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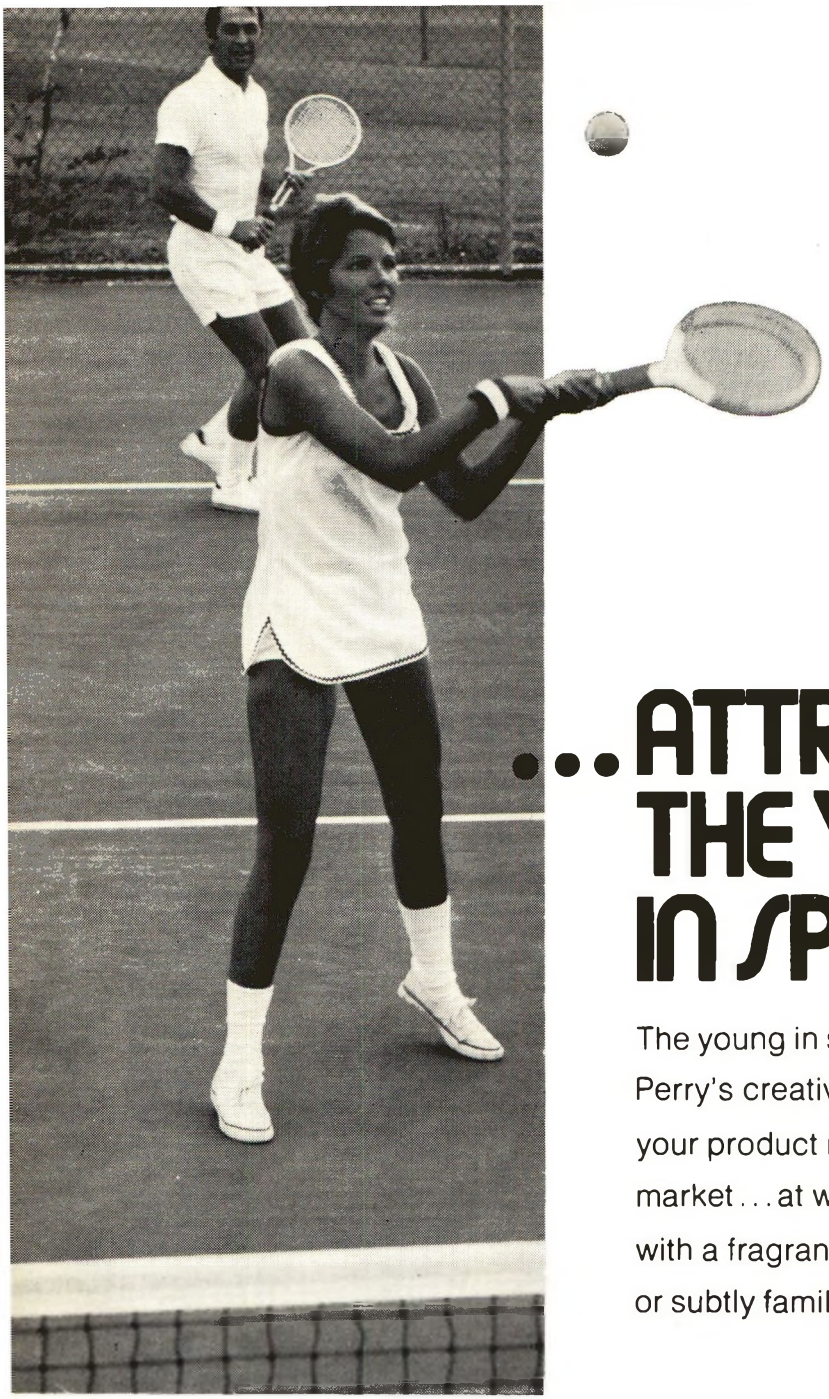

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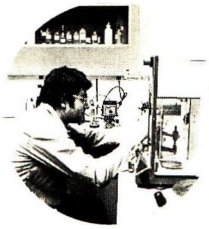

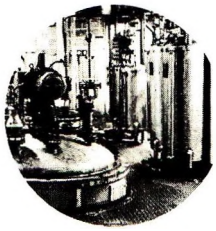

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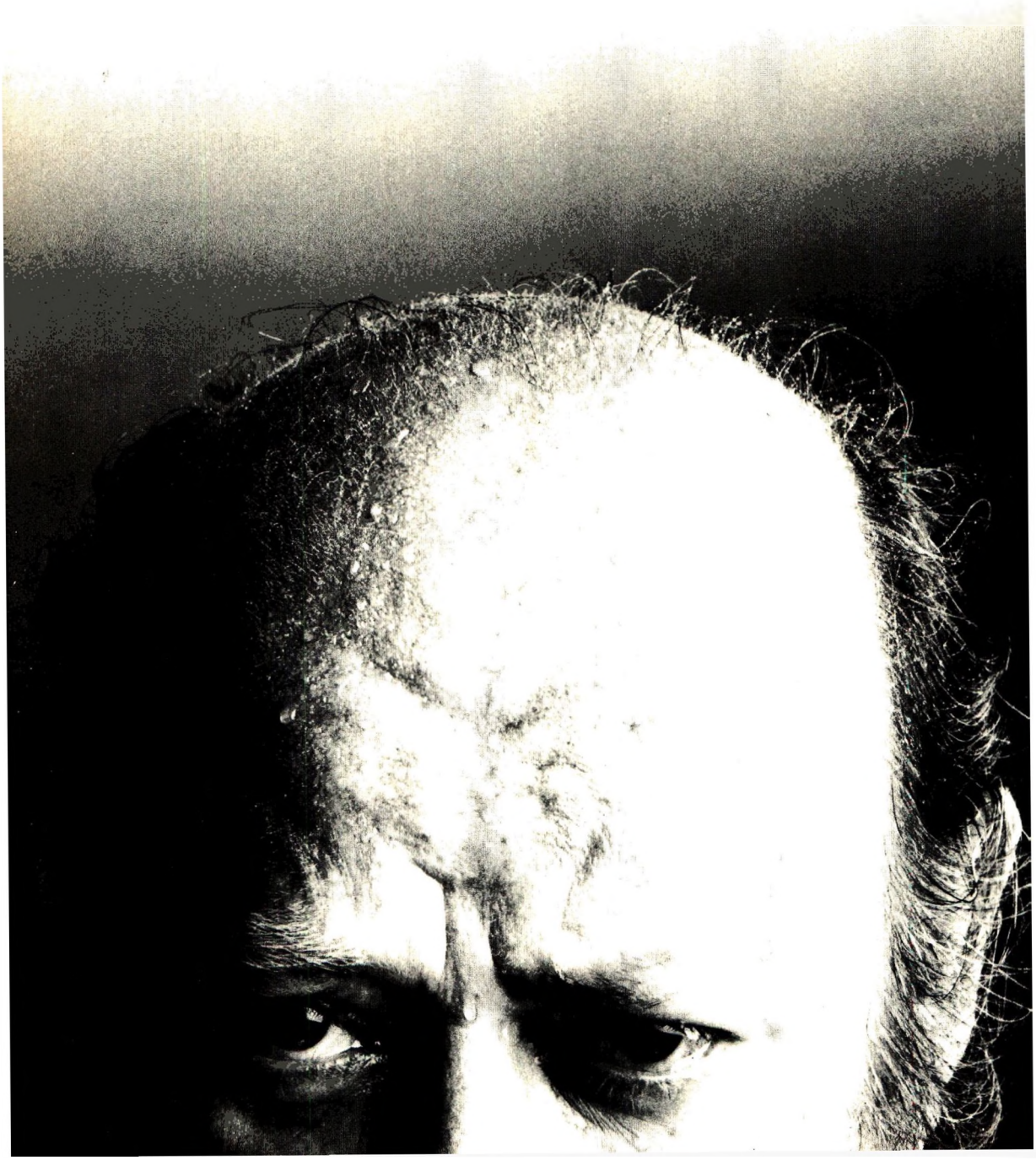

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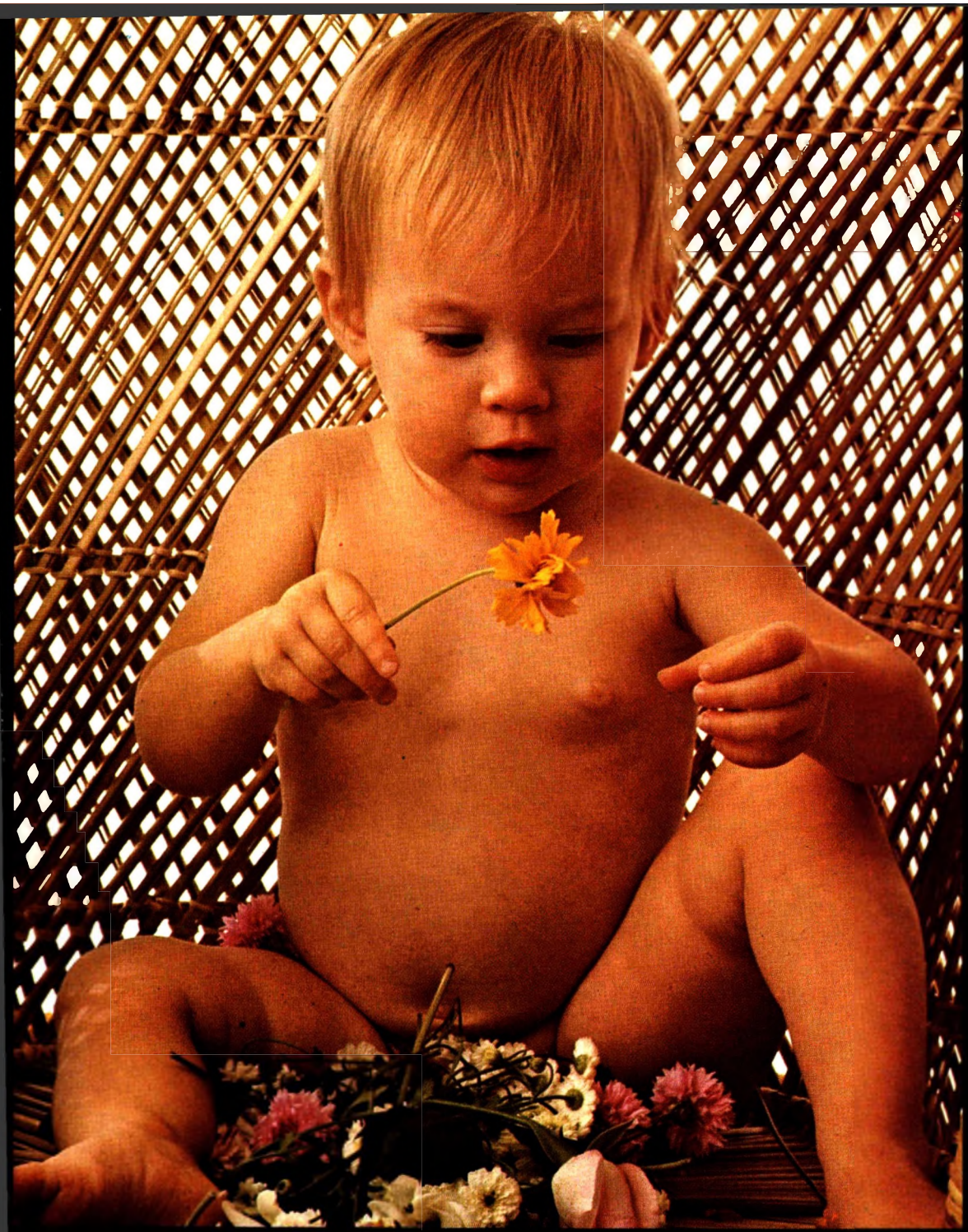

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SYNOPSES FOR CARD INDEXES

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

Age related baldness. Effect of topical treatment: J. H. Herndon, Jr., D. A. Leeber, and C. B. Read. *Journal of the Society of Cosmetic Chemists* **28,** 485 (September 1977)

Synopsis—Twenty-nine subjects, 10 women and 19 men, took part in a trial in which thorough cleansing of the scalp was used as therapy for age-related baldness (ARB). We measured changes in rates of hair loss, number of hairs identifiable per unit area of scalp, telogen/anagen ratio, and numbers of superficial squames removable per unit area of scalp skin. The subjects completed a two-month control period consisting of infrequent low intensity shampooing (no more often than every 3 to 7 days), then a three-month treatment period consisting of rigorous daily cleansing of hair and scalp. Following treatment, we noted a highly significant reduction in squames per unit area, but only trends toward improvement in rates of hair loss and in numbers of hairs counted per unit area of scalp. There was no observable change in telogen/anagen ratio in hair roots. We concluded that rigorous cleansing of hair and scalp could not be shown to affect significantly the course of ARB.

Identification of preservatives: H. Gottschalck and T. Oelschläger. *Journal of the Society of Cosmetic Chemists* **28,** 497 (September 1977)

Synopsis—Methods are described for identifying and quantifying the most important preservatives used in cosmetic products. Emulsions are separated into several homogeneous phases with the aid of solvents. After thin layer chromatographic separation (different layers; different developing liquids), the preservatives are identified with the aid of color reactions, reduction of fluorescence, spectral measurements, and RF values. The quantitative determination generally is performed by direct photometric evaluation of the thin layer plates (densitometry); the best conditions for assays are described. Dowicil 200 is determined quantitatively by splitting off of formaldehyde and subsequent reaction with dimedone. The amount of the dimedon derivative formed is determined gravimetrically or titrimetrically.

The effect of detergents on swelling of stratum corneum: Gerald J. Putterman, Nancy F. Wolejsza, Maria A. Wolfram, and Karl Laden. *Journal of the Society of Cosmetic Chemists* **28,** 521 (September 1977)

Synopsis—Several surfactants were tested for their ability to produce in-plane swelling (increase surface area) of squares of guinea pig stratum corneum. Highest levels of swelling were observed with the anionic surfactants sodium laurate and sodium lauryl sulfate, while little or no swelling was observed with the few cationic and nonionic surfactants examined. Although swelling in laurate was shown to be reversible, work index measurements revealed an irreversible weakening of the tissues. To gain insight into the mechanism of swelling the effects of protein denaturants and delipidizing agents were also evaluated. We conclude that protein denaturants, *per se*, do not cause stratum corneum swelling, but that swelling is due at a reversible conformation change resulting from cooperative binding of the detergent. Stratum corneum swelling could be of value for studying detergent-skin interactions and for predicting detergent penetration of skin and possible subsequent skin irritancy.

Some comparisons of benzoyl peroxide formulations: O. J. Lorenzetti, T. Wernet, and T. McDonald. *Journal of the Society of Cosmetic Chemists* **28**, 533 (September 1977)

Synopsis—The biological profile of several formulations of benzoyl peroxide are compared. The efficacy of benzoyl peroxide can be optimized by influencing formulation variables. A benzoyl peroxide formulation "A" is compared to some competitive products, C, D, and B. Dermal irritation in rabbits, acute toxicity in rats, efficacy against *Corynebacterium acnes*, as well as several formulation variables, such as particle size and vehicle interaction, are compared.

The selection of a candidate formulation is subjected to test involving acute toxicity, ocular irritation, skin irritation, and sensitization. The design of these tests should involve not only positive and negative controls, but also appropriate reference products which are already on the market. It is important when developing biological data to accumulate data on the finished product, since it is the finished product which will come into extensive contact with the skin in a clinical population.

All the formulations tested were equivalent in performance except for ocular irritation potential. Formulation with larger particle size distribution had a greater ocular irritation potential.

The electrostatic properties of human hair: Anthony C. Lunn and Robert E. Evans. *Journal of the Society of Cosmetic Chemists* **28**, 549 (September 1977)

Synopsis—Three factors have been studied which are significant in the development of electrostatic charge on hair fibers: (1) the charge generated by separation between hair fibers and brush or comb; (2) the mobility of charge on the fibers; and (3) the distribution of charge along the fiber length. Instrumentation has been developed to measure each of these parameters, and the effect upon them of quaternary ammonium compounds and other fiber treatments.

Quaternary antistatic agents are found to reduce substantially the charge generated on the fibers; the half-life of charge mobility varies with the quantity of agent on the hair. The density of charge is greatest near the fiber tips, corresponding to the region of a peak in the combing force. It is concluded that the mechanism of action of these antistatic agents is primarily one of lubrication; a reduction in combing force leads to a reduction of static charge generated on the hair.

The optical properties of human hair I. Fundamental considerations and goniophotometer curves: Robert F. Stamm, Mario L. Garcia, and Judith J. Fuchs. *Journal of the Society of Cosmetic Chemists* **28**, 571 (September 1977)

Synopsis—By using a goniophotometer and linearly polarized parallel white light incident obliquely on planar arrays of parallel oriented taut hair fibers, the light scattered and specularly reflected from the fibers has been recorded as a function of the angle of observation and direction of polarization in the exit beam. It can be categorized as being: (a) reflected from the air-cuticle interfaces on the near side (white light), from the cuticle-air interfaces on the far side (colored light), and from an interface probably consisting of a discontinuous wedge-shaped sheath of air parallel to the axis of the fiber; or (b) scattered from optical imperfections which are principally on the surface of the fibers. Specular reflection from the front air-cuticle interfaces is independent of hair color and permits an evaluation of Θ ($\sim 3°$), the angle of inclination of the scales to the axis of the fiber.

The optical properties of human hair II. The luster of hair fibers: Robert F. Stamm, Mario L. Garcia, and Judith J. Fuchs. *Journal of the Society of Cosmetic Chemists* **28**, 601 (September 1977)

Synopsis—Part I of this paper contains the results obtained with regard to the specular reflection and diffuse scattering of light by human hair fibers as studied by means of goniophotometry. Such data provide a means of measuring the luster of hair fibers. For evaluating the luster of hair, the method chosen employs white light polarized perpendicular to the plane of incidence and incident at 30° with observation being made from 0° to − 75° through an analyzer which is aligned with the polarizer. The integral of the trace of intensity versus the angle of observation yields the specular reflection (S) and diffuse scattering (D). The luster (contrast gloss) value is (S–D)/S. Numerical values extend from zero for bleached hair in very poor condition to ~ 0.85 for dark hair in excellent condition. Using 3 evaluations per sample, luster values have a 90 per cent confidence limit of ± 2.5 per cent of the mean value.

J. Soc. Cosmet. Chem., **28**, 485–496 (September 1977)

Age related baldness. Effect of topical treatment

J. H. HERNDON, JR., D. A. LEEBER, and C. B. READ *Division of Dermatology, Department of Internal Medicine and the Department of Medical Computer Science, The University of Texas Health Science Center, 5323 Harry Hines Blvd., Dallas, TX 75235.*

Received November 8, 1976.

Synopsis

Twenty-nine subjects, 10 women and 19 men, took part in a trial in which THOROUGH CLEANSING of the SCALP was used as therapy for AGE-RELATED BALDNESS (ARB). We measured changes in rate of hair loss, number of hairs identifiable per unit area of scalp, telogen/anagen ratio, and numbers of superficial squames removable per unit area of scalp skin. The subjects completed a two-month control period consisting of infrequent low intensity shampooing (no more often than every 3 to 7 days), then a three-month treatment period consisting of rigorous daily cleansing of hair and scalp. Following treatment, we noted a highly significant reduction in squames per unit area, but only trends toward improvement in rates of hair loss and in numbers of hairs counted per unit area of scalp. There was no observable change in telogen/anagen ratio in hair roots. We concluded that rigorous cleansing of hair and scalp could not be shown to affect significantly the course of ARB.

INTRODUCTION

As early as the 4th Century B.C. Aristotle noted that baldness affected men but not women, children, and eunuchs. Beginning with Sabouraud, numerous observers have remarked on the frequent concurrence of oily seborrhea with age-related baldness (ARB) (1–3). Although current teaching has abandoned the hypothesis that accumulation of sebum causes hair loss and accepted instead the notion that age-related hair loss develops due to an interplay between androgenic hormones and a dominantly-inherited trait (4), still the idea has persisted that excessive or qualitatively altered secretion of sebum may affect the development of ARB (5–7). Available evidence suggests that human sebaceous secretion falls with age (3). Older peoples' sebaceous glands also seem to be smaller and fewer in number (8). Despite these data, the proponents of a role for sebum-mediated injury can point to several studies that show toxic affects when human sebum is applied to animal skin. One group showed that whole human sebum and some of its unsaturated components caused noninflammatory depilation in rats, mice, and rabbits, though not in human children (9–12). Peroxide-rich fatty acids seemed most potent, although the paraffinic hydrocarbon fraction of sebum also caused hair loss in animals (14–15). Other analyses showed that human

sebum is unique among mammalian products in containing large amounts of triglyceride fatty acid, squalene, and mono-ester waxes (16), and that these components are produced maximally at the time of onset of ARB (17).

Despite its potential importance, we could not find published accounts of controlled trials of the influence of thorough removal of sebum on ARB in either sex. We were given an opportunity to examine this problem in the course of a study involving a group of men and women referred for excessive hair fall in whom other causes of alopecia had been excluded.

METHODS: POPULATION

We interviewed 73 men and women between ages 16 and 50 on referral from practicing dermatologists in the community. All complained of severe and continuous hair loss. A thorough history and dermatologic exam, including hematologic, serologic, X-ray, general physical, and other studies where indicated, was completed during the first visit. The subjects were questioned closely concerning drugs, vitamins, prior medical and lay therapy for hair loss, personal and family history of skin disease, recent febrile illness, pregnancy, endocrine disturbance, or hematologic disorder. Other possible causes of alopecia including infection with dermatophytes, treponema pallidum, or symptoms of connective tissue disease, alopecia areata, or trichotillomania were excluded by appropriate means.

The degree of baldness was graded by the investigator for all subjects. None of the women had temporal-crown thinning resembling the pattern often seen in men or in pathologically virilized women. Instead, all had diffuse loss beginning behind the frontal hairline and extending throughout the top of the scalp. This distribution has been termed female-pattern alopecia (18) and common female baldness (19), and has been blamed on thyroid deficiency (20) as well as inherited influences. All of our patients displayed normal thyroid and other endocrine function during evaluation, however.

In accepting female subjects, we ignored a history of taking birth control pills if two conditions were satisfied: (1) if the patient consistently adhered to 1 oral agent and schedule for a minimum of 6 months before beginning treatment; and (2) if her history of excessive hair loss extended a minimum of 6 months before beginning oral contraceptives, and her hair loss had not changed in severity while using the drug. Such agents have been shown to influence hair growth in animals (21), as has human pregnancy (22), but aside from a scattering of case reports (23), recent investigators have discovered no causal relationship between human ARB and estrogenic medication (24). It is true that some women have responded to withdrawal of estrogen supplements by developing hair loss for short periods (25). This phenomenon should not have affected our results, however, since all medications of this type were continued.

