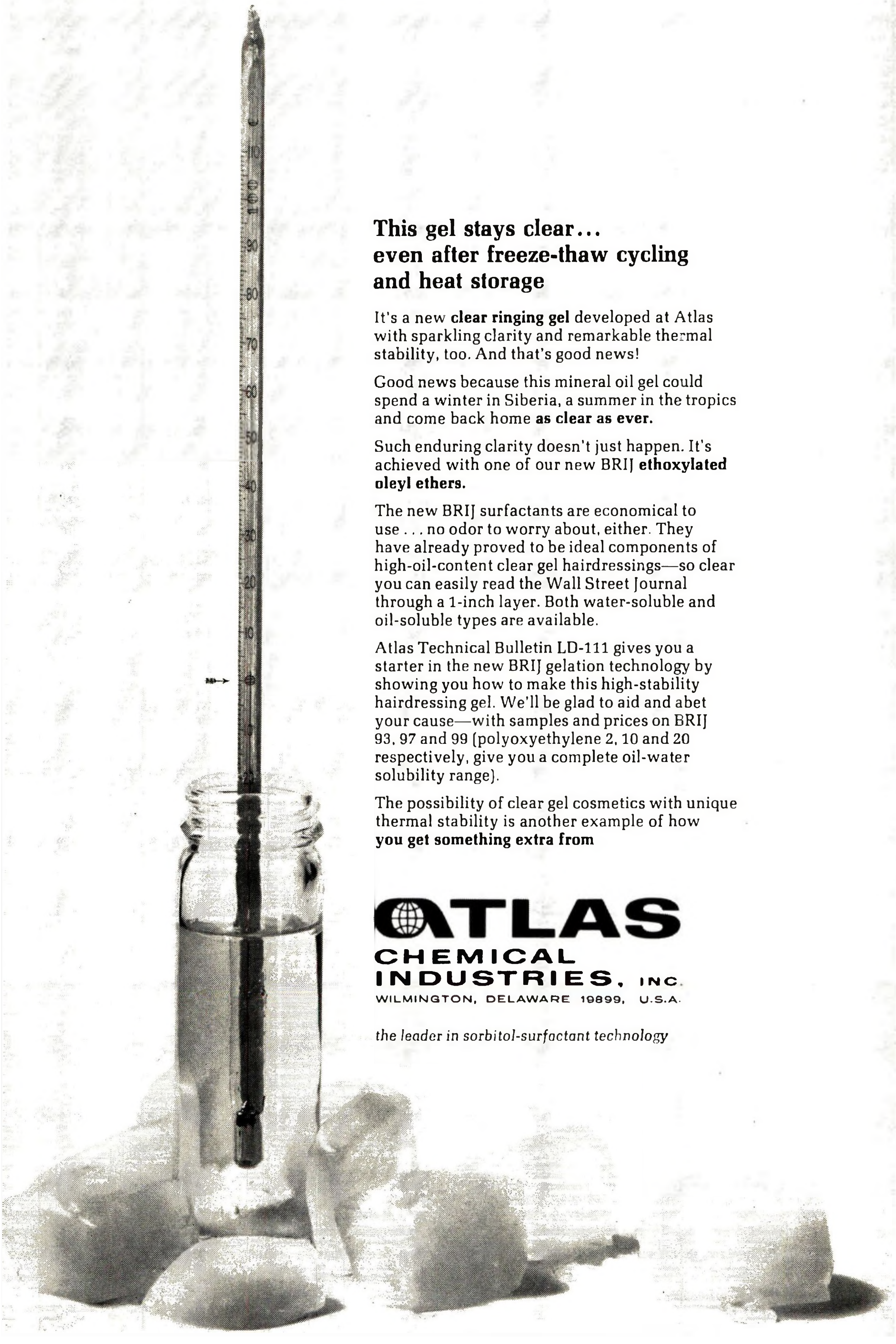

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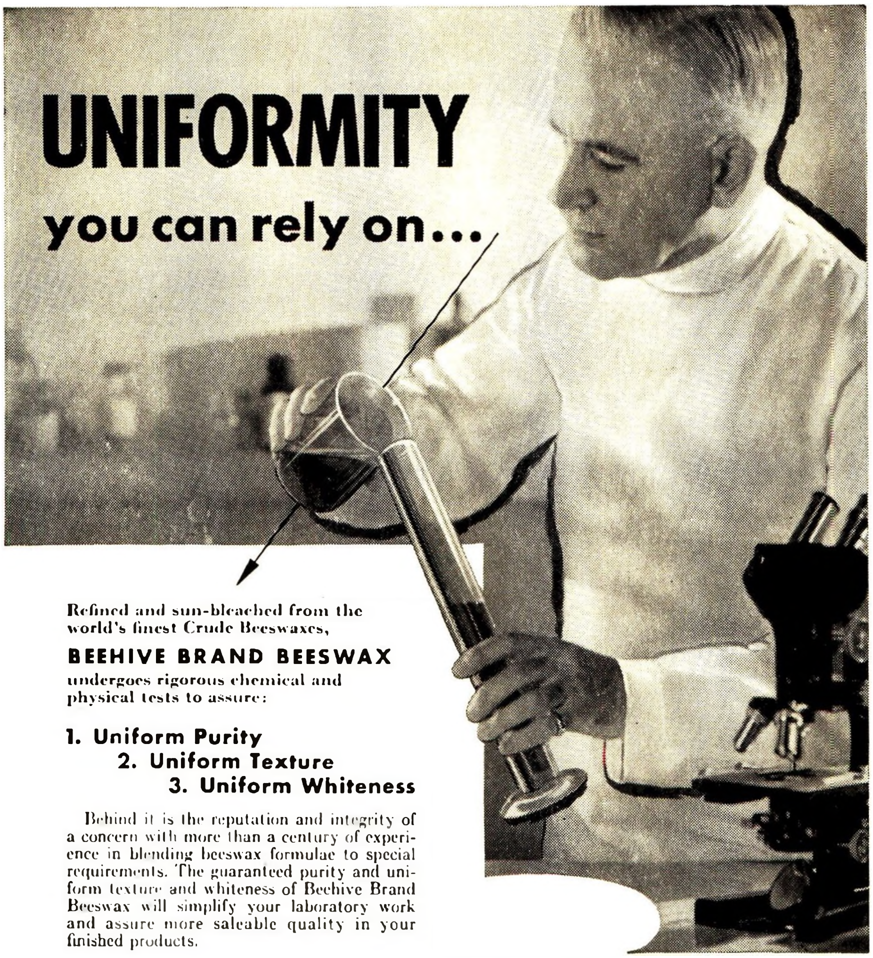

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