Using a mean value of 50 hairs lost per day as a threshold for entrance to the project, we studied 29 of the 73 subjects interviewed, 10 women and 19 men. Sixteen of the original 73 were excluded when they demonstrated hair loss of less than 50 per day, another 21 became drop-outs or displayed unreliability during the control period, one became pregnant, and one developed alopecia areata. Five subjects, 2 men and 3 women, withdrew from participation during the treatment period. In order to avoid biasing the results these 5 were assumed for statistical purposes to have experienced

Table I
Composition of Preparations Used in Treatment Regimen

A. Conditioner	
2-propanol	50
water	45
methyl ethyl ketone	4
Tween 80	0.39
smaller quantities of dye, perfume, allantoin, hexachlorophene and benzethonium chloride	
B. Cleanser	
inert oil	60
sulfonated vegetable oil	40
C. Shampoo	
water	58
ammonium lauryl sulfate	38.4
lauric diethanolamide	0.96
propylene glycol	0.96
smaller quantities of dichlorophene, methyl paraben, BHT, EDTA, dye and perfume	
D. Lotion	
2-propanol	88
water	9.8
polyethylene glycol 400	2.1
smaller quantities of hexachlorophene and estradiol NF (the latter at a level of 0.00004 per cent or 0.011 mg/fluid oz)	
E. Antiseptic dressing	
water	99.8
benzethonium chloride	0.19
smaller quantities of perfume and dye	

outcomes less favorable than any patient who completed the study, and are so included in the tables.

MEDICATIONS

During the control period, all subjects shampooed once every 3 to 7 days, using a mild unmedicated shampoo. During the treatment phase each subject was advised to apply in sequence each day the 5 liquid preparations whose compositions are given in Table I.

PROCEDURE

At the first interview each patient received a complete explanation of the protocol and signed a statement indicating informed consent. During an initial control period of 2 months we obtained 3 or more 24 h hair collections counted in an envelope. At each visit the examiner regraded the subject's signs and symptoms. A 1.5 × 1.5 cm site near the crown was clipped and photographed. The same area was located and reclipped at each return visit. The photos were later analyzed by applying a transparent 1 × 1 cm mask and visually enumerating hairs found growing within its area. Approximately 20 to 30 hairs were then plucked and separated into anagen and telogen categories under a hand lens (26). Next, a corneocyte count was made of squames removable from a 5.1 cm^2 area of the anterior forehead adjacent to the hair line (27).

Table II
Summary of Results in 29 Subjects Who Met 2 Conditions: 1) Initial Rate of Hair Loss Equaled or Exceeded 50 Hairs/Day; 2) Satisfactorily Completed a 2-Months Control Period and at Least 3 Months Treatment Period

	Women	Men	Total
Reduction in hair loss (> 20 per cent)	3/10	10/19	13/29 (45 per cent)
Increase in hairs/cm^2 (> 20 per cent)[a]	5/8	1/13	6/21 (29 per cent)
Subjective increase in hair	7/10	11/19	18/29 (62 per cent)

[a]Photographic counts of hair density were complete for only 8 women and 13 men, while complete measurements of daily loss constituted a criterion for inclusion in the study.

Table III
Reduction in Hair Loss: Men

Subject	Mean Daily Rate of Loss[a] Control Period	Treatment Period	Difference	Decrease as Per Cent Control[b]	Signed Rank
RW	114	39	75	66	16
JP	133	43	90	68	17
MG	109	92	17	16	4.5
EG	96	173	−77	−80	−19
GT	192	78	114	59	15
RB	210	107	103	49	14
EF	86	48	38	44	13
JHo	277	68	209	75	18
FE	89	54	35	39	12
JW	107	113	−6	−6	−2
RD	197	131	66	34	10
WL-C	58	47	11	19	7
RP	93	108	−15	−16	−4.5
HG	80	96	−16	−20	−8
JM	59	62	−3	−5	−1
GW	63	42	21	33	9
JHa	162	191	−29	−18	−6
DC	74	81	−7	−9	−3
DG	200	131	69	35	11
RD[c]	99	[c]	[c]	(−81)[c]	−20
TB[c]	105	[c]	[c]	(−82)[c]	−21
n = 21					$\Sigma R_i+ = 146.5$
					$\Sigma R_i- = 84.5$
					Wilcoxon Signed Rank Test: $0.067 < p < 0.081$

[a]Each value represents the mean of six determinations, 3 from each of 2 visits during control, and the same during treatment.
[b]Negative signs in this and the difference column refer to rises in number of hairs lost.
[c]These 2 patients dropped out after completing the control period, but before completing the treatment period. They were arbitrarily assigned the most unfavorable results on the table.

At the end of the 2-month control period, each subject began using a large square of flexible plastic screen folded over the drain during the daily shampoo in order to collect lost hair. In addition to prior procedures the subject was questioned closely at

each visit about adherence to the regimen, the volume of unused solutions remaining, as well as changes noted in hair and scalp. Side effects, if any, were also recorded. Three subjects complained of slight transient burning irritation after the use of lotion D, but did not find it sufficiently uncomfortable to interrupt the regimen. One person noted slight yellowing of gray hair following use of dressing E.

RESULTS

Nearly half of the 29 subjects who completed both control and treatment periods in satisfactory fashion noted reductions in hair loss of 20 per cent (more men than women), while almost 30 per cent displayed increases in hairs countable in the 1 cm^2 area (more women than men) (Table II). As shown in Table II, the percentage of those who noted improvement subjectively was twice the percentage of those who displayed measurable increases. None of these changes were found to be statistically significant, however, as noted below.

Table III shows a detailed analysis of the data for the possibility of a reduction in hair loss following treatment. When the results were corrected for the 2 subjects lost during the treatment phase, the findings in male subjects showed a favorable trend but failed to attain statistical significance.

As shown in Table IV, the data obtained in women showed only a slight trend toward reduced loss of hair, a trend which became smaller still when the results were corrected

Table IV
Reduction in Hair Loss: Women

Subject	Mean Daily Rate of Loss[a]		Difference	Decrease as Per Cent Control[b]	Signed Rank
	Control Period	Treatment Period			
PH	50	59	−9	−18	−4.5
DH	62	44	22	35	7
ER	54	45	9	17	3
PM	105	47	58	55	12
LS	200	231	−31	−16	−2
KH	74	77	−3	−4	−1
MM	82	120	−38	−46	−8
KA	71	88	−17	−24	−6
CJ	101	30	71	70	13
BY	113	93	20	18	4.5
BEY[c]	135	[c]	[c]	(−47)[c]	−9
BS[c]	79	[c]	[c]	(−48)[c]	−10
EM[c]	129	[c]	[c]	(−49)[c]	−11
n = 13					$\Sigma R_i+ = 39.5$ $\Sigma R_i- = 51.5$
					Wilcoxon Signed Rank Test: not significant

[a]Each value represents the mean of 6 determinations, 3 from each of 2 visits during control, and the same during treatment.

[b]Negative signs in this and the difference column refer to rises in number of hairs lost.

[c]These 3 patients dropped out after completing the control period, but before completing the treatment period. They were arbitrarily assigned the most unfavorable results on the table.

Table V
Variations in Rate of Hair Loss During Treatment: Men

	Hair Loss as Per Cent of Control Period		Changes[c]	
	Treatment Period First Half (1)[a]	Treatment Period Last Half (2)[b]	Per Cent Rise (1) → (2)	Per Cent Fall (1) → (2)
RW	31	39	8	
JP	29	32	3	
MG	94	114		
EG	149	174		
GT	45	32		13
RB	56	52		4
EF	63	41		22
JHo	27	27	—	—
FE	60	55		5
JW	152	95		
RD	92	45		47
WL-C	90	79		11
RP	101	124		
HG	171	165		
JM	110	80		30
GW	101	54		47
JHa	115	153		
DC	109	107		
DG	65	75	10	
		$\bar{X}$	7	22

[a]Each value represents the mean of 6 determinations, 3 from each of the first 2 months of the treatment period, but expressed as a per cent of the mean of that subject's control period collections.
[b]All comments in footnote [a] apply, except that values are derived from final 2 treatment visits (except in subjects RW, EG, JW, JM and GW), for whom only 1 final treatment visit was available.
[c]Changes were calculated only for those whose loss declined to 80 per cent of control or lower at some time during treatment. Values represent the difference between periods (1) and (2) expressed as a per cent of the control period.

for the 3 subjects who stopped in mid-treatment. Even excluding these 3, the number of subjects whose rates of loss increased following treatment was equal to the number whose loss declined.

In an attempt to exclude systematic error due to the changed circumstances of hair collection after the subjects began using the regimen, we also analyzed the results sequentially. In the event of a fall in hair collections due to therapeutic effectiveness of the regimen we would have expected to see a gradual, progressive decline in counts. If on the other hand, the losses became smaller because the patients were unable to collect hair as completely when shampooing daily, we would have expected to see a sudden drop in counts at the time of the shift in technique followed by random fluctuations. As shown in Table V, we found that 12 of 19 male subjects showed a decline in hair loss to 80 per cent or less of the mean value noted during the control period. Eight of those 12 did experience a decline, not at the onset, but during the body of the treatment period. That is, two-thirds of the responders displayed greater reductions in hair loss in the last half of the treatment period than in the first half.

The data were next analyzed for the possibility that the regimen had encouraged new or thicker hair to grow. Either greater longevity of existing anagen hairs or the stimula-

Table VI
Increase in Hair Per Unit Area of Scalp: Men

Subject	Mean Number of Hairs/cm²[a] Control Period	Treatment Period	Difference	Increase as Per Cent of Control	Signed Rank
JP	132	139	7	5	2
GT	169	171	2	1	1
RB	132	157	25	19	12
EF	140	154	14	10	7.5
JHo	107	125	18	17	11
FE	249	320	71	7	4.5
JW	99	110	11	11	9
RD	141	153	12	9	6
WL-C	66	70	4	6	3
RP	113	147	34	30	13
JM	109	120	11	10	7.5
GW	159	172	12	7	4.5
JHa	141	162	21	15	10
RD[b]	[b]	[b]	[b]	(0)[b]	
TB[b]	[b]	[b]	[b]	(0)[b]	
n = 15					$\Sigma R_i+ = 91$
					$\Sigma R_i- = 0$
					Wilcoxon Signed Rank Test: $P < 0.001$

[a]Each value represents the mean of 2 determinations, where possible on the first 2 visits of the control period and the last 2 visits of the treatment period.
[b]These 2 patients dropped out after completing the control period, but before completing the treatment period. They were arbitrarily assigned the most unfavorable results on the table.

Table VII
Increase in Hair Per Unit Area of Scalp: Women

Subject	Mean Numbers of Hairs/Cm² Control Period	Treatment Period	Difference	Increase as Per Cent of Control	Signed Rank
PH	89	129	30	33	9
ER	207	250	43	20	6
PM	148	194	46	31	8
LS	207	207	0	0	
KH	81	100	19	23	7
MM	186	281	95	51	10
KA	114	129	15	13	1
CJ	221	189	−32	−14	−2
BEY[b]	[b]	[b]	[b]	(−15)[b]	−3
BS[b]	[b]	[b]	[b]	(−16)[b]	−4
EM[b]	[b]	[b]	[b]	(−17)[b]	−5
n = 10					$\Sigma R_i+ = 41$
					$\Sigma R_i- = 14$
					Wilcoxon Signed Rank Test: $0.081 < p < 0.097$

[a]Each value represents the mean of 6 determinations, 3 from each of 2 visits during control, and the same during treatment.
[b]These 3 patients dropped out after completing the control period, but before completing the treatment period. They were arbitrarily assigned the most unfavorable results on the table.

tion of dormant, possibly empty, telogen follicles to re-enter anagen could have increased the number of hairs counted per unit area. Tables VI and VII present evidence for an increase in the density of hair in men, while showing a somewhat weaker trend toward improvement in women. Closer inspection of Table VI, however, shows that such increases were quantitatively slight, all but 1 being less than 20 per cent, and lacked biological if not statistical significance.

ARB is accompanied by gradual shortening in the anagen, or growing phase of each hair and lengthening in the telogen or dormant phase. In areas destined to become bald, the resultant hair also shrinks in diameter following each cycle until only a slender stub remains (28–29). We wondered whether the treatment regimen might influence the physiologic cues which govern these phases of growth, specifically whether we might find a greater proportion of anagen hairs in the scalp following treatment; the only method readily available for detecting such changes in the manual method of counting the total as well as number of telogen roots in a plucked sample. Table VIII shows that we were unable to detect significant changes during the treatment period in male subjects. Similar results were observed in women (data not shown).

Table VIII
Changes in Percentage of Hair Roots in Telogen Stage: Men

Subject	Percentage of Plucked Hair Roots in Telogen[a]		Difference[b]	Signed Rank
	Control Period	Treatment Period		
RW	29	20	9	10
JP	7	8	−1	−1.5
MG	26	8	16	14
EG	17	16	1	1.5
GT	18	10	8	8.5
RB	16	4	12	12
EF	33	12	21	16
JHo	50	9	41	20
FE	25	23	2	3
JW	8	41	−33	−17
RD	24	24	0	—
WL-C	9	19	−10	−11
RP	12	19	−7	−6.5
HG	4	23	−19	−15
JM	26	18	8	8.5
GW	22	29	−7	−6.5
JHa	10	25	−15	−13
DC	20	17	3	4.5
DG	42	48	−3	−4.5
RD[c]	11	[c]	(−34)[c]	−18
TB[c]	8	[c]	(−35)[c]	−19
n = 21				$\Sigma R_i+ = 98$
				$\Sigma R_i- = 112$
				Wilcoxon Signed Rank Test: not significant

[a]Each value represents the mean of at least 3 determinations.

[b]Since the values in the difference column represent differences between percentages, they have not been further normalized.

[c]These 2 patients dropped out after completing the control period, but before completing the treatment period. They were arbitrarily assigned the most unfavorable results on the table.

Table IX
Decrease in Superficial Squames Per Unit Area of Scalp: Men

Subject	Cells Per Cubic Millimeter in 2 ml Detergent Buffer[a]		Difference	Decrease as Per Cent of Control	Signed Rank
	Control Period	Treatment Period			
RW	587	347	240	41	8
JP	453	134	319	70	16
MG	477	537	−60	−13	−2
EG	338	359	−21	−6	−1
GT	276	134	142	51	11.5
RB	373	291	82	22	5
EF	186	150	36	19	4
JHo	488	250	238	49	10
FE	156	277	−121	−77	−18
JW	239	177	62	26	6
RD	289	126	163	56	14
WL-C	422	204	218	52	13
RP	349	135	214	61	15
HG	228	112	116	51	11.5
JM	287	326	−39	−14	−3
GW	818	227	591	71	17
JHa	537	277	260	48	9
DC	276	194	82	30	7
DG	797	147	650	82	21
RD[b]	383	[b]	[b]	−78	−19
TB[b]	589	[b]	[b]	−79	−20
n = 21					$\Sigma R_i+ = 168$
					$\Sigma R_i- = 63$
					Wilcoxon Signed Rank Test: $0.029 < p < 0.036$

[a]Two ml of detergent buffer were used in scrubbing 5.1 cm^2 near the anterior hairline. Each value represents the mean of at least 3 determinations.

[b]These 2 patients dropped out after completing the control period but before completing the treatment period. They were arbitrarily assigned the most unfavorable results on the table.

In contrast to effects on hair growth, the regimen did reduce significantly the cell counts obtainable from a given area of skin located near the hairline (Tables IX and X). The few counts which rose during treatment may have reflected frequent shampooing during the control period, something all subjects were urged to avoid.

DISCUSSION

Among potential sources of error in this study one must mention the problem of its design. While a double-blind cross-over arrangement might have seemed the best means of controlling bias, we felt it would have been difficult to achieve in this instance. Since the question was whether or not regular, thorough removal of sebum resulted in a reduction in hair fall, placebo therapy in the usual sense could not be used. Instead, the subjects were urged not to change their habits regarding shampooing during the control period, or if they washed frequently, to moderate their efforts.

Nor could we incorporate a phase involving a cross-over to placebo therapy after the treatment period. Such a design might have allowed us to correct for bias associated

Table X
Decrease in Superficial Squames Per Unit Area of Scalp: Women

Subject	Cells per Cubic Millimeter in 2 ml Detergent-Buffer[a]			Decrease as	Signed
	Control Period	Treatment Period	Difference	Per Cent of Control	Rank
PH	311	250	61	20	1
DH	281	357	−76	−27	−4
ER	410	258	152	37	7
PM	802	361	441	55	8
LS	463	364	99	21	2
KH	909	194	715	79	13
MM	620	231	389	63	10
KA	526	171	355	67	11
CJ	467	319	148	32	6
BY	163	210	−47	−29	−5
BEY[b]	770	211[b]	559	73	12
BS[b]	489	188[b]	301	62	9
EM[b]	274	339[b]	−65	−23	−3
n = 13					$\Sigma R_1+ = 79$
					$\Sigma R_1- = 12$
					Wilcoxon Signed Rank Test: $0.008 < p < 0.011$

[a]Two ml of detergent buffer were used to scrub an area of 5.1 cm^2 near the anterior hair line. Each value represents the mean of at least 3 determinations, except as noted below.
[b]Three patients completed the control period, but not the treatment period. The values given for the treatment period in their columns thus represent a single (or in the case of the EM column, 2) determination(s). Since these values were available to indicate a trend, it was not felt proper to assign arbitrarily unfavorable responses to the treatment periods, as was done in Table VII and previously.

with the duration of the study. But the motivation of our subjects was considered too tenuous for this refinement. Each patient cooperated in order to remedy his or her own hair loss and not for financial inducement. We could not obtain the patient's cooperation without offering the possibility of therapeutic benefit.

Instead of a post-study control period, we endeavored to maintain uniform methods of data collection throughout the study. This requirement was readily satisfied with photographs, cell counts, and other investigator-based techniques, but questions arose regarding the consistency of the technique of collecting hair. Two steps were taken to attempt to render hair collections during daily shampooing comparable with those collected after shampooing at 2 to 7 day intervals. Subjects were asked to avoid all but the gentlest massage during the daily treatment phase, and were also asked carefully to collect hairs lost while shampooing using multiply-folded plastic screening (supplied to them by the investigator) covering the drain area. Data shown in Table V suggests that in at least two-thirds of a sub-group of male subjects whose loss declined by 20 per cent or more improvement tended toward a linear relationship with duration of the regimen.

The effect of topically-applied estrogen in the regimen is difficult to evaluate. Lotion D contained estradiol - 17β at low concentration ($4.0 \times 10^{-8}M$[Table I]). Because of its polar character and molecular size, the permeability constant (kp) for this compound is an extremely low 0.003 cm h^{-1} (30), approximately the same as that of hydrocortisone. Taking together the two factors of low concentration and low permeability constant, it

seemed unlikely that estradiol reached physiologically meaningful concentrations in either sebaceous glands or hair follicles. In order to reach the threshold of suppressant effects on human sebaceous output, previous workers have found it necessary to use a concentration as high as 1 per cent when applying topically the more potent estrogen ethynyl estradiol (31).

In experiments on male rats, Clay, however (unpublished observations) found that application of estradiol -17β to the skin surface at 10 times the concentration used in the present study could cause testicular atrophy when certain conditions were observed: (1) animals were treated with the complete regimen first (that is, the epidermis was prepared with hydration and detergent before applying the steroid); (2) animals began receiving applications during the early weaning period and continued for 28 days. Rat stratum corneum is far thinner and more permeable to applied compounds than that of man, however, and no data were available to suggest that this degree of absorption occurs in humans. For this reason we suspect, but cannot prove, that the estradiol -17β incorporated in lotion D did not influence our findings.

CONCLUSIONS

Unfortunately, the final results of the trial were inconclusive. The data expressed no more than a trend in favor of an improvement following daily removal of sebum or other residues. The groups were small enough to be influenced by the defection of 5 subjects, whose presumed poor results reduced the favorable effect of those who completed the course. Although the data for hairs countable per unit area showed significant improvement in males, the magnitude of the rises was small and may have been biologically trivial.

Montagna has explained (32) an increase in countable hairs following the application of testosterone (33) by noting that certain physical and chemical agents can nonspecifically stimulate quiescent hair follicles, even those present in apparently bald areas of scalp. Such a nonspecific response may lead to 'the false impression that hair has "regrown" in such areas.' The possibility exists that this interpretation is unnecessarily nihilistic, since the regrowth is not false, but biologically trivial and possibly short lived.

In any event, our data would suggest that the sebum-induced causal hypothesis of ARB remains unproven.

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Indentifizierung und quantitative Bestimmung von Konservierungsmitteln in kosmetischen Produkten

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Synopsis — Methods are described for identifying and quantifying the most important preservatives used in cosmetic products. Emulsions are separated into several homogeneous phases with the aid of solvents. After thin layer chromatographic separation (different layers; different developing liquids), the preservatives are identified with the aid of color reactions, reduction of fluorescence, spectral measurements, and RF values. The quantitative determination generally is performed by direct photometric evaluation of the thin layer plates (densitometry); the best conditions for assays are described. Dowicil 200 is determined quantitatively by splitting off of formaldehyde and subsequent reaction with dimedone. The amount of the dimedone derivative formed is determined gravimetrically or titrimetrically.

1. Einleitung

Konservierungsmittel werden in einer Vielzahl von kosmetischen Produkten eingesetzt, um die mikrobielle Zersetzung bei der Lagerung und während des Gebrauchs zu verhindern.

Verschiedene Autoren berichteten über Methoden zur Indentifizierung von antimikrobiellen Mitteln:

König (1) trennte und identifizierte 16 halogenierte aromatische Verbindungen mittels Dünnschichtchromatographie, Wilson (2) verwendete ebenfalls die Dünnschichtchromatographie zur Indentifizierung von insgesamt 25 verschiedenen antimikrobiellen Mitteln. Die Trennung und Identifizierung von mehreren halogenierten Aromaten und der Nachweis von Irgasan DP 300 und Tribromsalicylanilid in Seife mittels Hochdruck-Flüssigchromatographie wurde von Wolf und Semionow (3) durchgeführt.

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Graber, Domsky und Ginn (4) extrahierten halogenierte Aromaten aus Seife und identifizierten die Verbindungen durch Dünnschichtchromatographie. König (5) arbeitete eine Methode aus, um 22 halogenierte aromatische Verbindungen nach Umwandlung in die silylierten Derivate gaschromatographisch zu trennen und zu identifizieren.

Einige Veröffentlichungen liegen auch vor über quantitative Bestimmungen von Konservierungsmitteln in kosmetischen Fertigprodukten:

Wilson (6) führte eine fluorometrische Bestimmung von Formaldehyd in kosmetischen Produkten durch, eine ähnliche Methode wurde von Sheppard und Wilson (7) für die quantitative Bestimmung von Formaldehyd-Abspaltern, wie Bronopol, Germall 115 und Hydroxymethyldimethylhydantoin ausgearbeitet. Ryder (8) beschrieb den dünnschichtchromatographischen Nachweis und die densitometrische Bestimmung von Germall 115. Cooper (9) führte quantitative Analysen von Methyl- und Propylparaben mittels Hochdruck-Flüssigchromatographie durch. Cropper, Platt und Puttnam (10) beschrieben die Bestimmung von Chlorhexidin in Zahnpasten. Die Verfasser Schwedt (11) und Wilson (12) bestimmten Hexachlorophen in kosmetischen Produkten.

Das Ziel unserer Arbeit war, mit Hilfe einer weitgehend einheitlichen Methode — Dünnschichtchromatographie und Densitometrie — die wichtigsten Konservierungsmittel in kosmetischen Produkten, insbesondere in Cremes, zu identifizieren und quantitativ zu bestimmen.*

2. Probenvorbereitung

Für die exakte Auftragung auf Dünnschichtplatten sind homogene, niedrig viskose Lösungen erforderlich. Zum Nachweis und zur Bestimmung von Konservierungsmitteln müssen Emulsionen (z. B. Cremes) deshalb vorher durch Behandlung mit Lösungsmitteln in mehrere homogene Phasen überführt werden. Das Verfahren hat den Vorteil, daß je nach Art der Lösungsmittel die Bestandteile der Cremes nach hydrophilem bzw. lipophilem Charakter vorklassiert werden. Auch die Konservierungsmittel

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* Für die folgenden antimikrobiellen Mittel, die vorwiegend in Desodorantien eingesetzt werden, haben wir ebenfalls analytische Bestimmungsmethoden ausgearbeitet:

Bromchlorophen, Hexachlorophen, Hibitan (Chlorhexidin), Irgasan DP 300, Irgasan CF 3, Trichlorcarbanilid (TCC), Tribromsalicylanilid (TBS), Raluben TL. Für die qualitative Prüfung diente ebenfalls die Dünnschichtchromatographie, die quantitative Bestimmung wurde durch Elution der entsprechenden Verbindungen mit geeigneten Lösungsmitteln von der Dünnschichtplatte und spektralphotometrische Messung der Lösungen vorgenommen. Die Umstellung dieser Methode auf die densitometrische Auswertung ist in Arbeit.

werden auf diese Weise grob vorgetrennt. Eine vollständige Auftrennung wird dabei im allgemeinen nicht erreicht, so daß es zur Erzielung quantitativer Ergebnisse im allgemeinen erforderlich ist, alle Phasen auf Konservierungsmittel zu untersuchen.

Nichtemulsionsartige Produkte können, gegebenenfalls nach Verdünnung (z. B. Shampoos), direkt auf die Dünnschichtplatte aufgetragen werden.

2. 1. W/O-Emulsionen oder O/W-Emulsionen

Die angegebenen Mengen gelten für Gehalte an Konservierungsmitteln von 0,05 % bis 0,5 %. 50 g Creme werden mit 80–200 ml Tetrachlorkohlenstoff und 10 ml Essigsäure gerührt, bis keine Cremeteile mehr vorhanden sind. Nach Homogenisierung mit dem Ultra-Turrax (ca. 3 Min.) wird das Gemisch zur Phasentrennung in einen Scheidetrichter gegeben. Sollte die Trennung zu langsam verlaufen, werden noch 10–30 ml Isopropylalkohol zugegeben. Bei nicht ausreichender Trennung kann zusätzlich ein Essigsäure-Wassergemisch (15–30 ml) hinzugegeben werden. Je nach untersuchter Creme entsteht manchmal noch eine dritte Phase, bestehend aus nicht gelösten Fettbestandteilen. Diese Phase wird dann ebenfalls abgetrennt und mit Tetrachlorkohlenstoff zu einer homogenen Aufschlämmung verrührt. Die Phasen können für die dünnschichtchromatographische Prüfung eingeengt oder verdünnt werden je nach Konservierungsmittel-Konzentration.

2. 2. O/W-Emulsionen[*]

Auch hier gelten die Mengen für Gehalte an Konservierungsmitteln von 0,05 % bis 0,5 %. 50 g Creme werden mit 80 ml Isopropylalkohol, 10 ml dest. Wasser und 10 ml Essigsäure p. a. mit einem Korbrührer vorgerührt, bis keine gröberen Cremepartikel mehr vorhanden sind. Dann wird kurze Zeit (ca. 3 Min.) mit einem Ultra-Turrax homogenisiert. Das Gemisch wird zur Phasentrennung zentrifugiert und die dabei entstehende klare Phase abgetrennt. Die zurückbleibende Fettphase wird mit 100 ml Tetrachlorkohlenstoff verrührt und mit einem Ultra-Turrax homogenisiert. Die Phasen können verdünnt oder eingeengt werden je nach Konservierungsmittel-Konzentration.

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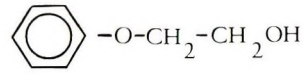
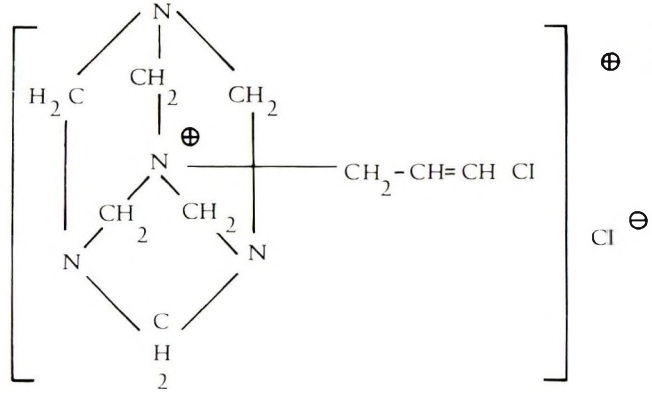
[*] Die in Abschnitt 2.1. beschriebene Methode hat sich nicht in allen Fällen für die Trennung von O/W-Emulsionen bewährt, in einigen Fällen ist das im Abschnitt 2. 2. erläuterte Verfahren besser geeignet.

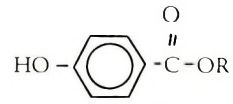
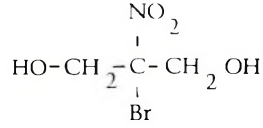
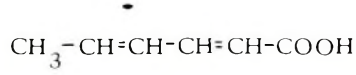
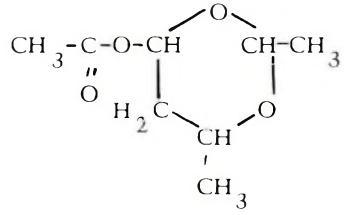
3. Untersuchte Substanzen

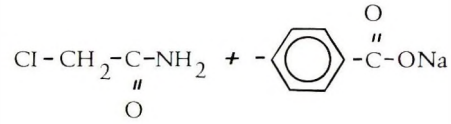
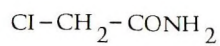
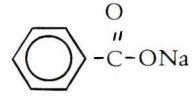
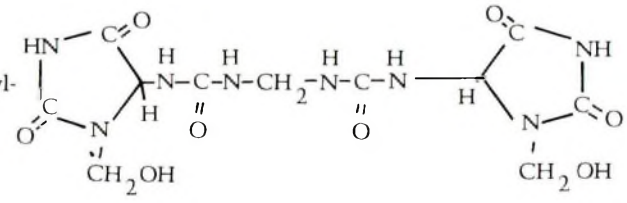
In der folgenden Tabelle sind die Handelsnamen, die chemischen Bezeichnungen, die Strukturformeln (soweit bekannt) und die Bezugsquellen der untersuchten Konservierungsmittel angegeben.

Tabelle 1

Untersuchte Konservierungsmittel

Handelsname	Chem. Bezeichnung	Struktur	Bezugsquelle
1. Phenoxyäthylalkohol, Äthylenglykolmono-phenyläther			Haarmann u. Reimer
2. Dowicil 200	1-(3-Chlorallyl)-3, 5, 7,-triaza-1-azonia-adamantanchlorid		The Dow Chemical Corp.

Handelsname	Chem. Bezeichnung	Struktur	Bezugsquelle
3. Nipaester Parabene	p-Hydroxybenzoesäure-ester (PHB-Ester)	 R = CH_3 / C_3H_7	Nipa-Laboratorium, Merck
4. Bronopol	2-Brom-2-nitro-propandiol (1,3)		The Boots Comp. Ltd.
5. Sorbinsäure bzw. Kaliumsorbat			Hoechst AG
6. Giv-Gard DXN-CO (Dioxin CO)	6-Acetoxy-2,4-dimethyl-m-dioxan		Givaudan

Handelsname	Chem. Bezeichnung	Struktur	Bezugsquelle
7. Konservierungsmittel CA 24	Chloracetamid-Natriumbenzoat-Mischung		Biochema, Dr. Lehmann & Co.
8. Cloracetamid			Merck
9. Natriumbenzoat			Merck
10. Germall 115	Imidazolidinyl-harnstoffverbindung bzw. Methan-bis (N,N'-(5-ureido-2,4-diketo-1-hydroxymethyl-imidazolidin *		Sutton Laboratories (Lieferant Chemag)

* Letztere Bezeichnung lt. J. Soc. Cosmet. Chem. **25,** 655 (1974).

4. Sprühreagenzien für Dünnschichtchromatographie / Detektion

1. Phenylhydrazin-4-sulfonsäure (für Dowicil 200, Bronopol, Germall 115).

   3,5 g Phenylhydrazin-4-sulfonsäure Hemisulfat (Fluka) werden in 10 ml Wasser und 20 ml N-Natronlauge gelöst (pH-Wert der Lösung 7 bis 9). Beim Besprühen muß die Platte gleichmäßig durchfeuchtet werden, ohne daß die Reagenzlösung von der Platte abläuft. Die Platte wird dann bei maximal 25° C vor einem Ventilator getrocknet. Die trockene Platte wird mit einer Mischung von 30 ml 2 N-Natronlauge und 40 ml Aceton, die vor dem Besprühen gut geschüttelt wird, besprüht. Man erhält tiefrote Flecken. Soll die Platte für einen Zeitraum von mehr als 1 Stunde konserviert oder quantitativ vermessen werden, so wird sie nach voller Ausbildung der Rotfärbung zur Neutralisation in eine mit CO_2-Atmosphäre gefüllte Kammer gestellt. Die Flecken färben sich hierbei gelbbraun, der Untergrund bleibt hell. Danach wird die Platte im Kaltluftstrom getrocknet. Die Sprühreagenzien sind täglich neu anzusetzen.

2. Echtblausalz B = Di-o-anisidintetrazoniumdichlorid (für p-Hydroxybenzoesäureester und andere kupplungsfähige Phenole). Es wird eine 5 % ige, wässerige Lösung von Echtblausalz B verwendet. Die Platte wird damit vorbesprüht, mit 0,1 N-Natronlauge nachgesprüht und bei 150° C im Trockenschrank getrocknet. Rotfärbung der Flecken.

3. Echtrotsalz RC (Fluka) = diazotiertes Zinkdoppelsalz des 2-Amino-4-chloranisols (für Giv-Gard DXN-CO, Bronopol).

   Es wird eine 1 % ige wässerige Lösung von Echtrotsalz RC verwendet. Bei quantitativen Bestimmungen von Giv-Gard sind neutrale oder alkalische Fließmittel nicht geeignet, da der Untergrund zu stark verfärbt wird, bei Verwendung von sauren Fließmitteln wird ein fast farbloser Untergrund erhalten. Die Platte wird nach dem Trocknen vor dem Ventilator (ca. 15 Min.) möglichst gleichmäßig mit der Echtrotsalz-Lösung besprüht, dann 1 Stunde lang bei 60° - 70° C im Umlufttrockenschrank getrocknet (für quantitative Bestimmung unerläßlich, da sonst uneinheitliche Färbung des Plattenuntergrundes). Rotorange Flecken. Bei quantitativen Bestimmungen von Bronopol muß mit 10 % iger wässeriger Natriumcarbonat-Lösung ($Na_2CO_3\,10H_2O$) nachgesprüht werden, da sonst die Farbstoffbildung zeitlich verzögert eintritt. Neutrale Fließmittel verwendbar.

4. Chlor-Pyrazolon-Cyanid* (für Chloracetamid). Die Platte wird einige Minuten lang in eine Chloratmosphäre eingestellt, danach wird das überschüssige Chlor im Trockenschrank bei 100° C entfernt.

   Lösung a: 0,2 M 1-Phenyl-3-methylpyrazolon-(5) in Pyridin
   Lösung b: N-Kaliumcyanidlösung.

   Lösung a und Lösung b in gleichen Volumina gemischt, die Platte wird damit besprüht. Leuchtend rote Flecken, nach kurzer Zeit nach blau umschlagend. Flecken verblassen schnell, für quantitative Bestimmung daher nicht geeignet.

5. Kaliumhexacyanoferrat(III)-Natriumpentacyanonitrosylferrat** (für Germall 115).

   Lösung a: Natronlauge 10 % ig
   Lösung b: Natriumpentacyanonitrosylferrat 10 % ig in Wasser
   Lösung c: Kaliumhexacyanoferrat-(III) 10 % ig in Wasser

   Die Lösungen a, b, c werden im Volumenverhältnis 1 : 1 : 1 gemischt, die Mischung wird mit 3 Teilen Wasser verdünnt. Die Lösung muß mindestens 20 Min. lang bei Raumtemperatur stehen. Vor Gebrauch wird diese Lösung mit dem gleichen Volumen Aceton vermischt. Rote Flecken. Für quantitative Bestimmungen geeignet.

6. Ninhydrin (für Chloracetamid, Nachweis in Form der Umsetzungsprodukte Glycinamid und Glycin). 0,3 g Ninhydrin und 3 ml Essigsäure in 100 ml Butanol-1. Die Platte wird bis zur gleichmäßigen Durchfeuchtung damit besprüht, dann im Kaltluftstrom getrocknet. Anschließend 10—20 Min. bei 50—60° C im Trockenschrank aufbewahren. Intensiv violette Flecken.

7. Fluoreszenzminderung.

   Bei Verwendung von Platten mit Fluoreszenzindikator. Betrachten der Platten unter der UV-Lampe bei 254 nm. Fluoreszensminderung tritt auf bei Phenoxyäthylalkohol, p-Hydroxybenzoesäureestern, Bronopol, Sorbinsäure / Kaliumsorbat, Natriumbenzoat.

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* Nach E. Stahl „Dünnschicht-Chromatographie", 2. Auflage, S. 821.

** Nach E. Stahl „Dünnschicht-Chromatographie", 2. Auflage, S. 844.

8. Spektrale Vermessung von UV-aktiven Verbindungen (für Phenoxyäthylalkohol, p-Hydroxybenzoesäureester, Bronopol, Sorbinsäure, Natriumbenzoat).

   Bei einer Creme unbekannter Rezeptur ist allein aufgrund der Fluoreszenzminderung und des RF-Wertes noch nicht mit Sicherheit festgestellt, daß es sich z. B. um Phenoxyäthylalkohol (bzw. p-Hydroxybenzoesäureester, Bronopol, Sorbinsäure oder Natriumbenzoat) handelt. Es kann auch eine andere UV-aktive Verbindung mit gleichem RF-Wert vorliegen oder ein Gemisch des betreffenden Konservierungsmittels mit einer Fremdsubstanz. Um die Unsicherheit auszuschalten, muß der Fleck densitometrisch vermessen werden. Das geschieht, indem man von dem Fleck bei verschiedenen Wellenlängen, am besten im Abstand von 5 nm, in kurzen räumlichen Abständen auf einem Schreiber Remissions-Orts-Kurven aufnimmt. Die Maxima der Einzelwerte miteinander verbunden ergeben die typische Spektralkurve der Substanz. Z. B. die Maxima der Absorption von Phenoxyäthylalkohol liegen bei 260 nm (schwach) und 205 nm (stark) mit einem Minimum bei 225 nm. Ist die Kurve des fraglichen Flecks identisch mit der Kurve der reinen Verbindung, so ist bewiesen, daß es sich um diese Verbindung handelt. Sind beide Kurven nicht identisch, so muß durch Variation der Fließmittel oder der Schicht eine andere Trennung durchgeführt werden.

Absorptions-Maxima und -Minima:

	Maxima	Minima
Phenoxyäthylalkohol	205 nm (stark) 260 nm (schwach)	225 nm
p-Hydroxybenzoesäureester	210 nm (schwach) als Schulter 255 nm (stark)	223 nm
Bronopol	200 nm — 210 nm (langsam ansteigend von ca. 350 nm an, wenig spezifisch)	—
Sorbinsäure/Kaliumsorbat	260 nm (stark)	—
Benzoesäure (Natriumbenzoat)	223 nm (stark) 275 nm (schwach)	207 nm 255 nm

5. Dünnschichtchromatographische Trennung — qualitative Prüfung

Zur qualitativen Prüfung auf Konservierungsmittel werden 2—5 µl Lösung auf eine Dünnschichtplatte aufgetragen. Nach Entwicklung mit dem geeigneten Laufmittel erfolgt die Detektion in unterschiedlicher Weise je nach Art des Konservierungsmittels.

In Tabelle 2 sind die untersuchten Konservierungsmittel, die jeweils verwendeten Dünnschichtplatten, die Laufmittel, die RF-Werte und die Art der Detektion verzeichnet.

Tabelle 2

Dünnschichtchromatographische Bedingungen für die Trennung und Identifizierung von Konservierungsmitteln:

Konservierungsmittel	DC-Platten	Laufmittel	RF-Wert	Detektion
Phenoxyäthylalkohol	SIL G 25 UV 254 Macherey-Nagel & Co.	Toluol 50 Tetrachlorkohlenstoff 20 Essigsäureäthylester 23 Essigsäure 3 ohne Kammersättigung	0,40	Fluoreszenzminderung bei UV 254 nm *s. Anm. 1*
Dowicil 200 *s. Anm. 2*	Polyamid G 1600 LS 254 Schleicher & Schüll	1-Propanol 75 Wasser 25	0,92	Phenylhydrazin-4-sulfonsäure intensivrot

Konservierungsmittel	DC-Platten	Laufmittel	RF-Wert	Detektion
p-Hydroxybenzoe-säureester	Kieselgel 60 F 254 Merck	nacheinander: Fließmittel A = Toluol 50 Tetrachlor-kohlenstoff 20 Essigsäure-äthylester 23 Essigsäure 3 ohne Kammer-sättigung	Methylester 0,45 Propylester 0,50	Fluoreszenzminderung bei UV 254 nm *s. Anm. 1* Echtblausalz B rot
		und Fließmittel B = Toluol 80 Äthanol 20	Methylester 0,30 Propylester 0,31	
	Polyamid G 1600 LS 254 Schleicher & Schüll	Toluol 95 Essigsäure 10	Methylester 0,14 Propylester 0,25	
Bronopol	SIL G 25 UV 254 Macherey-Nagel & Co.	Toluol 50 Tetrachlorkohlenstoff 20 Essigsäureäthylester 23 Essigsäure 3 ohne Kammersättigung	0,18	Fluoreszenzminderung bei UV 254 *s. Anm. 1* oder Echtrotsalz RC rotbraun
	Polyamid G 1600 LS 254 Schleicher & Schüll	A. 1-Propanol 75 Wasser 25	0,65	Phenylhydrazin-4-sulfon-säure intensivrot oder Echtrotsalz RC rotbraun
		B. Benzol 80 Äthanol 20	0,27	
		C. Toluol 95 Essigsäure 10	0,04	
	Silgur 25 UV 254 Macherey-Nagel & Co.	Toluol 80 Äthanol 20 Essigsäure 2	0,34	Fluoreszenzminderung bei UV 254 *s. Anm. 1* oder Echtrotsalz RC rotbraun

Konservierungsmittel	DC-Platten	Laufmittel	RF-Wert	Detektion
Sorbinsäure / Kaliumsorbat	Kieselgel F 254 Merck	nacheinander: Fließmittel A = Toluol 50, Tetrachlorkohlenstoff 20, Essigsäureäthylester 23, Essigsäure 3	0,34	Fluoreszenzminderung bei UV 254 *s. Anm. 1*
		und Fließmittel B = Toluol 80, Äthanol 20	0,42	
	SIL G 25 UV 254 Macherey-Nagel & Co.	Petroläther (40/60) 50, Tetrachlorkohlenstoff 40, Chloroform 20, Ameisensäure 8, Essigsäure 2 (obere Phase)	0,24	
	Polyamid G 1600 LS 254 Schleicher & Schüll	Toluol 95, Essigsäure 10	0,64	
Giv-Gard DXN-CO	Kieselgel 60 Merck *s. Anm. 3*	Benzol 80, Aceton 20, Essigsäure 2	0,51 (stark) 0,10 (schwach)	Echtrotsalz RC rotorange
CA 24 (Chloracetamid)	Kieselgel 60 F 254 Merck	1-Propanol 60, Wasser 40, Essigsäure 0,25	0,62	Chlor-Pyrazolon-Kalium-cyanid intensivrot, nach blau umschlagend
	Kieselgel 60 Merck	1-Propanol 60, Wasser 40, Essigsäure 0,25 *s. Anm. 4*	0,17 (Glycin) 0,34 (Glycinamid)	Nachweis als Glycinamid/Glycin *s. Anm. 5* mit Ninhydrin violett

Konservierungsmittel	DC-Platten	Laufmittel	RF-Wert	Detektion
Natriumbenzoat	Kieselgel 60 F 254 Merck	Toluol 80 Aceton 20 Essigsäure 2	0,45	Fluoreszenzminderung bei UV 254 *s. Anm. 1*
Germall 115	Kieselgel 60 Merck	1-Propanol 60 Wasser 30 Essigsäure 10	0,50	Kaliumhexacyanoferrat III / Natriumpentacyanonitrosylferrat rot
		Athanol 70 Dimethylformamid 15 Essigsäure 15	0,69	
		1-Butanol 80 Wasser 20 Essigsäure 20 (obere Phase)	0,26	
	Polyamid G 1600 LS 254 Schleicher & Schüll	1-Propanol 60 Wasser 30 Essigsäure 10	ca. 0,9	Phenylhydrazin-4-sulfonsäure intensivrot
		1-Propanol 80 Ammoniaklsg. (33%ig) 20 ohne Kammersättigung	0,40	Kaliumhexacyanoferrat III / Natriumpentacyanonitrosylferrat rot

Anmerkung 1: Bei einer unbekannten Rezeptur gilt das in Abschnitt 4.8. Gesagte.

Anmerkung 2: Dowicil 200 zersetzt sich in wässeriger Lösung relativ rasch, bei teilweise zersetzten Lösungen treten weitere Flecken im Dünnschichtchromatogramm mit den RF-Werten 0,72; 0,68; 0,55 auf.

Anmerkung 3: Bei Verwendung von Kieselgel mit Fluoreszenzindikator wird der Nachweis stark abgeschwächt.

Anmerkung 4: Die relative Luftfeuchtigkeit sollte mindestens 50 % betragen, da sonst Schwanzbildung auftritt.

Anmerkung 5: Zu 25 ml Chloracetamid-enthaltende wässerige Lösung (Gehalt 0,01 bis 0,1 %) werden 50 ml 30 %ige Amoniaklösung gegeben. Die Mischung wird 35 Min. lang am Rückfluß auf 70° erhitzt, dann auf 0° abgekühlt. Zur Entfernung des Ammoniaks wird die Mischung mit der gleichen Menge Isopropylalkohol vermischt und auf 0° gekühlt. Die Mischung wird am Rotationsverdampfer unter Wasserstrahlpumpen-Vakuum auf ca. 25 ml eingeengt, wobei die Temperatur langsam auf 30° gesteigert wird, um Siedeverzug zu vermeiden. Je nach vermutetem Gehalt an Chloracetamid wird mit Alkohol auf 50 bis 150 ml aufgefüllt. Mit dieser Lösung werden dünnschichtchromatographische Prüfungen durchgeführt.

6. Quantitative Bestimmungen

6.1. Methodik der Densitometrie

Die quantitativen Bestimmungen werden durch die direkte photometrische Auswertung der Dünnschichtplatten durchgeführt.

Gerät: Zeiss Chromatogramm — Spektralphotometer PMQ II in der Meßanordnung Monochromator-Probe (M-Pr).

Die Messungen werden in der Anordnung Remission, z. T. in der Anordnung Simultan (simultane Remissions- und Transmissionsmessung) durchgeführt.
Die Meßwellenlänge und weitere apparative Details sind in der Tab. 3 ververzeichnet.

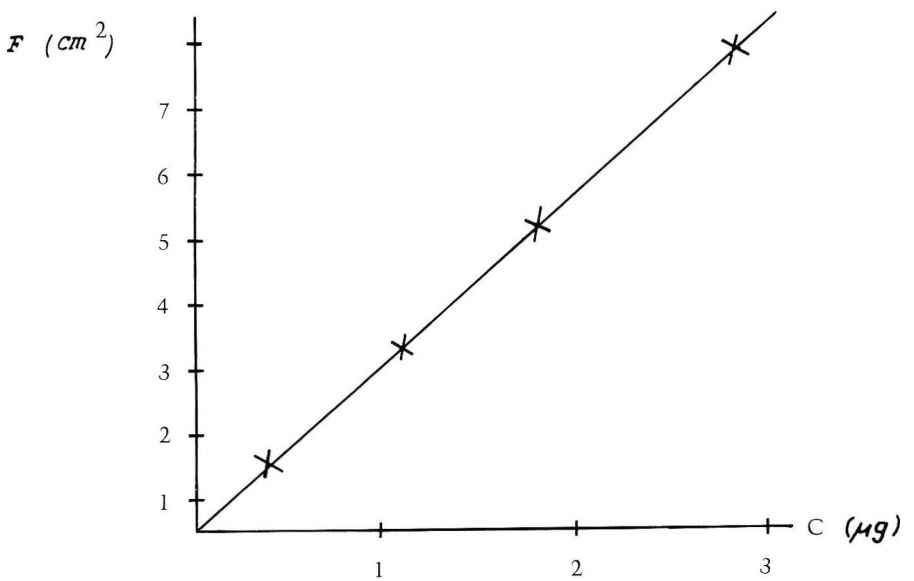
Die quantitative Bestimmmung wird in der üblichen Weise ausgeführt:

Auftragen der Probelösung, die das zu bestimmende Konservierungsmittel enthält, mit Mikrokapillaren auf die Dünnschichtplatte; im allgemeinen werden drei Meßflecken aufgetragen. Auftragen der entsprechenden Vergleichslösungen, die das Konservierungsmittel in reiner Form in bekannter Konzentration enthalten, auf die Dünnschichtplatte; im allgemeinen werden 8 Eichflecken aufgetragen, zur Kontrolle der

Reproduzierbarkeit werden je zwei Eichflecken gleicher Konzentration aufgegeben. Die Eichmengen müssen einen Bereich umfassen, in dem voraussichtlich auch die Menge des Meßflecks liegt, z. B. bei einer Meßfleckmenge von ca. 1 µg sollten die Eichmengen zwischen 0,2 µg und 3 µg liegen. Die Auftragevolumina von Meß- und Eichlösungen werden jeweils gleich gewählt, um möglichst gleiche Fleckgrößen zu erhalten.

Die Flecken der zu bestimmenden Substanz werden möglichst gleichmäßig zwischen den Eichflecken angeordnet, um Unterschiede der Plattenbeschaffenheit auszugleichen. Das Auftragsvolumen sollte 5 µl nicht überschreiten.

Nach Entwicklung der Dünnschichtplatte und gegebenenfalls Detektion durch Sprühreagenzien (Details s. Tab. 3) erfolgt die photometrische Auswertung (Details s. Tab. 3). Aus den erhaltenen Remissions-Orts-Kurven werden die Flächen der Einzelkurven im allgemeinen aus Höhe × Halbwertsbreite berechnet, z. T. (s. Tab. 3) auch durch Planimetrie oder gravimetrisch (Ausschneiden und Wägen). Die endgültige quantitative Bestimmung erfolgt anhand von Eichkurven (Peakflächen aufgetragen gegen Menge an Konservierungsmittel), als Beispiel s. Bestimmung von Phenoxyäthylalkohol.



Eichkurve zur Ermittlung des Gehaltes an Phenoxyäthylalkohol

Tabelle 3

Kurzbeschreibung der chromatographischen Trennbedingungen, der Detektion und der apparativen Details bei der photometrischen Auswertung für quantitative Bestimmungen.

Konservierungsmittel	Dünnschichtplatte	Fließmittel	Detektion	Meßwellenlänge	Meßanordnung	Bemerkungen
Phenoxyäthylalkohol	SIL G UV 254 Macherey-Nagel & Co.	Toluol 50 Tetrachlorkohlenstoff 20 Essigsäureäthylester 23 Essigsäure 3 ohne Kammersättigung	Absorption im UV-Bereich	220 nm 271 nm	Remission	
Dowicil 200	Polyamid G 1600 LS 254 Schleicher & Schüll	1-Propanol 75 Wasser 25	Phenylhydrazin- 4-sulfonsäure	410 nm *	Remission	Messung quer zur Laufrichtung. Flächenauswertung gravimetrisch oder durch Planimetrie
p-Hydroxybenzoe- säureester	Polyamid G 1600 LS 254 Schleicher & Schüll	Toluol 95 Essigsäure 10	Absorption im UV-Bereich	254 nm	Remission	
Bronopol	Polyamid G 1600 LS 254 Schleicher & Schüll	Benzol 80 Äthanol 20	Absorption im UV-Bereich Echtrotsalz RC	220 nm 475 nm	Remission Remission	wegen Instabilität frische Eichlösungen verwenden

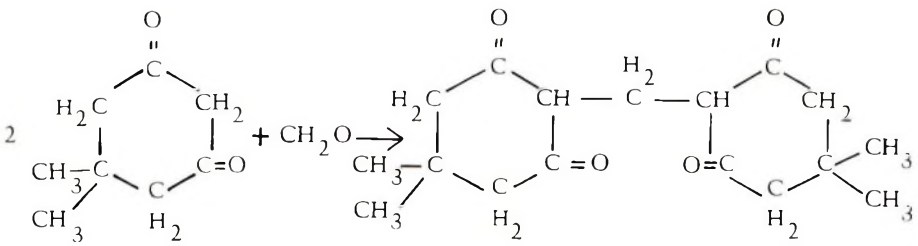
* Die densitometrische Bestimmung des Dowicil 200 verläuft unbefriedigend und ist nur als halbquantitative Methode zu werten. Exaktere Werte wurden erhalten durch die unten beschriebene Methode der Umsetzung mit Dimedon und gravimetrischer Bestimmung.

Konservierungsmittel	Dünnschichtplatte	Fließmittel	Detektion	Meßwellenlänge	Meßanordnung	Bemerkungen
Sorbinsäure	SIL G UV 254 Macherey-Nagel & Co.	Petroläther (40 / 60) 50 Tetrachlorkohlenstoff 40 Chloroform 20 Ameisensäure 8 obere Essigsäure 2 Phase	Absorption im UV-Bereich	260 nm	Remission	
Giv-Gard DXN-CO	Kieselgel 60 Merck (ohne Fluoreszenz-indikator)	Benzol 80 Aceton 20 Essigsäure 2	Echtrotsalz RC	550 nm	Remission	
Chloracetamid als Glycinamid / Glycin (nach Umsetzung mit NH_3)	Kieselgel 60 Merck	1-Propanol 60 Wasser 40 Essigsäure 0,25	Glycinamid } Ninhydrin Glycin } Ninhydrin	400 nm (Glycinamid u. Glycin)	Simultan (R : T = 100:40)	Da bei der Umsetzung mit Ammoniak sowohl Glycinamid als auch Glycin entsteht, müssen beide Verbindungen als Eichsubstanzen verwendet werden.
Natriumbenzoat	Kieselgel 60 F 254 Merck	Toluol 80 Aceton 20 Essigsäure 2	Absorption im UV-Bereich	233 nm	Remission	
Germall 115	Polyamid G 1600 LS 254 Schleicher & Schüll	1-Propanol 80 Ammoniak (33 %) 20 ohne Kammersättigung	Kaliumhexacyanoferrat III-Natriumpentacyanonitrosylferrat	550 nm	Remission	

6. 2. Bestimmung von Dowicil 200

Wenn durch qualitative Dünnschichtchromatographie bzw. durch densitometrische Auswertung (halbquantitative Methode, s. o.) das Vorliegen von Dowicil 200 abgesichert ist, muß für die exakte Bestimmung von Dowicil 200 eine gesonderte Methode angewendet werden.

Die Methode beruht darauf, daß aus Dowicil 200 durch Erhitzen mit Mineralsäure Formaldehyd abgespalten wird (6 Mol CH_2O aus 1 Mol Dowicil 200), der mit Dimedon zum entsprechenden Derivat umgesetzt wird — die Menge an Dimedon-Derivat wird dann gravimetrisch oder durch Titration mit Natronlauge festgestellt. *



Wichtig bei dieser Methode ist, daß die Umsetzung mit Dimedon bei einem exakt eingestellten pH-Wert 4,6 durchgeführt wird und daß Dimedon in einem stöchiometrischen Überschuß von ca. 10 % eingesetzt wird (bei völlig unbekanntem Gehalt sind daher gegebenenfalls mehrere Probebestimmungen erforderlich). Die gravimetrische Bestimmung kann durch die titrimetrische Bestimmung kontrolliert werden.

Für die gravimetrische Bestimmung gilt:

1 g Dowicil 200 = 0,72 g CH_2O = 6,99 g Dimedonderivat

Für die titrimetrische Bestimmung gilt:

1 g Dowicil 200 = 6,99 g Dimedonderivat = 23,9 ml N-Natronlauge.

Im einzelnen wird diese Methode wie folgt durchgeführt:

25 g des zu untersuchenden Fertigproduktes werden in einen Dreihalskolben eingewogen und mit 100 ml ca. 15 %iger Salzsäure versetzt. Die Mischung wird unter kräftigem Rühren an einem Liebigkühler destilliert,

* Umsetzung von Formaldehyd mit Dimedon gemäß Houben-Weyl, Methoden der Organischen Chemie, Bd. II (1953), S. 456.

bis die Innentemperatur ca. 120° erreicht hat. Das erhaltene Destillat wird mit Salzsäure und Natriumacetat auf einen pH-Wert von 4,6 eingestellt. Zu dieser Lösung gibt man eine auf ca. 80° erwärmte wässerige Lösung von Dimedon, die das Reagenz in etwa 10 %igem molaren Überschuß enthält (Verhältnis von geschätzter Formaldehydmenge zu eingesetztem Dimedon ca. 1 : 10) und verdünnt mit Wasser auf 300 ml Die Mischung bleibt dann zur quantitativen Kristallisation des Reaktionsproduktes 12 Stunden lang stehen oder wird 10 Min. auf ca. 80° — 90° erhitzt, dann auf Raumtemperatur abgekühlt und 30 Min. stehen gelassen. Der Niederschlag wird auf einer Filterfritte (G-3) abgesaugt, mit ca. 50 ml kaltem Wasser gewaschen und bei 60 ° zur Gewichtskonstanz getrocknet.

Dowicilgehalt des Musters in %:

$$= \frac{0{,}143 \times \text{Auswaage Dimedonderivat (g)} \times 100}{\text{Einwaage des Musters (g)}}$$

Zur titrimetrischen Bestimmung wird der Niederschlag der gravimetrischen Bestimmung in Äthanol gelöst und mit 0,1 N-Natronlauge gegen Phenolpthalein titriert.

Dowicilgehalt des Musters in %:

$$= \frac{0{,}00418 \times \text{Verbrauch 0,1 N-NaOH (ml)} \times 100}{\text{Einwaage des Musters (g)}}$$

6.3. Ergebnisse bei der Analytik von Fertigprodukten

Im folgenden (Tab. 4) sind die Ergebnisse der quantitativen Bestimmung von Konservierungsmitteln in kosmetischen Fertigprodukten (Cremes, Shampoos u. dgl.) verzeichnet. Bei der Analytik der Cremes wurde, wie in Abschnitt 2 — Probenvorbereitung — beschrieben, eine Phasentrennung durchgeführt, die Konservierungsmittel wurden jeweils in den einzelnen Phasen bestimmt. Die Durchführung der Bestimmungen erfolgte nach den in Tab. 3 gemachten Angaben.

Tabelle 4

Ergebnisse der quantitativen Bestimmung von Konservierungsmitteln in Fertigprodukten:

Produkt-Typ	eingesetztes Konservierungsmittel — Gehalt	Konservierungsmittel gef.		analytisch ermittelter Wert in % d. Th.	
Creme A 1	Nipagin L forte 0,300 %	CCl_4-Phase 0,262 % H_2O-Phase 0,065 %	0,327 %	109	*s. Anm. 1 a*
Creme A 1	Nipagin L forte 0,300 %	CCl_4-Phase 0,293 % H_2O-Phase 0,046 %	0,339 %	113	*s. Anm. 1 a*
	Phenoxyäthylalkohol 0,400 %	CCl_4-Phase 0,364 % H_2O-Phase 0,058 %	0,422 %	105	
Creme A 1	Nipagin L forte 0,300 %	CCl_4-Phase 0,191 % H_2O-Phase 0,079 %	0,270 %	90	*s. Anm. 1 a*
	Phenoxyäthylalkohol 0,400 %	CCl_4-Phase 0,296 % H_2O-Phase 0,149 %	0,445 %	111	
Lotion A 1	Nipagin L forte 0,300 %	CCl_4-Phase 0,274 % H_2O-Phase 0,026 %	0,300 %	100	*s. Anm. 1 a*
	Phenoxyäthylalkohol	CCl_4-Phase 0,342 % H_2O-Phase 0,064 %	0,406 %	102	
Shampoo A	CA 24 — 0,200 %	Chloracetamid 0,119 % Natriumbenzoat 0,086 %		103	
Shampoo A	CA 24 — 0,200 %	Chloracetamid 0,122 % Natriumbenzoat 0,086 %		104	
Shampoo B	CA 24 — 0,100 %	Chloracetamid 0,066 % Natriumbenzoat 0,032 %		98	

Produkt-Typ	eingesetztes Konservierungsmittel — Gehalt	Konservierungsmittel gef.			analytisch ermittelter Wert in % d. Th.	
Shampoo B	CA 24 — 0,100 %	Chloracetamid Natriumbenzoat	0,072 % 0,032 %		104	
Shampoo C	CA 24 — 0,100 %	Chloracetamid Natriumbenzoat	— 0,034 %		106	*s. Anm. 2 a*
Shampoo G	CA 24 — 0,200 %	Chloracetamid Natriumbenzoat	— 0,061 %		95	*s. Anm. 2 a*
Shampoo D	CA 24 — 0,200 %	Chloracetamid Natriumbenzoat	0,131 % —		96	*s. Anm. 2 a*
Shampoo E	CA 24 — 0,100 %	Chloracetamid Natriumbenzoat	— 0,032 %		100	*s. Anm. 2 a*
Creme B 1	Phenoxyäthylalkohol-0,180 %	CCl_4-Phase H_2O-Phase	0,100 % 0,078 %	0,178 %	99	
Creme B 2	Phenoxyäthylalkohol-0,194 %	CCl_4-Phase H_2O-Phase „Fettphase"	0,165 % 0,018 % 0,006 %	0,189 %	97	
Creme B 3	Phenoxyäthylalkohol-0,185 %	CCl_4-Phase H_2O-Phase „Fettphase"	0,147 % 0,025 % 0,008 %	0,180 %	97	
	Dowicil 200 — 0,200 %	H_2O-Phase	0,102 %		52	*s. Anm. 3 a*
Creme A 2	Dowicil 200 — 0,400 %	nach Dimedon-Methode	0,41 %		102	
Creme A 2	Dowicil 200 — 0,400 %	nach Dimedon-Methode	0,41 %		102	

Produkt-Typ	eingesetztes Konservierungsmittel — Gehalt	Konservierungsmittel gef.	analytisch ermittelter Wert in % d. Th.
Creme A 2	Dowicil 200 — 0,400 %	nach Dimedon-Methode 0,40 %	100
Creme A 3	Dowicil 200 — 0,200 %	nach Dimedon-Methode 0,172 %	86
Creme B 4	p-Hydroxybenzoesäure-methylester — 0,208 %	CCl_4-Phase 0,151 % H_2O-Phase 0,041 % „Fettphase" 0,024 % } 0,216 %	104
	p-Hydroxybenzoesäure-propylester — 0,200 %	CCl_4-Phase 0,159 % H_2O-Phase 0,009 % „Fettphase" 0,024 % } 0,192 %	96
Creme B 5	Bronopol — 0,193 %	Wasser-Alkohol-Phase 0,177 % (UV-Absorption)	91
Creme B 5	Bronopol — 0,193 %	Wasser-Alkohol-Phase 0,176 % (UV-Absorption)	91
Creme B 5	Bronopol — 0,193 %	Wasser-Alkohol-Phase 0,175 % (UV-Absorption)	91
Shampoo F	Bronopol — 0,050 %	0,04 % Echtrotsalz RC)	80
Lotion A 2	Bronopol — 0,100 %	CCl_4-Phase 0,041 % H_2O-Phase 0,057 % } 0,098 % (UV-Absorption)	98
Creme B 4	Kaliumsorbat — 0,196 %	CCl_4-Phase 0,144 % H_2O-Phase 0,036 % „Fettphase" 0,008 % } 0,188 %	96

Produkt-Typ	eingesetztes Konservierungsmittel — Gehalt	Konservierungsmittel gef.			analytisch ermittelter Wert in % d. Th.	
Creme B 6	Phenoxyäthylalkohol — 0,188 %	CCl_4-Phase H_2O-Phase „Fettphase"	0,161 % 0,020 % 0,006 %	0,187 %	99	
Creme B 7	Phenoxyäthylalkohol — 0,193 %	CCl_4-Phase H_2O-Phase „Fettphase"	0,156 % 0,022 % 0,014 %	0,192 %	99	
	Giv-Gard DXN-CO-O, 188 %	CCl_4-Phase H_2O-Phase „Fettphase"	0,147 % 0,023 % 0,014 %	0,184 %	98	
Creme B 8	Phenoxyäthylalkohol — 0,182 %	CCl_4-Phase H_2O-Phase „Fettphase"	0,152 % 0,024 % 0,006 %	0,182 %	100	
	Germall — 0,206 %	H_2O-Phase	0,170 %		83	*s. Anm. 4 a*

Anmerkung 1 a: p-Hydroxybenzoesäuremethylester und -propylester in Nipagin L forte als Summe der Einzelwerte.

Anmerkung 2 a: Hier wurde jeweils nur das eine der beiden Konservierungsmittel quantitativ bestimmt. Aus dem Erfahrungswert von ca. 68 % Chloracetamid und 32 % Natriumbenzoat für CA 24 ergeben sich die in Spalte 4 angegebenen Zahlen.

Anmerkung 3 a: Bezüglich des durch Dünnschichtchromatographie gefundenen niedrigen Wertes s. Bemerkungen in den Abschnitten 6.1. und 6.2.

Anmerkung 4 a: Die Nachweisempfindlichkeit für Germall 115 ist nicht sehr hoch, sie ist nicht ausreichend für die Bestimmung in der Tetrachlorkohlenstoff-Phase, so daß häufig etwas zu niedrige Werte gefunden werden.

Zusammenfassung

Es werden Methoden beschrieben zur Identifizierung und zur quantitativen Bestimmung der wichtigsten Konservierungsmittel in kosmetischen Fertigprodukten.

Bei der Untersuchung von Emulsionen werden diese zunächst durch Behandlung mit Lösungsmitteln in mehrere homogene Phasen überführt. Die Konservierungsmittel werden nach dünnschichtchromatographischer Trennung (verschiedene Schichten, verschiedene Fließmittel) durch Farbreaktionen, Fluoreszenzminderung, spektrale Vermessung und RF-Werte identifiziert. Die quantitative Bestimmung erfolgt in den meisten Fällen durch direkte photometrische Auswertung der Dünnschichtplatten (Densitometrie) — die optimalen Bedingungen werden beschrieben.

Dowicil 200 wird quantitativ bestimmt, indem Formaldehyd abgespalten und anschließend mit Dimedon umgesetzt wird — die Menge an Dimedonderivat wird gravimetrisch oder titrimetrisch ermittelt.

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The effect of detergents on swelling of stratum corneum

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Synopsis

Several surfactants were tested for their ability to produce in-plane SWELLING (increase surface area) of squares of GUINEA PIG STRATUM CORNEUM. Highest levels of swelling were observed with the anionic surfactants sodium laurate and sodium lauryl sulfate, while little or no swelling was observed with the few cationic and nonionic surfactants examined. Although swelling in laurate was shown to be reversible, work index measurements revealed an irreversible weakening of the tissues. To gain insight into the mechanism of swelling the effects of protein denaturants and delipidizing agents were also evaluated. We conclude that protein denaturants, *per se*, do not cause stratum corneum swelling, but that swelling is due to a reversible conformation change resulting from cooperative binding of the detergent. Stratum corneum swelling could be of value for studying detergent-skin interactions and for predicting detergent penetration of skin and possible subsequent skin irritancy.

INTRODUCTION

Among the properties of skin which have been shown to be altered by detergent treatment are its permeability, extractability of amino acids and Folin-Ciocalteu positive material (protein) and liberation of reactive sulfhydryl groups (1). In terms of dimensional changes Choman (2) observed increases in the thickness of epidermis-free calf skin and human abdominal skin which were produced by treatment with sodium alkyl sulfates of different chain lengths and concluded that sodium lauryl sulfate produced the greatest increase. In order for swelling to occur a concentration near or above the critical micelle concentration (CMC) of each alkyl sulfate was required. In their ultrastructural study of the action of 1 per cent sodium lauryl sulfate on rat skin Tovell and coworkers (3) noted a marked thickening of the epidermis and stratum corneum resulting from treatment with the detergent.

Scheuplein and Ross (4) soaked stratum corneum in 5 per cent sodium laurate for 24 h and observed a visible expansion in the plane of the tissue. These authors also noted that Von Götte (5) had previously observed an expansion of isolated epidermis after

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treatment with anionic detergents. Since the measurement of surface area would be a convenient means of evaluating stratum corneum-detergent interactions, we have utilized the method to confirm the results for sodium laurate (4) and examine other detergents. To gain an insight into the mechanism of this swelling phenomenon we have also determined the effect of other agents known to interact with protein or lipid on stratum corneum surface area and have evaluated the effect of sodium laurate on a rheological property of stratum corneum.

MATERIALS

Stratum corneum was obtained from Hartley guinea pigs. Excised, epilated* skin was exposed to ammonia vapor (6). The sheets were air dried and stored under ambient conditions.

Analytical grade reagents were used without further purification. These included urea, guanidine hydrochloride, dimethylsulfoxide, formic acid, ammonium thioglycollate, dithiothreitol, lithium bromide, N-methyl-2-pyrrolidone, chloroform, methanol, and ethyl ether. The sources of surfactants used in this work are listed in Table I.

METHODS

IN-PLANE SWELLING

Squares of stratum corneum 20 × 20 mm were soaked in water for 1 h. The squares were lifted out of the water on plastic screens and their dimensions were determined with a ruler calibrated in millimeters. The squares were then immersed in the appropriate solution for 16 h after which they were removed on plastic screening, and their dimensions were again determined. Swelling is expressed as the percent change in area after exposure to the second solution as compared to the first solvent, water.

MECHANICAL TESTING OF STRATUM CORNEUM

Strips of stratum corneum, prepared according to procedures previously described (7), were immersed in water for 4 h and stretched 5 per cent of their original length. After relaxation they were exposed to a test material for 1 h, followed by transfer to water and a second stretching after 4 h. The results are expressed in terms of a work index (7) where:

$$\text{work index} = \frac{\text{work required to stretch strip after treatment}}{\text{work required to stretch strip before treatment}}$$

STRATUM CORNEUM MODIFICATION

1. *Oxidation:* Performic acid was prepared by combining 9 parts of concentrated formic acid (98 per cent) with 1 part hydrogen peroxide (30 per cent) and letting the mixture stand for 2 h at room temperature. The performic acid was diluted 1:5 with water just before using on stratum corneum in a bath ratio of 100:1 at 15–20°C for 30 min. The stratum corneum was rinsed well in deionized water. An 88 per cent oxida-

*Zip Wax®, Jean Jordeau Inc., New York.

Table I
Surfactants Studied

Name	Concentration	Manufacturer	CMC[a]
Sodium laurate	.05 *M*	Eastman Organic Chemicals, Rochester, NY	2.4×10^{-2} *M*
Sodium lauryl sulfate	.05 *M*	Fisher Scientific Corp., Fairlawn, NJ	8.1×10^{-3} *M*
Ammonium lauryl sulfate	.05 *M*	Continental Chemical Co., Clifton, NJ	6.0×10^{-3} *M*
Triethanolammonium lauryl sulfate	.05 *M*	Alcolac Inc., Baltimore, MD	4.0×10^{-3} *M*
Sodium dodecylbenzene sulfonate	.05 *M*	Pfaltz and Bauer, Inc., Flushing, NY	1.2×10^{-3} *M*
Sodium myristal ether sulfate	.05 *M*	Standapol ES-40 Conc.—Henkel, Inc., Teaneck, NJ	1.4×10^{-3} *M*
Sodium lauryl ether sulfate	.05 *M*	Sipon ES—Alcolac Inc., Baltimore, MD	4.8×10^{-3} *M*
Sodium alkyl sulfonate	.05 *M*	Ultrawet K—ARCO Chemical Co., Philadelphia, PA	9.0×10^{-3} *M*
Sodium oleate	.05 *M*	Fisher Scientific Corp., Fairlawn, NJ	2.6×10^{-3} *M*
Sodium hexanoate	.05 *M*	Eastman Organic Chemicals, Rochester, NY	1.6 *M*
Lauryl isoquinolinium bromide (Q-75)	.05 *M*	Q-75—Onyx Chemical Co., Jersey City, NJ purified from Isothan	4.8×10^{-3} *M*
Stearyl dimethyl benzyl ammonium chloride	20 per cent	Triton X-400—Rohm & Haas Co., Philadelphia, PA	8.5×10^{-6} *M*
Brij 35, pH 4.8	.05 *M*	Atlas Chemical Co., Wilmington, DE	6.0×10^{-5} *M*
Octylphenoxy polyethoxy ethanol	1 per cent	Triton X-100—Rohm & Haas Co., Philadelphia, PA	2×10^{-3} per cent

[a] Values obtained from (17).

Table II
Effect of Anionic Surfactants on Stratum Corneum Swelling

Surfactant	Conditions	Per cent Swelling	Standard Deviation	n[a]
Sodium laurate	.05 *M*, pH 9.8	16.7	±9.7	37
Sodium lauryl sulfate	.05 *M*, pH 10	13.1	±3.5	97
Ammonium lauryl sulfate	.05 *M*	9.1	±2.9	4
Triethanolammonium lauryl sulfate	.05 *M*	12.2	±2.3	4
Sodium dodecylbenzene sulfonate	.05 *M*	11.9	±10.8	4
Sodium myristyl ether sulfate	.05 *M*	−0.1	±1.4	7
Sodium lauryl ether sulfate	.05 *M*	6.6	±2.9	4
Sodium lauryl triether sulfate	.05 *M*	3.9	±3.8	4
Sodium oleate	.05 *M*	15.1	±7.9	6
Sodium hexanoate	.05 *M*	0.0	±0.0	4

[a]Number of measurements.

tive fission of disulfide bonds was obtained as determined by amino acid analyses of acid hydrolysed samples.

2. *Reduction and Alkylation:* For the reduction of stratum corneum 0.02 *M* dithiothreitol was used at 200:1 bath ratio for 1 h at 39°C. After reduction stratum corneum was alkylated with 2.5 per cent acrylonitrile in 1 per cent borate buffer (pH 9.1) for 30 min at 35°C in a 50:1 bath ratio. Alternatively, the stratum corneum was alkylated with 2 per cent iodoacetate in borate buffer (pH 8) for 2 h at 35°C in a 100:1 bath ratio. The reaction flask was evacuated during the reaction.

DELIPIDIZATION

Delipidization was obtained with $CHCl_3$:MeOH(2:1) for 90 min at room temperature followed by 5 min extraction with water.

RESULTS

Several anionic surfactants at concentrations above their CMC (Table I) were tested for their ability to produce in-plane swelling (increase surface area) of guinea pig stratum corneum squares. The results given in Table II confirm the observation of Scheuplein and Ross (4) for sodium laurate and indicate that sodium lauryl sulfate produces the same effect. The increase in surface area obtained with sodium laurate is illustrated in Fig. 1. The sodium cation is not necessary for the effect since similar levels of swelling were found when ammonium and triethanolammonium lauryl sulfate were used. Sodium dodecyl benzene sulfonate and sodium oleate also gave high levels of in-plane swelling, while sodium hexanoate gave no measurable swelling. This absence of swelling with hexanoate could be a direct effect of using a short chain molecule (i.e., a short chain molecule might not interact with stratum corneum as readily as the longer laurate) or the effect might be indirect in that the concentration of hexanoate employed, although equal to that of the other anionic surfactants, was below its CMC (Table I). (In this regard, 0.005 *M* sodium lauryl sulfate produced no measurable swelling

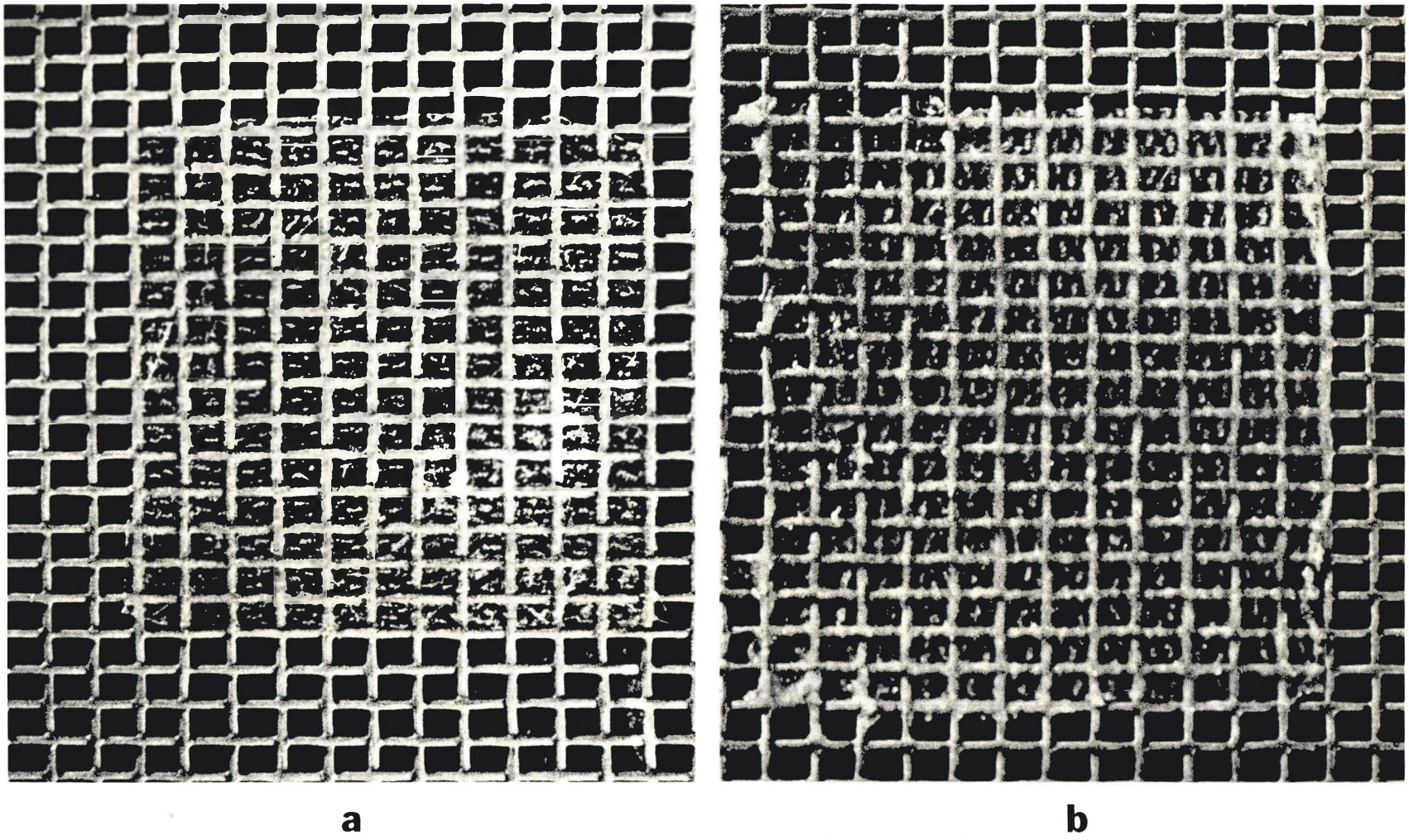

Figure 1. Illustration of in-plane swelling of stratum corneum in sodium laurate: a) following initial water soak; b) the same piece of stratum corneum following sodium laurate soak

Table III
Effect of Cationic and Nonionic Surfactants on Stratum Corneum Swelling

Surfactant	Conditions	Per cent Swelling	Standard Deviation	n[a]
Laurylisoquinolinium bromide (Isothan Q-75)	.05 *M*	3.9	±3.8	4
Stearyldimethylbenzylammonium chloride (Triton X-400)	20 percent	1.6	±0.7	4
Polyoxyethylene (23) lauryl ether (Brij 35)	.05 *M*, pH 4.8	3.4	±3.4	4
Octylphenoxypolyethoxyethanol (Triton X-100)	0.1 percent	3.1	±0.9	4

[a]Number of measurements.

Table IV
Effects of Protein Denaturants and Lipid Solvents on Stratum Corneum Swelling

Reagent	Type[a]	Per cent Swelling	Standard Deviation	n[b]
8 *M* urea	D	0	±0.0	4
5 *M* guanidine-HCl	D	4.1	±1.6	4
0.1 *M* ammonium thioglycollate	D	0	±0.0	4
0.1 *M* DTT	D	0	±0.0	4
50 per cent LiBr	D	0	±0.0	4
80 per cent dimethylsulfoxide in water	L	0	±0.0	4
80 per cent N-methylpyrrolidone in water	L	0	±0.0	4
Chloroform: methanol (2:1)	L	0.6	±1.0	10
ethyl ether	L	−4.1	±1.5	6
0.3 per cent performic acid, 15°C	D	26.3	±12.9	10

[a]D is a protein denaturant; L is a lipid solvent.
[b]Number of measurements.

Table V
Effect of Pretreatment on Sodium Lauryl Sulfate-Induced Swelling of Stratum Corneum

Pretreatment[a]	Per cent Swelling in[b] 0.05M NaLS (pH 6)	Standard Deviation	n[b]
H_2O	13.1	±3.5	97
$CHCl_3$:MeOH delipidized	24.3	±6.2	8
DMSO	36.8	±2.8	4
DTT reduced	14.2	±0.1	4
DTT-acrylonitrile alkylated	16.0	±6.3	10
DTT-iodoacetate alkylated	23.4	±5.2	8
Performic acid oxidized	−1.7[c]	±3.2	4

[a]Abbreviations: DMSO-dimethyl sulfoxide; DTT-dithiothreitol.
[b]Number of measurements.
[c]Performic acid oxidation induced a swelling of 26 per cent, which was not reversible in water. No additional swelling occurred upon exposure to NaLS.

while readily detectable swelling was generated in 0.01 *M* sodium lauryl sulfate.) That a hydrophobic chain in the surfactant favors stratum corneum swelling is indicated by a comparison of results obtained for sodium lauryl sulfate and sodium lauryl ether sulfate (1 mol of ethylene oxide). Sodium lauryl ether sulfate with 3 mol of ethylene oxide

yielded an even lower level of stratum corneum swelling. Sodium myristyl ether sulfate (1 mol of ethylene oxide) produced no swelling indicating that the combination of increasing polarity and a C_{14} alkyl group instead of C_{12} eliminated swelling.

To determine whether the in-plane swelling of stratum corneum was produced only by anionic surfactants, two cationic surfactants (Triton X-400) and Isothan Q-75) and two nonionic surfactants (Brij 35 and Triton X-100) were evaluated. The results shown in Table III indicate that little swelling is obtained with these surfactants compared to levels found for long chain anionic surfactants.

Since sodium lauryl sulfate has been used to denature proteins,* other agents which denature proteins (probably by means of a different mechanism) were evaluated for their ability to swell stratum corneum (Table IV). Reagents which are strong hydrogen bond formers (5 *M* guanidine hydrochloride, 8 *M* urea), reducing agents (ammonium thioglycollate, dithiothreitol), and 50 per cent lithium bromide produced little or no stratum corneum swelling. Performic acid oxidation run under mild conditions (0.3 per cent performic acid, 15°C, 30 min) produced extensive swelling which probably reflects its greater efficiency (compared to reducing agents) in cleaving disulfide bonds as well as the effect of introducing hydrophilic negative sites into the keratin. Agents capable of removing lipid (80 per cent dimethyl sulfoxide,† 80 per cent N-methyl pyrrolidone in water,† and chloroform:methanol (2:1 by volume) produced no swelling.

Not only was stratum corneum swelling measured in the protein denaturants cited above but stratum corneum soaked in some of these agents was subsequently exposed to the known swelling agent sodium lauryl sulfate. The results are summarized in Table V. Delipidizing agents and reducing agents appear to enhance sodium lauryl sulfate induced swelling while performic acid oxidation does not. Since per cent swelling in sodium lauryl sulfate is calculated by comparing the stratum corneum dimensions in the surfactant to its dimensions in water following the pretreatment, it would appear that the tissues have reached their maximum capacity of swelling in performic acid.

Since the greatest increases in swelling were produced by sodium laurate and sodium lauryl sulfate, these surfactants were further examined. If surfactant-induced swelling was specifically due to the extraction of proteins or lipids from the stratum corneum, one would expect that the swelling effect would be irreversible. However, reversibility of the effect was demonstrated by alternately swelling stratum corneum in sodium laurate and returning it to its original size in water (Table VI).

Although the swelling in sodium laurate appeared to be reversible, it seemed reasonable to examine the effect of laurate on other properties of the stratum corneum. Thus, stratum corneum strips were first stretched on the Instron extensometer approximately 5 per cent in water, and after relaxation were exposed to either water, 0.05 *M* sodium laurate at pH 9.8 or 0.05 *M* sodium acetate at pH 9.8 for 1 h followed by transfer to water and a second stretching. The work index (defined in the Methods Section of this paper) would be 1.0 if the treatment had no effect and <1 if the treat-

*Sodium lauryl sulfate has been used as a denaturing agent in the determination of protein molecular weights (8).

†These aprotic solvents are also capable of forming hydrogen bonds and have often been classified as protein denaturants.

Table VI

Sodium Laurate (NaL) Induced Swelling of Stratum Corneum—Reversibility Studies[a,b]

	Per Cent Swelling in 1 Per Cent NaL	Standard Deviation	Per Cent Swelling in H_2O[c]	Standard Deviation	Per Cent Swelling in 1 Per Cent NaL	Standard Deviation	Per Cent Swelling in H_2O[c]	Standard Deviation
Animal I	24.6	± 4.9	−1.4	±2.4	22.8	±3.4	0.6	±2.7
Animal II	25.3	±12.5	0.0	±0.0	20.1	±7.6	−6.4	±2.7

[a] 0.05 *M* sodium laurate, pH 9.8.

[b] Each value represents a measurement on 3 pieces of stratum corneum.

[c] Recovery time in water is 4 h.

Table VII
Effect of Sodium Laurate (NaL) on Work Index of Stratum Corneum

Treatment	Work Index	Standard Deviation	n[a]
Water	0.98	±0.07	7
1 per cent sodium acetate, pH 9.8, 60 min	0.88	±0.07	5
1 per cent NaL, pH 9.8, 60 min	0.50	±0.17	7

[a]Number of measurements.

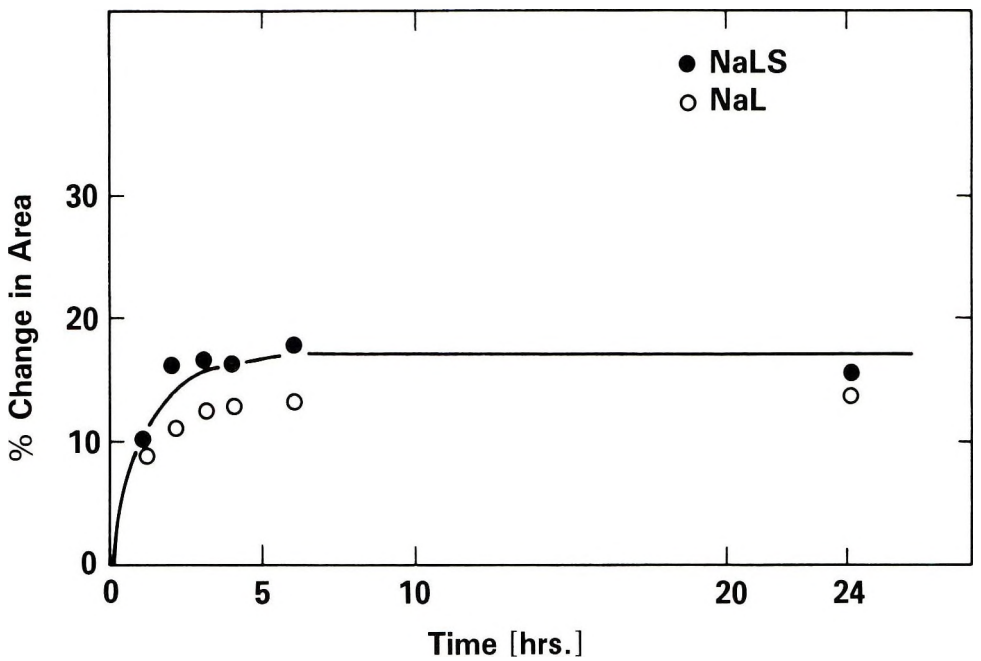

Figure 2. Rate of in-plane swelling in sodium lauryl sulfate (NaLS) and sodium laurate (NaL)

ment produced weakened stratum corneum. The data in Table VII indicate that water and sodium acetate had little effect on the strength of the tissue while sodium laurate produced a notable weakening. Rate studies of stratum corneum swelling in sodium laurate and sodium lauryl sulfate (Fig. 2) justified the brief exposure to surfactant employed in the mechanical test.

DISCUSSION

The use of in-plane swelling of guinea pig stratum corneum is an admittedly insensitive means of determining surfactant–skin interactions. Nevertheless, the procedure is simple, requires little time by an experimenter and no sophisticated equipment. That the values obtained for a given surfactant can differ with the source of the stratum corneum (animal to animal) and even with the site on an animal (piece to piece) is evident from the high standard deviations. Thus, in comparing surfactants, stratum corneum

from the same animal and from neighboring sites should be used. Fortunately, we have observed that although the magnitude may be variable from study to study, the relative order of magnitude remains the same and surfactants can easily be classified as producing little or no swelling, or producing readily measurable swelling. Scheuplein and Ross (4) soaked human stratum corneum in 5 per cent sodium laurate for up to 72 h and observed an expansion in area ranging from 50 to 80 per cent.

In discussing the mechanism by which anionic detergents swell stratum corneum while cationic and nonionic surfactants appear to have little effect, it seems reasonable to briefly consider the literature on globular proteins. As summarized by Tanford (9) amphiphilic substances (ionic or polar derivatives of hydrocarbons) can combine with proteins in at least 3 distinct modes of interaction. (1) Association with specific binding sites of native proteins (serum albumin and β-lactoglobulin behave in this manner); (2) Cooperative association between protein and a large number of detergent molecules without major conformational changes (serum albumin with alkyl sulfates and sulfonates having short hydrocarbon chains); (3) Cooperative association with gross denaturation of the protein. The 3 types of binding occur with detergent monomers rather than micelles. In fact, micelle formation can be considered to be in competition with protein binding. Nevertheless, to insure a maximum concentration of monomer, our studies were performed well above the CMC except where noted.

Since nonionic detergents have much lower CMC than anionic detergents, fewer monomers would be present in a solution of nonionic detergent so that binding type 3 would be less likely to occur with a nonionic detergent (10). It should be noted that little or no swelling was observed with nonionic detergents.

Tanford and coworkers (11) also compared the interaction of anionic lauryl sulfate and tetradecyltrimethylammonium ions with serum albumin and other globular proteins and concluded that both detergents yield type 3 interaction. However, with the cationic detergent type 3 binding occurred very close to its CMC while with lauryl sulfate the binding occurred far below its CMC. Less cationic detergent was bound than anionic detergent. The authors concluded that the difference between the 2 types of detergent was that the anionic detergent would cluster around the longer cationic sites in the protein (arginyl and lysyl side chains) which could accommodate more detergent molecules than the shorter anionic sites in the protein (glutamyl, aspartyl) around which cationic detergents would cluster. In a subsequent paper, however, Tanford and coworkers (12) studied the binding of the same cationic detergent as well as lauryl sulfate to apoproteins of human serum high density lipoprotein and observed cooperative interaction with the cationic detergent at a much lower equilibrium detergent concentration than observed previously with water-soluble proteins. They also concluded that binding the cationic and anionic detergent had resulted in a change in conformation which was unlike the denatured state observed with globular proteins. That little swelling was observed with the cationic surfactants we used might be due to the low CMC for Triton X-400, or it might reflect the inability of the stratum corneum to undergo cooperative binding with these particular surfactants. Preliminary work suggests that dodecyltrimethylammonium chloride may produce levels of swelling similar to lauryl sulfate. The results of the 2 studies just cited indicate the difficulty in choosing the appropriate soluble protein to simulate the insoluble stratum corneum. However, as the interests of academic scientists turn more toward membranous proteins, more choices for the cosmetic chemist/skin biologist should be available.

In reviewing the effects of chemicals on skin dimensions we should note the observation of Wildnauer that soaking stratum corneum in formic acid resulted in an increase in length of the tissue which he attributed to denaturation of the protein (13). Not all denaturing media induce this effect as indicated by our results shown in Table IV. Imokawa and coworkers (14, 15) used the change in optical rotation induced by soaking bovine serum albumin in several detergents as a means of estimating a detergent's ability to cause protein denaturation; they obtained positive correlation between a detergent's denaturing ability and its ability to produce "skin roughness" *in vivo*.

Scheuplein and Ross (4) observed that while concentrated urea solution had no effect on skin permeability to water, 1 per cent solutions of laurate and lauryl sulfate enhanced skin permeability. Interestingly, we observed no swelling in 8 *M* urea (Table IV), but notable swelling in the anionic surfactants. Not only was the swelling induced by laurate reversible ((4) and Table IV), but much of the barrier function was shown to be recoverable after resoaking the stratum corneum in water (4).

The observation of the reversibility of laurate-induced swelling and the observation that the birefringence of the stratum corneum, which is greatly diminished by soaking in 5 per cent laurate, is restored after resoaking in water led Scheuplein and Ross (4) to conclude that laurate had induced a reversible $\alpha \rightarrow \beta$ conversion of the stratum corneum protein with an uncoiling of the filaments, which was accompanied by a gross expansion of the tissue and high influx of water.

We conclude that denaturation does not cause stratum corneum swelling, but that swelling is due to a reversible conformation change resulting from cooperative binding of the appropriate detergent. The binding is neither type 2 nor type 3 but is probably most like that described above for the apoproteins of serum high density lipoproteins. Our observation on the effect of laurate, however, indicates irreversible effects as well. Prottey and Ferguson (16) have observed the extraction of proteins and amino acids by anionic detergents. Lauryl monoethoxysulfate can extract protein (16) but causes little swelling suggesting that protein extraction may be responsible for weakening but not for swelling.

Our results suggest that stratum corneum swelling could be of value for studying detergent-skin interactions and for predicting detergent penetration of skin and possibly subsequent skin irritancy.

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Some comparisons of benzoyl peroxide formulations

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Synopsis

The BIOLOGICAL PROFILE of several FORMULATIONS of BENZOYL PEROXIDE are compared. The efficacy of benzoyl peroxide can be optimized by influencing formulation variables. A benzoyl peroxide formulation "A" is compared to some competitive products, C, D, and B. Dermal irritation in rabbits, acute toxicity in rats, efficacy against *Corynebacterium acnes*, as well as several formulation variables, such as particle size and vehicle interaction, are compared.

The selection of a candidate formulation is subjected to test involving acute toxicity, ocular irritation, skin irritation, and sensitization. The design of these tests should involve not only positive and negative controls, but also appropriate reference products which are already on the market. It is important when developing biological data to accumulate data on the finished product, since it is the finished product which will come into extensive contact with the skin in a clinical population.

All the formulations tested were equivalent in performance except for ocular irritation potential. Formulations with larger particle size distribution had a greater ocular irritation potential.

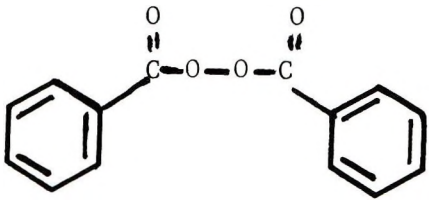
INTRODUCTION

Benzoyl peroxide is an old and established treatment agent with keratolytic and antibacterial action. This compound is formed by the reaction of alkaline (sodium) hydrogen peroxide with benzoyl chloride in water. It was described as a therapeutic aid in the treatment of burns, ulcerations, and various infected cutaneous and mucous membrane lesions, and more recently it has been found to be among the most effective mode of acne therapy (1).

There are many methods to treat acne vulgaris, including unblocking the pilosebaceous duct, strengthening the wall of the duct, decreasing the amount of sebum secreted, or changing the composition of the sebum to make it less of an irritant (2).

Among the most popular method of treatment of acne is the use of benzoyl peroxide. The topical use of drying and peeling medications has long been a mainstay of the therapy of acne vulgaris. It is now fairly well agreed that the initial local changes in acne consist of desquamation and hyperkeratosis of the follicular orifice of the functioning sebaceous gland, thus producing an obstruction and dilation of the glandular opening with retention of the sebum. The effect of these peeling agents is obvious. The most

STRUCTURE



USE - A desquamating antimicrobial agent used in treatment of acne.

MECHANISM OF ACTION -
- slow oxygen releaser providing antimicrobial activity
- scaling (comedolytic)
- reduction of free fatty acids (FFA) released during metabolism of surface bacteria

Figure 1. What is benzoyl peroxide?

direct way to interrupt this process that leads to the formation of acne lesions is by peeling away of the rim of the hyperkeratotic orifice. Many agents have been utilized to this end, some more successfully than others.

The purpose of this paper is to review the profile of several benzoyl peroxide formulations, which have been investigated in our laboratories. Evaluations were based on studies undertaken on acute toxicity, ocular irritation, dermal irritation, as well as several formulation variables as particle size and vehicle interaction (3, 4) (Fig. 1).

For brevity, data on two formulations A and C will be presented at 10 per cent concentration of benzoyl peroxide. These were selected because they represented the 2 extremes in formulation response variables and the data is representative. Formulations D and B gave response intermediate between A and C.

MATERIALS AND METHODS

Several standard methodologies were used for these studies and will be briefly mentioned.

ACUTE ORAL TOXICITY

Swiss albino mice weighing approximately 20 g* were utilized. The mice were acclimated to laboratory conditions for 1 week prior to use. The animals were maintained on Purina Chow† and tap water provided *ad libitum*. The test formulation was appro-

*Obtained from Mouse House, Marlow OK.

†Ralston Purina.

priately diluted with the vehicle to achieve the desired dosage of 50 ml/kg by the oral route. Administration was accomplished with the aid of a 3-ml syringe adapted with a 20-gauge olive tipped needle. Each dose level was administered to 5 males and 5 females. A separate group of 5 males and 5 females received the vehicle. The animals were observed for a period of 7 days for untoward signs and lethality and the LD_{50} calculated by the Probit method (5).

OCULAR IRRITATION EVALUATION

New Zealand albino rabbits without regard to sex and weighing approximately 2 kg were obtained from a local supplier.* The animals were acclimated to laboratory conditions for 1 week prior to initiation of the test. The animals were maintained on Purina Chow and tap water provided *ad libitum.* Only animals judged free of ocular defects by macroscopic and biomicroscopic examination were utilized.

The ocular irritation studies followed modifications of guidelines established by the Hazardous Substances Act. Procedures were modified by the addition of a 20-sec wash group. Three treatment groups of 6 eyes each were established for each test formulation. All groups received 0.1 ml of the test formulation in both eyes of each rabbit. Each eye was washed with a total of 300 ml of metered running tap water over a 2-min period. The time of eye washing after exposure to the formulation was different for each group. Group I eyes were washed at 20 sec after exposure; Group II eyes were washed 5 min after exposure; and Group III eyes were not washed until 24 h after exposure to the formulation. Appropriate sham control groups with washings on Day 0 and Day 1 were included for comparative purposes. A separate group of rabbits served as an untreated control. Sham control and untreated control groups were run each time the study was performed. After treatment, all eyes were examined at 1 h and at 1, 2, 3, 7, 14, and 21 days. All control groups of rabbit eyes were observed in conjunction with treatment animals. The conjunctiva was graded macroscopically by the method of Draize (6). The cornea, anterior chamber, iris, and lens were graded with the aid of a biomicroscope by the method of Baldwin, McDonald, and Beasley (7). Scores and incidences of each parameter were subjectively evaluated and used to rank the formulations either more or less irritating than similar competitor products.

DERMAL IRRITATION EVALUATION

Benzoyl peroxide formulations were tested in New Zealand albino rabbits of mixed sex and weighing about 2.5 kg. The animals were maintained on Purina Chow and tap water provided *ad libitum.* The backs of 15 rabbits were clipped free of hair and divided into 4 quadrants with each quadrant measuring approximately 2 in. on each side. The quadrants were labeled A, B, C, and D.

Quadrants A and D in the first 6 rabbits were unabraded, while quadrants B and C of the same 6 rabbits were abraded with a Berkeley Scarifier.† Quadrants A and B of these first 6 rabbits received benzoyl peroxide 10 per cent, while quadrants C and D of

*Krauss Rabbitry, Palestine, TX.

†Berkeley Biologics, Berkeley, CA.

the same 6 rabbits received the competitive formulations. Quadrants A and B of the next 6 rabbits received the positive control, quadrants A, B, C, and D of 3 separate rabbits served as untreated control quadrants. Each test formulation was applied at 0.5ml/dose, once a day for 3 consecutive days. After each application, the sites were covered with 3 × 3 in. gauze pads. The gauze pad was secured with an elastic adhesive bandage. At the end of each of the 3 24-h periods, the bandages were removed and dermal sites graded by the method of Draize (6).

PHYSICAL MEASUREMENTS

Particle size determinations were conducted using a Zeiss microscope* under standard 300 X magnification and 100 X magnification. Particle size determination was expressed as the per cent of particles which appeared within a certain micron range.

The formulations studied were marketed products from several manufacturers. They consisted of some ingredients which were common to the formulations tested, i.e., A, B, C, and D (Table I).

Table I
Ingredients Common to Benzoyl Peroxide Formulations Evaluated

Labeled as A, B, C, and D
Benzoyl Peroxide
Polyoxyethylene lauryl ether
Alcohol
Colloidal magnesium aluminum silicate
Hydroxypropylmethyl cellulose
Citric Acid
Carbomer 940
Diisopropanolamine
Disodium Edetate
Dimethicone
Acetone
Propylene glycol
Sodium lauryl sufate
Fragrance
H_2O
Triethanolamine

RESULTS

For purposes of this paper representative data will be presented only on formulation A among the best and formulation C as representative of the worst. Formulation D and B fell in between.

*Carl Zeiss.

Table II
Comparative Acute Toxicity of Benzoyl Peroxide Formulations, 10 Per Cent

Formulation	Dose ml/kg	Number of Animals	Deaths/ Toral Animals	LD50 (95 Per cent C.L.) mg/Kg
A	25	10	10/10	14.07 (12.73–15.56)
	16.5	10	8/10	
	12.5	10	3/10	
	10	10	0/10	
C				
	25	10	10/10	12.09 (10.88–13.44)
	16.5	10	9/10	
	12.5	10	7/10	
	10	10	1/10	
Control (vehicle)	0	10	0/10	

ACUTE LD50

Animals which received the test formulations were lethargic, prostrate, and exhibited evidence of labored respiration within 4 h. Changes in the general appearance and behavior were more pronounced at the higher dose levels, especially for animals who died during the study. The mortalities occurred in a dose-response pattern for calculation of an oral LD_{50} for the various benzoyl peroxide formulations. The acute oral toxicity is expressed in Table II. There were no mortalities for the vehicle treated animals. Formulation A was less toxic (not significant) from formulation C.

OCULAR IRRITATION

Conjunctival congestion observed at the 1- through 24-h period was high in incidence for all treatment groups. Beginning on Day 7 through Day 21, minimal to moderate conjunctival congestion at a high to moderate incidence was observed for all test groups which received benzoyl peroxide formulations. Eyes which received the 10 per cent concentration exhibited severe conjunctival congestion at a high incidence on Days 7, 14 and 21, minimal conjunctival congestion was observed at the 1-h observation period for the Day 0 controls. Thereafter, variable instances of minimal conjunctival congestion at a low to moderate incidence was observed for the Day 0 controls. Likewise, Day 1 controls and untreated controls exhibited minimal conjunctival congestion at a low to moderate incidence throughout the entire test period (Table III). There was less severity for A after 24 h than for formulation C.

Moderate conjunctival swelling at a high incidence was observed in the 5-min and 24-h wash groups which received 10 per cent benzoyl peroxide for the 1-through 72-h observation period. At the 1-h observation period, moderate conjunctival swelling at a high incidence was observed for the 20-sec wash group for eyes which received the 10 per cent formulation; thereafter, the same eyes exhibited minimal conjunctival swelling at a high incidence through the 72-h observation period at which time swelling was not observed for the remainder of this treatment group. For the 5-min and 24-h wash groups in eyes which received 10 per cent benzoyl peroxide on Days 7 and 14, minimal conjunctival swelling at a low to moderate incidence was observed, while no swelling

Table III
Conjunctival Congestion for Rabbits After Single Topical Ocular Instillation of Benzoyl Peroxide 10 Per Cent

Formulation	Wash Time[c]		Conjunctival Congestion 1 h	24 h	48 h	72 h	7 day	14 day	21 day
A	20 sec	$\bar{x}$[a]	6.0	6.0	5.3	6.0	2.3	3.0	1.0
		Inc.[b]	6/6	6/6	6/6	6/6	5/6	6/6	3/6
A	5 min	$\bar{x}$	6.0	6.0	6.0	6.0	4.0	4.0	3.5
		Inc.	6/6	6/6	6/6	6/6	6/6	4/4[d]	4/4
A	24 h	$\bar{x}$	6.0	6.0	6.0	5.7	4.7	3.7	2.7
		Inc.	6/6	6/6	6/6	6/6	6/6	6/6	6/6
C	20 sec	$\bar{x}$	6.0	6.0	6.0	5.7	5.3	4.0	5.0
		Inc.	6/6	6/6	6/6	6/6	6/6	6/6	6/6
C	5 min	$\bar{x}$	6.0	6.0	6.0	6.0	6.0	5.3	6.0
		Inc.	6/6	6/6	6/6	6/6	6/6	6/6	6/6
C	24 h	$\bar{x}$	6.0	6.0	6.0	6.0	6.0	5.0	5.3
		Inc.	6/6	6/6	6/6	6/6	6/6	6/6	5/6
Day 0 Controls	Day 0	$\bar{x}$	2.3	1.3	0.0	0.0	0.0	1.3	0.3
		Inc.	6/6	3/6	0/6	0/6	0/6	4/6	1/6
Day 1 Controls	Day 1	$\bar{x}$	0.0	0.7	0.3	0.0	0.3	2.3	0.7
		Inc.	0/6	2/6	1/6	0/6	1/6	5/6	2/6
Untreated Controls	—	$\bar{x}$	1.0	0.0	0.7	0.3	0.3	1.7	0.0
		Inc.	3/6	0/6	2/6	1/6	1/6	5/6	0/6

[a]Maximum score: Congestion = 6. Mean score calculated by summing individual scores and dividing by the number of observations.
[b]Number of eyes with response/number of eyes in test group.
[c]Interval of time after dosing until eye was washed.
[d]Number less than 6 indicates mortality not related to treatment.

was observed for the 5-min wash group at the 21-day observation period but a single instance of minimal conjunctival swelling was observed for the 24-h wash group. Moderate conjunctival swelling at a high incidence was observed at the 1-through 72-h observation period for all 3 treatment groups receiving 10 per cent formulations. On Day 7, minimal conjunctival swelling at a high incidence was observed for the 20-sec wash group, while moderate conjunctival swelling at a high incidence was observed for the 5-min and 24-h wash groups for eyes which received the benzoyl peroxide formulations. Swelling was not observed for any control eyes (Table IV). Swelling was less severe for A after 24 h than for C.

Moderate conjunctival discharge at a high incidence was observed at the 1- and 24-h observation periods for 3 treatment groups receiving the benzoyl peroxide formulations. For the 20-sec wash group, minimal conjunctival discharge at a high incidence was observed at the 48-h and 72-h observation periods with a discharge not being observed for the remainder of the test period. For the 5-min wash group, moderate conjunctival discharge at a high incidence was observed at the 48-h and 72-h observation periods with minimal conjunctival discharge at a low to moderate incidence being observed on Days 7 and 14 and with discharge being absent on Day 21. In the 24-h wash group, moderate conjunctival discharge at a high incidence was observed at the 48- and

Table IV
Conjunctival Swelling for Rabbits After Single Topical Ocular Instillation of Benzoyl Peroxide 10 Per Cent

Test Formulation	Wash Time[c]		Conjunctival Swelling						
			1 h	24 h	48 h	72 h	7 day	14 day	21 day
A	20 sec	$\bar{x}$[a]	3.7	2.0	2.0	1.7	0.0	0.0	0.0
		Inc.[b]	6/6	6/6	5/6	5/6	0/6	0/6	0/6
A	5 min	$\bar{x}$	3.7	3.3	3.3	3.3	1.3	1.3	0.0
		Inc.	6/6	6/6	6/6	6/6	4/6	3/4	0/4
A	24 h	$\bar{x}$	4.0	3.3	3.3	3.3	1.0	0.7	0.3
		Inc.	6/6	6/6	6/6	6/6	3/6	2/6	1/6
C	20 sec	$\bar{x}$	3.7	3.3	3.7	3.0	2.3	0.7	0.3
		Inc.	6/6	6/6	6/6	5/6	5/6	2/6	1/6
C	5 min	$\bar{x}$	4.0	4.3	5.3	4.7	3.7	2.7	1.7
		Inc.	6/6	6/6	6/6	6/6	6/6	6/6	5/6[d]
C	24 h	$\bar{x}$	3.7	3.7	4.0	4.3	3.0	2.7	1.3
		Inc.	6/6	6/6	6/6	6/6	6/6	4/6	3/6
Day 0 Controls	Day 0	$\bar{x}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		Inc.	0/6	0/6	0/6	0/6	0/6	0/6	0/6
Day 1 Controls	Day 1	$\bar{x}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		Inc.	0/6	0/6	0/6	0/6	0/6	0/6	0/6
Untreated Controls	—	$\bar{x}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		Inc.	0/6	0/6	0/6	0/6	0/6	0/6	0/6

[a]Maximum score: Swelling = 8. Mean score calculated by summing individual scores and dividing by the number of observations.
[b]Number of eyes with response/number of eyes in test groups.
[c]Interval of time after dosing until eye was washed.
[d]Number less than 6 indicates mortality not related to treatment.

72-h observation periods with minimal conjunctival discharge at a low incidence being observed on days 7 and 14 and discharge being absent on Day 21. Moderate conjunctival discharge at a high incidence was observed for the 1-h observation period for eyes which received benzoyl peroxide formulations.

Moderate to severe conjunctival discharge at a high incidence was observed at the 24-, 48-, and 72-h and Day 7 observation periods for all treatment groups. Minimal conjunctival discharge at a moderate incidence was observed on Days 14 and 21 for the 20-sec wash group for eyes which received 10 per cent benzoyl peroxide formulations. Moderate conjunctival discharge at a moderate incidence was observed on Day 14 for the 5-min and 24-h wash groups, while discharge had diminished to a minimal intensity at a moderate incidence by Day 21. The second instance of minimal conjunctival discharge was observed at the 1-h observation period for the Day 0 controls; thereafter, the eyes in this treatment group did not exhibit discharge in the remainder of this 21-day test period. Discharge was not observed for the Day 1 controls and untreated controls (Table V). Formulation A after the 24-h treatment had minimal discharge compared to formulation C. All eyes were normal relative to light reflex (pupillary response and lens) for eyes receiving benzoyl peroxide formulations and control formulations.

Table V
Conjunctival Discharge for Rabbits After Single Topical Ocular Instillation of Benzoyl Peroxide 10 Per Cent

Test Formulation	Wash Time[c]		Conjunctival Discharge 1 h	24 h	48 h	72 h	7 day	14 day	21 day
A	20 sec	$\bar{x}$[a]	3.7	4.7	2.7	2.0	0.0	0.0	0.0
		Inc.[b]	6/6	6/6	5/6	5/6	0/6	0/6	0/6
A	5 min	$\bar{x}$	4.3	5.3	5.0	4.7	2.7	0.5	0.0
		Inc.	6/6	6/6	6/6	6/6	4/6	1/4[d]	0/4[d]
A	24 h	$\bar{x}$	3.7	4.3	4.7	4.7	1.0	0.3	0.0
		Inc.	6/6	6/6	6/6	6/6	2/6	1/6	0/6
C	20 sec	$\bar{x}$	3.0	5.0	5.3	5.3	4.0	1.0	0.7
		Inc.	6/6	6/6	6/6	6/6	5/6	3/6	2/6
C	5 min	$\bar{x}$	4.3	6.0	6.0	6.0	5.3	3.3	2.0
		Inc.	6/6	6/6	6/6	6/6	6/6	5/6	4/6
C	24 h	$\bar{x}$	3.3	5.7	6.0	6.0	5.0	4.0	2.3
		Inc.	6/6	6/6	6/6	6/6	6/6	4/6	4/6
Day 0 Controls	Day 0	$\bar{x}$	0.3	0.0	0.0	0.0	0.0	0.0	0.0
		Inc.	1/6	0/6	0/6	0/6	0/6	0/6	0/6
Day 1 Controls	Day 1	$\bar{x}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		Inc.	0/6	0/6	0/6	0/6	0/6	0/6	0/6
Untreated Controls	—	$\bar{x}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		Inc.	0/6	0/6	0/6	0/6	0/6	0/6	0/6

[a]Maximum score: discharge = 6. Mean score calculated by summing individual scores and dividing by the number of observations.
[b]Number of eyes with response/number of eyes in test group.
[c]Interval of time after dosing until eye was washed.
[d]Number less than 6 indicates mortality not related to treatment.

Relative to flare, a single incidence of minimal aqueous flare was observed at the 24-h observation period for the 20-sec wash group. Flare was not observed in the remainder of the 21-day period for all treatment groups (benzoyl peroxide formulations). Minimal aqueous flare at a low to moderate incidence was observed at the 1-, 24-, and 48-h observation periods for the 5-min wash group for eyes which received benzoyl peroxide formulations; thereafter, aqueous flare was not observed in the remainder of the 21-day test period for this treatment group. Minimal aqueous flare at a low to moderate incidence was observed at 1, 24, and 48 h for the 24-h wash group for eyes which received benzoyl peroxide formulations; thereafter, aqueous flare was not observed in the remainder of the 21-day test period. Minimal aqueous flare at a low to high incidence was observed at the 1-, 24-, and 48-h observation periods for the 20-sec wash group for the eyes receiving various benzoyl peroxide preparations; thereafter, aqueous flare was not observed during the remainder of the 21-day test period. Minimal aqueous flare at a low to high incidence was observed at 1, 24, 48, and 72 h for the 5-min and 24-h wash groups for eyes which received some of the benzoyl peroxide formulations; thereafter, aqueous flare was not observed for the remainder of the 21-day test period. Aqueous flare was not observed for the control eyes. Flare in general was minimal in all benzoyl peroxide formulations.

Table VI
Iritis for Rabbits After Single Topical Ocular Instillation
Of Benzoyl Peroxide 10 Per Cent

Test Formulation	Wash Time[c]		Iritis 1 h	24 h	48 h	72 h	7 day	14 day	21 day
A	20 sec	$\bar{x}$[a]	0.0	0.5	0.0	0.0	0.0	0.0	0.0
		Inc.[b]	0/6	2/6	0/6	0/6	0/6	0/6	0/6
A	5 min	$\bar{x}$	0.0	0.7	0.5	0.3	0.0	0.0	0.0
		Inc.	0/6	3/6	2/6	2/6	0/6	0/4[d]	0/4
A	24 h	$\bar{x}$	0.0	0.5	0.2	0.2	0.3	0.0	0.0
		Inc.	0/6	2/6	1/5	1/5	1/4	0/6	0/6
C	20 sec	$\bar{x}$	0.7	1.5	1.7	0.3	0.5	0.0	0.0
		Inc.	4/6	5/6	4/6	2/6	1/4	0/6	0/6
C	5 min	$\bar{x}$	0.2	1.0	1.8	1.8	0.0	0.0	0.0
		Inc.	1/6	3/6	4/5	4/4	0/3	0/3	0/3
C	24 h	$\bar{x}$	0.2	0.7	1.3	1.8	0.5	0.0	0.0
		Inc.	1/6	3/6	4/6	4/4	1/2	0/2	0/3
Day 0 Controls	Day 0	$\bar{x}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		Inc.	0/6	0/6	0/6	0/6	0/6	0/6	0/6
Day 1 Controls	Day 1	$\bar{x}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		Inc.	0/6	0/6	0/6	0/6	0/6	0/6	0/6
Untreated Controls	—	$\bar{x}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		Inc.	0/6	0/6	0/6	0/6	0/6	0/6	0/6

[a]Mean score calculated by summing individual scores and dividing by the number of observations. Maximum score: iritis = 4.
[b]Number of eyes with response/number of eyes in test group.
[c]Interval of time after dosing until eye was washed.
[d]Number less than 6 indicates mortality not related to treatment.

Relative to iritis, 2 instances of minimal iritis was observed at the 24-h observation period for the 20-sec treatment group for eyes receiving the benzoyl peroxide formulations. Minimal iritis at a low incidence was observed for the 24-, 48-, and 72-h periods for the 5-min wash group. Iritis was not observed for the remainder of the observation periods for these two groups. Minimal iritis at a low incidence was observed at 24, 48, and 72 h on Day 7 for the 24-h wash group for eyes which received benzoyl peroxide formulations. Iritis was not observed for any other observation period. Minimal iritis at a low to moderate incidence was observed at 1, 24, 48, and 72 h and again on Day 7 for the 20-sec and 24-h wash groups for eyes which received some of the benzoyl peroxide formulations. Iritis was not observed on Days 14 or 21. Minimal iritis at a low to high incidence was observed at 1, 24, 48, and 72 h for eyes for the 5-min wash group for eyes which received some benzoyl peroxide formulations; iritis was not observed on Days 7, 14, and 21. Iritis was not observed for any control eyes (Table VI). Minimal iritis was observed in formulation C with none observed with formulation A.

With regard to severity of corneal cloudiness, a low to high incidence was observed on the 1-, 24-, and 48-h observation periods for the 20-sec wash group for eyes which received various benzoyl peroxide formulations; thereafter, corneal cloudiness was not observed for any eye in this treatment group. The area (of involvement relative to the

Table VII
Severity of Corneal Cloudiness for Rabbits After Single Topical Ocular Instillation of Benzoyl Peroxide 10 Per Cent

Test Formulation	Wash Time[c]		Severity of Corneal Cloudiness						
			1 h	24 h	48 h	72 h	7 day	14 day	21 day
A	20 sec	$\bar{x}$[a]	0.7	1.2	0.3	0.0	0.0	0.0	0.0
		Inc.[b]	4/6	5/6	2/6	0/6	0/6	0/6	0/6
A	5 min	$\bar{x}$	1.3	2.3	2.3	2.3	1.0	0.2	0.3
		Inc.	6/6	6/6	6/6	6/6	5/6	1/4[d]	1/4
A	24 h	$\bar{x}$	1.0	1.5	1.7	1.7	1.8	0.7	1.0
		Inc.	5/6	5/6	4/6	4/6	4/6	4/6	3/6
C	20 sec	$\bar{x}$	1.0	1.7	2.2	2.0	2.2	0.7	0.5
		Inc.	6/6	6/6	6/6	5/6	5/6	4/6	3/6
C	5 min	$\bar{x}$	1.0	1.8	2.7	3.2	3.5	2.5	3.0
		Inc.	6/6	6/6	6/6	6/6	6/6	6/6	6/6
C	24 h	$\bar{x}$	1.0	2.0	2.3	3.2	3.3	2.8	2.3
		Inc.	6/6	6/6	6/6	6/6	5/6	5/6	4/6
Day 0 Controls	Day 0	$\bar{x}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		Inc.	0/6	0/6	0/6	0/6	0/6	0/6	0/6
Day 1 Controls	Day 1	$\bar{x}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		Inc.	0/6	0/6	0/6	0/6	0/6	0/6	0/6
Untreated Controls	—	$\bar{x}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		Inc.	0/6	0/6	0/6	0/6	0/6	0/6	0/6

[a]Mean score calculated by summing individual scores and dividing by the number of observations. Maximum scores: corneal cloudiness = 4.
[b]Number of eyes with response/number of eyes in test group.
[c]Interval of time after dosing until eye was washed.
[d]Number less than 6 indicates mortality not related to treatment.

total surface of cornea) of corneal cloudiness was approximately 25 to 50 per cent. Minimal corneal cloudiness at a moderate to high incidence was observed at 1, 24, 48, and 72 h and again on Day 7 for the 5-min and 24-h wash groups for the eyes which received various benzoyl peroxide formulations. On Days 14 and 21, minimal corneal cloudiness at a low to moderate incidence was observed for the same treatment groups (Table VII). Area for corneal cloudiness for these treatment groups on Day 7 was 50 to 100 per cent and on Day 14 approximately 24 per cent. Minimal to moderate corneal cloudiness at a high incidence was observed at 1, 24, 48, and 72 h and again on Days 7 and 14 for the 20-sec, 5-min, and 24-h wash groups for eyes which received some of the benzoyl peroxide formulations. On Day 21, minimal corneal cloudiness at a moderate incidence was observed for the 20-sec wash group, while moderate corneal cloudiness at a moderate to high incidence was observed for the 5-min and 24-h wash groups for eyes which received benzoyl peroxide formulations. The corneal area through Day 14 for each of the 3 treatment groups was approximately 75 to 100 per cent, while on Day 21 it was approximately 25 to 50 per cent. Corneal cloudiness was not observed for any control group (Table VIII). A greater severity of corneal involvement was noted for formulation C than for formulation A at the 20-sec period.

Table VIII
Area of Corneal Cloudiness for Rabbits After Single Topical Ocular Instillation of Benzoyl Peroxide 10 Per Cent

Test Formulation	Wash Time[c]		Area of Corneal Cloudiness						
			1 h	24 h	48 h	72 h	7 day	14 day	21 day
A	20 sec	$\bar{x}$[a]	1.5	2.0	0.3	0.0	0.0	0.0	0.0
		Inc.[b]	4/6	5/6	2/6	0/6	0/6	0/6	0/6
A	5 min	$\bar{x}$	4.0	4.0	3.8	3.8	2.3	0.3	0.3
		Inc.	6/6	6/6	6/6	6/6	5/6	1/4[d]	1/4
A	24 h	$\bar{x}$	2.7	2.7	2.7	2.7	2.0	1.7	0.8
		Inc.	5/6	5/6	4/6	4/6	4/6	4/6	3/6
C	20 sec	$\bar{x}$	3.2	3.8	3.3	3.0	2.3	1.8	1.3
		Inc.	6/6	6/6	6/6	5/6	5/6	4/6	3/6
C	5 min	$\bar{x}$	3.8	3.8	4.0	4.0	3.5	3.5	2.7
		Inc.	6/6	6/6	6/6	6/6	6/6	6/6	6/6
C	24 h	$\bar{x}$	4.0	4.0	4.0	4.0	3.2	3.2	2.5
		Inc.	6.6	6.6	6.6	6.6	5/6	5/6	4/6
Day 0 Controls	Day 0	$\bar{x}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		Inc.	0/6	0/6	0/6	0/6	0/6	0/6	0/6
Day 1 Controls	Day 1	$\bar{x}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		Inc.	0/6	0/6	0/6	0/6	0/6	0/6	0/6
Untreated Controls	—	$\bar{x}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		Inc.	0/6	0/6	0/6	0/6	0/6	0/6	0/6

[a]Mean score calculated by summing individual scores and dividing by the number of observations. Maximum scores: corneal cloudiness = 4.
[b]Number of eyes with response/number of eyes in test group.
[c]Interval of time after dosing until eye was washed.
[d]Number less than 6 indicates mortality not related to treatment.

Infrequent instances of minimal intensity of *fluorescein staining* occupying less than 25 per cent of the corneal surface area was observed for eyes which received all test formulations, while fluorescein staining was not observed for any control eye.

Relative to pannus, in the 24-h wash group which received benzoyl peroxide formulation, pannus at a moderate incidence was observed on Days 7, 14, and 21. Pannus was not observed for the 20-sec or 5-min wash groups for eyes which received benzoyl peroxide formulations "A" at 10 per cent. Moderate to marked pannus was observed on Days 7, 14, and 21 for the 5-min and 24-h wash groups for eyes which received benzoyl peroxide formulations "C." Pannus was not observed for any control eyes (Table IX). Pannus for formulation C was more severe than for A.

DERMAL IRRITATION

Minimal to moderate dermal edema and erythema at a high incidence was observed for the rabbits which received the positive control test formulation on each of the 3 test days. Dermal edema and erythema was not observed for the test sites receiving any of the benzoyl peroxide formulations or for the untreated control sites.

Table IX
Pannus for Rabbits After Single Topical Ocular Instillation of Benzoyl Peroxide 10 Per Cent

Test Formulation	Wash Time[c]		1 h	24 h	48 h	72 h	7 day	14 day	21 day
A	20 sec	$\bar{x}$[a]	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		Inc.[b]	0/6	0/6	0/6	0/6	0/6	0/6	0/6
A	5 min	$\bar{x}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		Inc.	0/6	0/6	0/6	0/6	0/6	0/4[d]	0/4
A	24 h	$\bar{x}$	0.0	0.0	0.0	0.0	0.7	1.0	0.7
		Inc.	0/6	0/6	0/6	0/6	2/6	3/6	2/6
C	20 sec	$\bar{x}$	0.0	0.0	0.0	0.0	1.0	1.0	0.0
		Inc.	0/6	0/6	0/6	0/6	3/6	4/6	0/6
C	5 min	$\bar{x}$	0.0	0.0	0.0	0.0	1.8	1.8	1.7
		Inc.	0/6	0/6	0/6	0/6	6/6	6/6	5/6
C	24 h	$\bar{x}$	0.0	0.0	0.0	0.0	1.7	1.5	1.3
		Inc.	0/6	0/6	0/6	0/6	5/6	5/6	4/6
Day 0 Controls	Day 0	$\bar{x}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		Inc.	0/6	0/6	0/6	0/6	0/6	0/6	0/6
Day 1 Controls	Day 1	$\bar{x}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		Inc.	0/6	0/6	0/6	0/6	0/6	0/6	0/6
Untreated Controls	—	$\bar{x}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		Inc.	0/6	0/6	0/6	0/6	0/6	0/6	0/6

[a]Maximum score = 2.
[b]Number of eyes with response/number of eyes in test group.
[c]Interval of time after dosing until eye was washed.
[d]Sacrificed in moribund condition on day 7.

PARTICLE SIZE DETERMINATION

Figure 2 demonstrates the various particle sizes which are observed under the Zeiss microscope. The range is shown in Table X. Particle size distribution varied between less than 20 μ to greater than 40 μ. A comparative study of particle size to a patch test undertaken in our clinic demonstrated that the larger particle size correlated with the greater amount of immediate type of irritation observed in Formulation C. However, some vehicle effects determined a late type of irritation, which will be described in the discussion.

DISCUSSION

The *acute oral LD50 in mice* for benzoyl peroxide 10 per cent (A) was 14 ml/kg. This oral LD_{50} is statistically equivalent to that of competitor products, C, D, and B, whose oral LD_{50} was 12, 10, and 12 ml/kg, respectively. Based upon the scale of Spector (8) and converting g/kg to ml/kg, benzoyl peroxide 10 per cent formulation has a rating of practically nontoxic. For an average 6-month-old 10 kg child, approximately 140 ml would have to be ingested before approaching the oral LD_{50} in this mouse study. For the average 70 kg adult, approximately 980 ml of benzoyl peroxide 10 per cent would have to be orally ingested before approaching the oral LD_{50} in this mouse study. Based

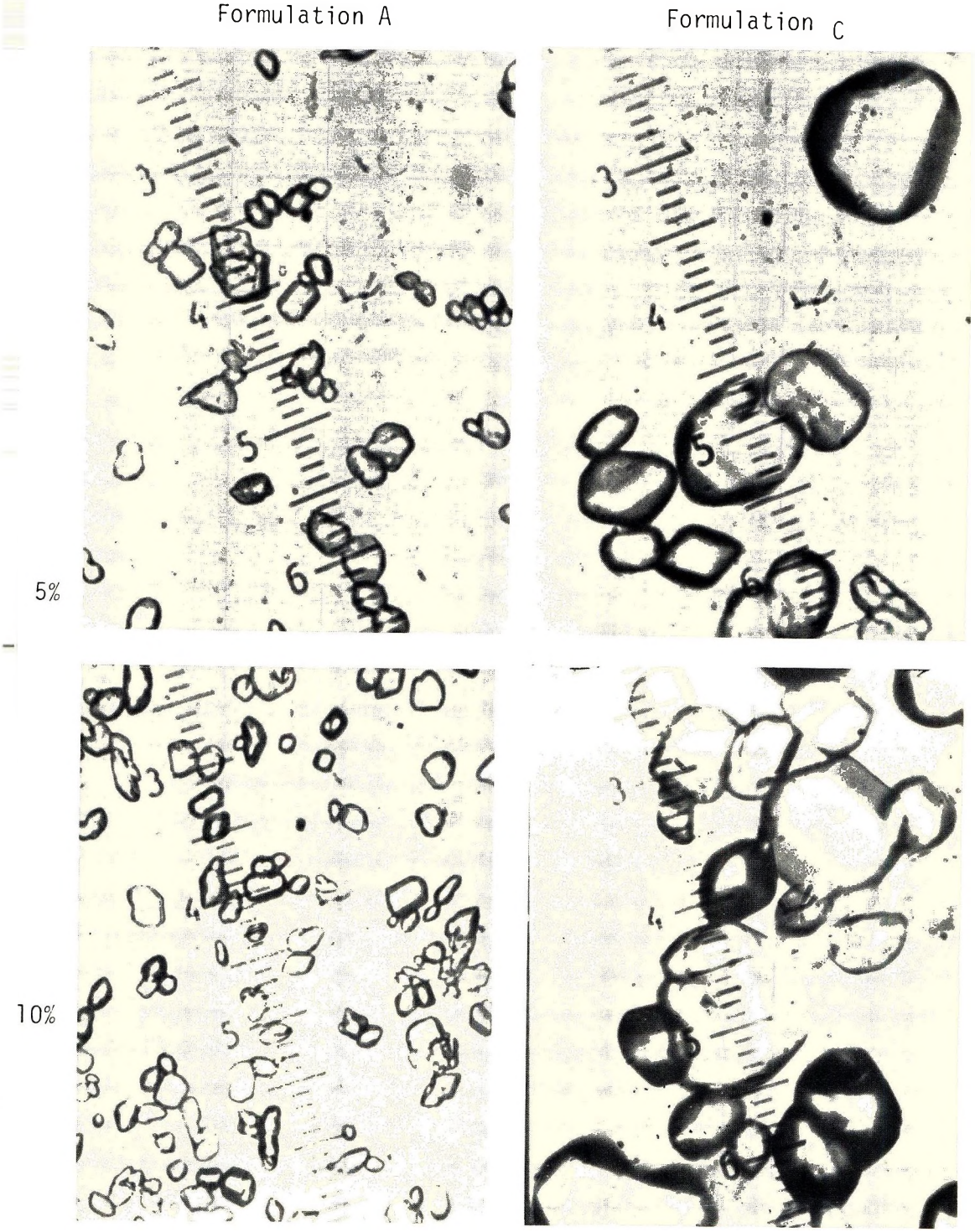


Figure 2. Representative particle size of various benzoyl peroxide formulations at 312.5 × magnification. Micron Scale illustrated.

Table X
Particle Size of Various BPO Formulations Per Cent

	Found in Different Formulations	
Particle Size (μ)	A	C
<20	90	50
>20, <40	10	40
>40	1	10

upon this acute oral toxicity study in mice, benzoyl peroxide 10 per cent is considered not to represent an acute oral hazard should accidental oral ingestion occur.

Topical ocular instillation of benzoyl peroxide 10 per cent (A) and marketed competitor products (C, D, and B) induced substantial ocular changes characterized by severe conjunctival congestion, swelling, discharge, minimal iritis and flare, moderate to severe corneal cloudiness, and evidence of pannus. These ocular changes are interpreted to be indicative of a test formulation which has a marked ocular irritation potential. Based upon these studies, it is concluded that precautionary labeling should accompany all benzoyl peroxide 10 per cent formulations. It is recommended that a precautionary statement state, "avoid contact with eyes and mucous membranes."

In the *dermal irritation* studies, 1 mortality occurred with formulation C and vehicle groups. It is not considered to be treatment related but related to the handling of the animals. Observed dermal irritation was minimal to none for all formulations.

Benzoyl peroxide 10 per cent A and C, D, and B induced comparable minimal dermal erythema during the 3-day dermal test, which is substantially less than that for the positive control. The positive control test formulation has been reported to cause dermal erythema and edema in experimental animals (9). This amount of dermal erythema observed for the benzoyl peroxide formulation is considered to be indicative of a low dermal irritation potential. Based on this rabbit study, it is concluded that benzoyl peroxide 10 per cent A has a low dermal irritation potential, equivalent to that for marketed competitor products, C, D, and B. It is also concluded that all benzoyl peroxide 10 per cent formulations do not represent an acute dermal hazard for intended clinical use.

The particle size relationships observed could be linked to observed increased ocular irritation. Particle sizes for benzoyl peroxide A, D, and B were of a lesser magnitude than for formulation C (Table X, Fig. 2).

In a clinical test, C was much more irritating in 24-h occlusive patch test. Surprisingly, one formulation D appeared minimally irritating (Grade 1) of all formulations initially, but produced a delayed response 48 h after removal of the patch. The significance of this response can be related to vehicle differences and is still under investigation.

The effect of benzoyl peroxide formulations on cutaneous bacteria has been reported to be most significant on anaerobes, which comprise about 98 per cent of *Corynebacterium acnes* (10). This reduction of anaerobes appear to be unrelated to free fatty acid (Table XI). Vehicles play an important part of optimizing the antibacterial properties

Table XI
Effect of Per Cent Benzoyl Peroxide Treatment on Cutaneous Bacteria[d]

		Mean Number Bacteria/ cm^2 (N = 16 to 19)	Mean Free Fatty Acid Control Per Cent
Before treatment			
	Anaerobes[a]	6.6123[b]±0.1107[c]	27.25±1.60
	Aerobes	4.8751 ±0.1392	
Treatment period			
3 days	Anaerobes	4.8813 ±0.1768	16.73±0.99
	Aerobes	3.8308 ±0.2010	
7 days	Anaerobes	4.8476 ±0.2046	14.30±1.16
	Aerobes	3.7820 ±0.2661	
14 days	Anaerobes	4.2918 ±0.2649	11.62±1.72
	Aerobes	3.5116 ±0.2455	

[a]*C. acnes* comprise about 98 per cent of the anaerobes.
[b]Numbers expressed as $\log_{10}$ values.
[c]Standard error of the mean. All treatment period vlaues are significant at $P<0.001$.
[d]Anderson *et al.* (10).

of benzoyl peroxide. Many vehicles contain polyoxethylene lauryl ether, which is known to enhance topical preparations because of its own surface-active and desquamating properties (11). It appears that possibly benzoyl peroxide formulations can be optimized so that even lower concentrations can be as effective as currently marketed strengths.

SUMMARY

In summary, several formulations of benzoyl peroxide have been evaluated for safety. One formulation had a trend toward greater ocular irritation potential which was related to larger particle size distribution (formulation C). No significant difference between formulation A and C was found among the acute toxicity or dermal irritation studies. Manufacturers of benzoyl peroxide formulation must be aware of differing responses that can be obtained dependent on formulation variables such as particle size, quality of raw materials, and manufacturing conditions.

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The electrostatic properties of human hair

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Synopsis

Three factors have been studied which are significant in the development of ELECTROSTATIC CHARGE on HAIR FIBERS: (1) the charge generated by separation between hair fibers and brush or comb; (2) the mobility of charge on the fibers; and (3) the distribution of charge along the fiber length. Instrumentation has been developed to measure each of these parameters, and the effect upon them of quaternary ammonium compounds and other fiber treatments.

Quaternary antistatic agents are found to reduce substantially the charge generated on the fibers; the half-life of charge mobility varies with the quantity of agent on the hair. The density of charge is greatest near the fiber tips, corresponding to the region of a peak in the combing force. It is concluded that the mechanism of action of these antistatic agents is primarily one of lubrication: a reduction in combing force leads to a reduction of static charge generated on the hair.

INTRODUCTION

While the phenomenon of static electrification, first recorded by the ancient Greeks, has intrigued physicists over the centuries, our knowledge and understanding of electrostatics as related to practical problems remains even today at an elementary level. Yet problems associated with the buildup of electrostatic charge on a body are of commercial importance in many industries. For example, static electrification has been of major concern to textile manufacturers and users, especially since the development of synthetic polymers, and, of course, to the plastics industry itself. In the hair-care industry, problems arise from static charges in brushed or combed hair, particularly at low humidity levels. The fibers are mutually repelled by these charges, thereby showing the phenomenon of "flyaway" which is unattractive and which makes hair hard to comb or to keep in place.

Substantial efforts have been made to develop means to ameliorate electrostatic problems. On human hair, cationic quaternary ammonium compounds are in common use for this purpose. Little is known of the mechanism of action of such antistatic agents, however, and in such circumstances it is difficult to develop improved materials.

Hypothetical reasoning led us to believe that 3 principal factors contribute to the severity of the "flyaway" of human hair. The first is the magnitude of charge which is generated by the contact and subsequent separation of hair and comb. The second factor is the mobility of charge and its rate of dissipation from the fibers. The third factor is the distribution of charge along the length of the combed fibers. In principle, the desired objective of reduced electrostatic effects can be approached by altering each one of these factors. Either a reduction in the magnitude of charge generated or an increase in the mobility of that charge can be effective. Mutual repulsion of fibers can also be altered by changing the distribution of charge density along the length of the fiber.

The generation of static charges when unlike objects are rubbed together arises from an unequal transfer of charges across the interface between two bodies in contact. When the bodies are separated, they are each left with net charges of opposite sign and of magnitude equal to the differential charge transferred. Theoretical aspects of this process are discussed by Vick (1), Arthur (2), and Hersh and Montgomery (3). The charge generated by rubbing filaments together has been studied experimentally by Hersh and Montgomery (4). Henry *et al.* (5) measured both charge magnitude and the rate of its decay from rubbed textile fabrics. Barber and Posner (6) measured the charge generated by combing human hair. Mills *et al.* (7) also attempted to measure the charge generated by combing hair, but the method employed did not permit a distinction to be made between generation and dissipation mechanisms.

The rate of dissipation of charge to electrical ground depends on the ease of movement of charges on the body, a property which we here call "charge mobility." A complementary phenomenon, the rate at which charge develops on the body in the presence of an electrostatic potential, is similarly determined by the charge mobility. Charge mobility is itself dependent primarily on the conductivity of the material (5,8). Shashoua (9) measured the rates of build up and decay of charge from films and fabrics. Ballou (10) measured decay rates from textiles; he also considered charge generated on moving yarns. Unfortunately, little information is available on the mobility of charge on human hair.

The distribution of charge along the length of a fiber, although noted by Ballou (10) as important, has received very little investigation. The only other discussion of such phenomena is by Sprokel (11), who studied the variation of charge along a running textile yarn.

In a published work, the relative importance of charge generation, mobility, and distribution to the incidence and control of electrostatic charges is rarely considered, and a clear distinction between them is not always drawn. Instrumentation has, therefore, been developed at these laboratories to study each of these parameters separately, on treated and untreated hair, with the intention of evaluating their relative importance and of elucidating the mechanism of action of antistatic agents on human hair.

EXPERIMENTAL

HAIR TRESSES: TREATMENT AND CONDITIONING

For the work reported here, virgin brown hair*was used. Test tresses were cut perpendicularly to a length of 20 cm and glued at the root ends to a plastic tab, on which the hair was spread over a width of 3.8 cm. The weight of hair in each tress was 1.3 ± 0.1 g.

In order to get reproducible results in charge mobility measurements, it was important to spread the hair uniformly over the 3.8 cm width of the tab. A mounting jig containing a fixed fine-toothed comb was employed to facilitate sample preparation; the hair fibers were spread evenly across the comb before being glued.

Before use, the tresses were cleaned with a solution of sodium lauryl sulfate, then rinsed thoroughly. When the effect of antistatic and other treatments was to be studied, these materials were typically applied as follows: 0.6 cc of the particular shampoo, creme rinse, or antistat agent was applied to the wet hair, worked in manually for 40 sec, rinsed in running tap water for 20 sec, and then air dried. All treatments discussed below were rinsed in this manner before being dried, unless otherwise specified.

As is well known, relative humidity is a critical variable in electrostatic experiments. All experiments were conducted in an environment controlled to ± 1 per cent RH at 23 ± 0.5°C. To avoid errors arising from the hysteresis in the water uptake of hair (12), tresses were always brought to equilibrium at the test humidity from a higher humidity level. It was found necessary to condition the hair for at least 40 h at the test humidity before making measurements, in order to obtain consistent results.

THE MEASUREMENT OF CHARGE GENERATED BY COMBING

The generation of electrostatic charge by the separation of 2 bodies is a notoriously variable procedure subject to considerable irreproducibility, and highly sensitive to test conditions such as surface contamination (13). For this reason, many workers have eschewed measurements of charge generation, preferring to determine electrical resistivity or charge mobility rates (8,9). Nevertheless, the process of charge generation is critically important, and it was considered essential that it be studied. A method was developed to measure the generation of charge under conditions simulating actual use, i.e., the combing of hair, with a procedure designed to control the variables as closely as possible.

The apparatus used is shown in Fig. 1. The hair tresses, comb, and Faraday cage were all enclosed in a humidity controlled box which was maintained at 23°C. Both tress and comb were carefully insulated from electrical ground during the combing operation, to ensure that no charge would be lost by conduction to ground before measurement. The tress was held in a polystyrene insulated grip while being combed, and the comb was mounted in a polystyrene handle. Some experiments were also performed with the comb grounded. Commercially available combs of various materials were used.

*DeMeo Brothers, New York, N.Y.

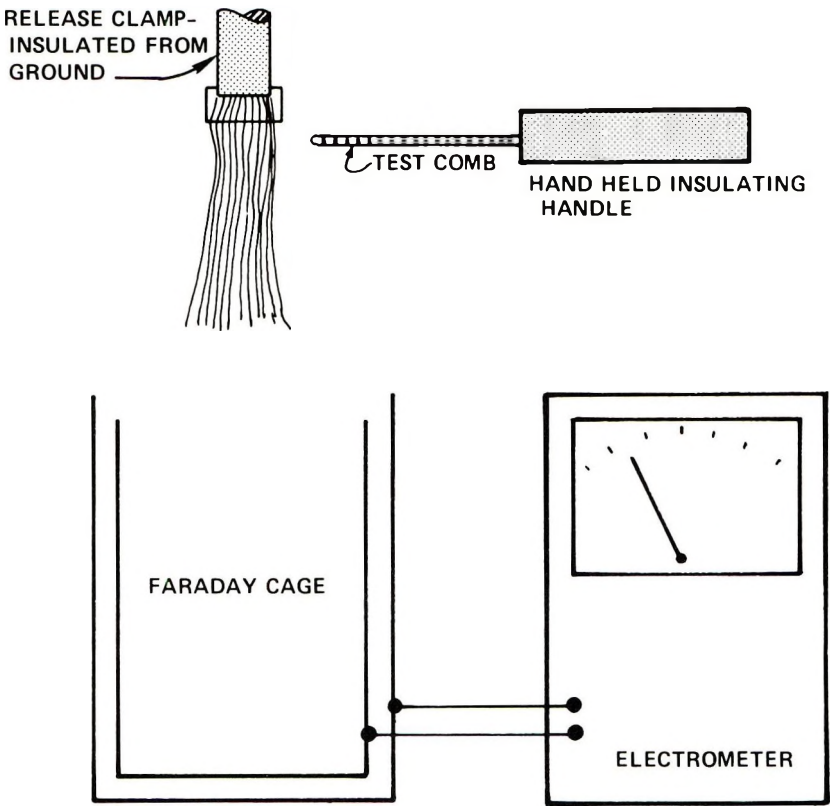


Figure 1. Apparatus used to measure electrostatic charges generated on hair tresses by combing

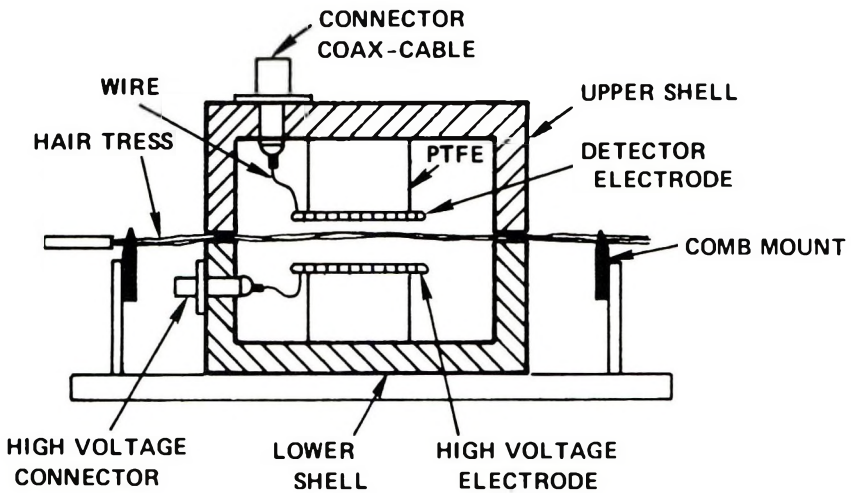
Residual charges on the tress were first removed by exposure to a radioactive polonium deionizer. The tress was hand combed for the requisite number of strokes with the insulated comb. Charge was then measured by releasing the tress from the polystyrene-insulated grip and depositing it in a Faraday cage, which was connected to an electrometer.* The capacitance of the Faraday cage and connecting cables was 100 pF, which was negligible compared to the capacitance of the electrometer. The charge Q on the tress could, therefore, be read directly from the electrometer scale.

The principle sources of error were variations in the relative humidity, variations between replicate tresses, and the irreproducibility of hand combing. For accurate measurements, 3 to 5 replicate tresses were used, with 5 successive determinations on each tress. In this way the charge Q could be determined with a 95 per cent confidence interval of ± 15 per cent.

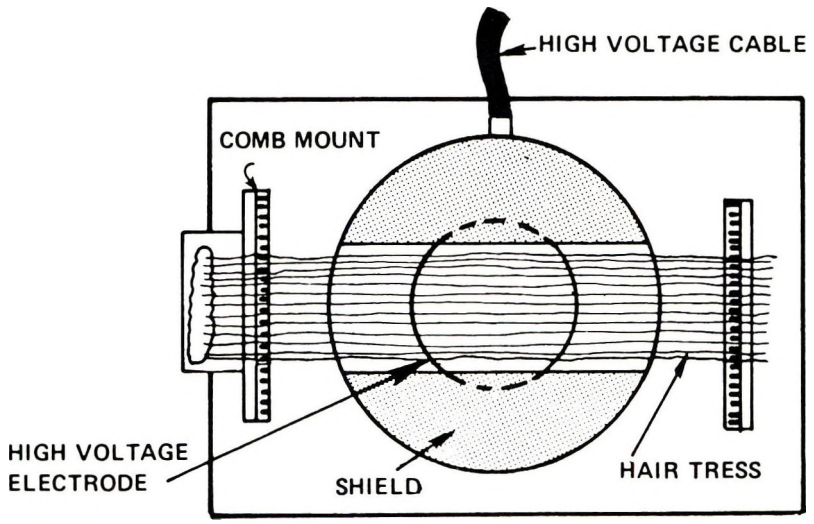
THE MEASUREMENT OF CHARGE MOBILITY ON HAIR

The mobility of electrostatic charge on a body can be characterized by the rate at which charges build up on and decay from it. The half-life of charge induction, τ^C, is the time

*Model 610 BR, Keithley Instruments, Cleveland, OH.



(a)



(b)

Figure 2. Faraday shell apparatus for measurement of charge mobility, with hair tress in position: (a) side view; (b) exposed top view (upper shell removed)

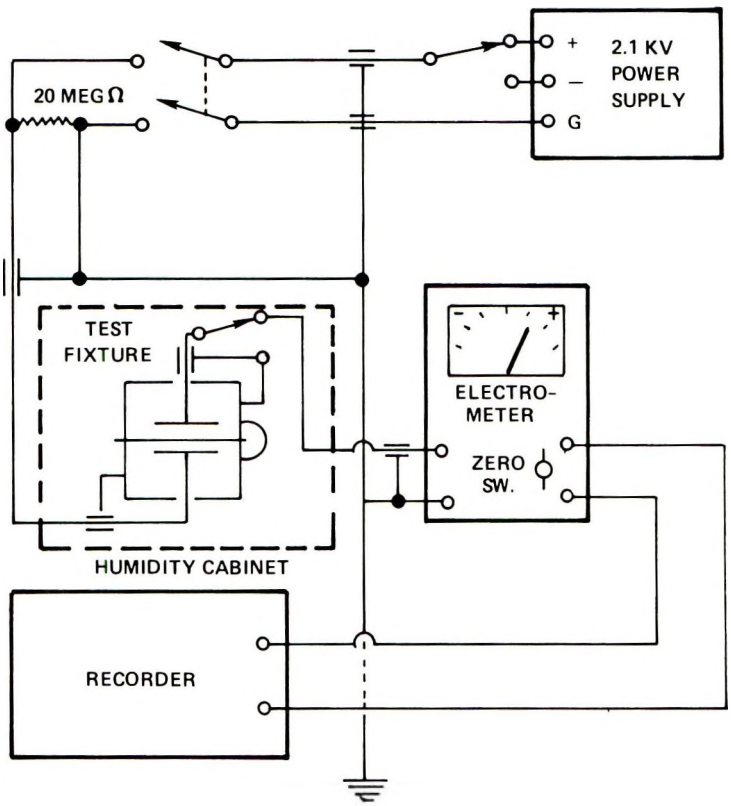


Figure 3. Wiring diagram for charge mobility measurements

required for charge to build up to one-half of its equilibrium value when the body is exposed to a high potential. The half-life of charge decay, τ^D, is the time taken for charge to diminish to one-half of its initial value when the charged body is connected to electrical ground. A perfect conductor charges and discharges instantaneously, and, therefore, has a charge mobility half-life of zero. Charges on a perfect insulator, however, are immobile, and the half-life is infinite in such a material. Poor insulators such as human hair have finite half-lives which vary widely with surface condition and with relative humidity.

The experimental procedure used in this work for the measurement of charge mobility is a modification of an ASTM method for the determination of charge mobility on flexible plastic films (14). The apparatus is shown schematically in Figs. 2 and 3. The principle of operation is as follows. The fibers of the hair tress, connected to electrical ground at each end, are charged by induction from a high voltage electrode. The charge on the hair is monitored by a detector electrode. The rate at which charge builds up is characterized by the half-life of charge induction. When the high voltage source is removed, the charge on the hair diminishes to zero at a rate characterized by the half-life of charge decay. The basic principle of the method is similar to that used by Shashoua (9) with the exception that in his case the specimen was charged directly, whereas, in the present procedure, it is charged by induction and thereby, acquires a charge of polarity opposite to that of the voltage source.

The test fixture, which we call here a Faraday shell, was constructed according to the ASTM description. The apparatus consists of 2 cylindrical brass shells, 10 cm in diameter. Each cell contains an electrode 5 cm in diameter which is insulated from ground by a polytetrafluoroethylene (PTFE) spacer. The electrodes are recessed 0.6 cm from the plane of the specimen. The walls of the fixture are grounded and are heavy to provide good electrical contact with the sample. The Faraday shell and the hair tresses under test were placed in a chamber of controlled relative humidity at 23°C.

Safety interlocks, which disconnect the high voltage source, were contained in a box which covered the test fixture. This ensured that the high voltage supply could not deliver a lethal shock to the operator.

The hair tress was spread uniformly over a 3.8 cm width by inserting the tress at the plastic tab end in one of the combs mounted adjacent to the shells. A hand-held comb was inserted behind the fixed comb and pulled across the shell; the tress was then affixed in the comb on the opposite side. The final position of the tress is shown in Fig. 2. The combs were used solely as a guide for specimen mounting, and were *not* used to generate charge on the tress. Any residual charges on the specimen after mounting were removed with a radioactive deionizer before closing the shells together.

In addition to the provision of combs adjacent to the Faraday shell for mounting the specimen, the other important modification of the ASTM procedure was the partial enclosure of the bottom shell; this shell was covered with a thin brass sheet with the exception of a 4 cm width in which the specimen was mounted (Fig. 2). The purpose of this modification was to shield the detector electrode in the upper shell from stray fields of the charging electrode leaking around the specimen.

In operation, a potential of $\pm$ 2100 V is applied to the electrode in the lower shell by a high voltage source at time zero. The upper detector electrode is used to monitor the electrostatic field potential, and is connected to an electrometer and chart recorder (see Fig. 3). At time zero, the detector electrode instantaneously charges by induction to a potential opposite to that of the charging electrode. Since hair is not a perfect conductor, the charge initially induced on the hair is zero. Charge builds up on the hair by induction at a finite rate; this charge has a polarity opposite to that of the high voltage source. Since the total charge within the Faraday shells is zero from Gauss' Law (15), the charge on the detector electrode decreases correspondingly. When the hair is fully charged, the charge on the detector electrode falls to zero.

The output of the chart recorder during this process is shown in Fig. 4, together with a representation of the state of charge on the hair and on the two electrodes as the hair is charged and discharged. The charge, $Q(t)$, on the hair at time t is related to the voltage, $V(t)$, on the detector electrode as follows:

$$\frac{Q(t)}{Q_0} = 1 - \frac{V(t)}{V_0} \tag{1}$$

during charging, and

$$\frac{Q(t)}{Q_0} = -\frac{V(t)}{V_0} \tag{2}$$

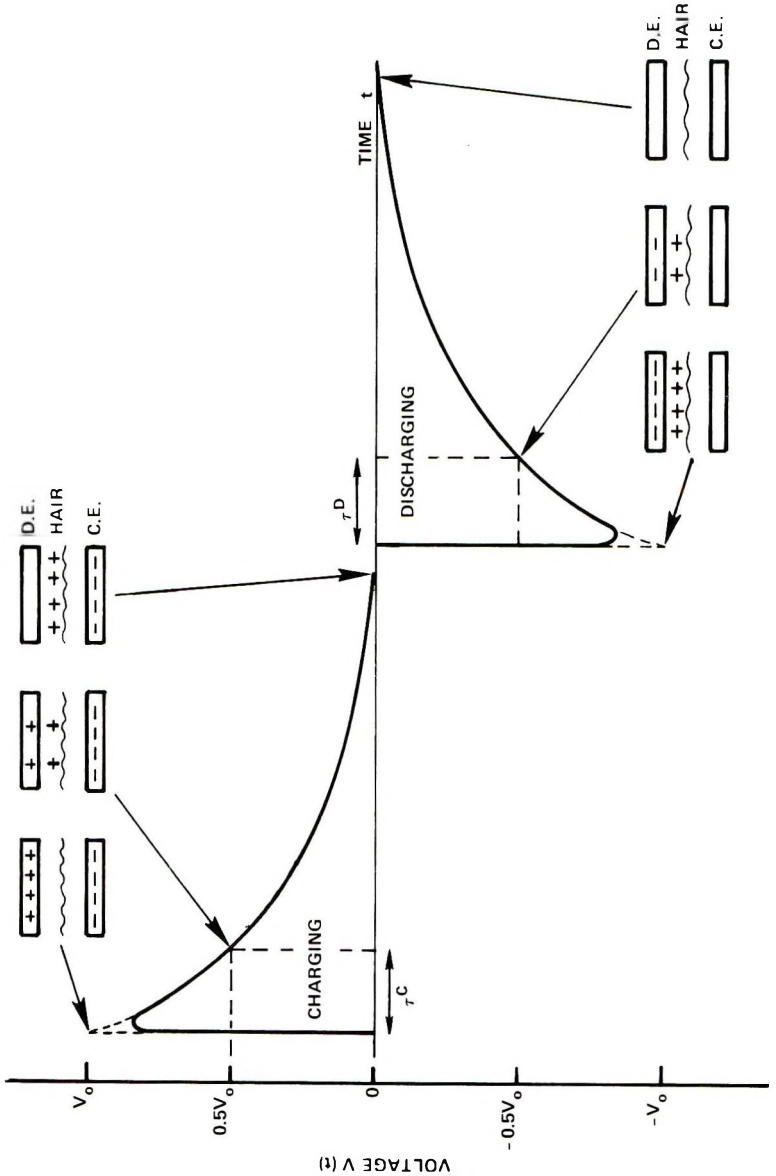


Figure 4. Voltage on detector electrode V(t) during charging and discharging of the hair (schematic). State of charge on charging electrode (CE), hair fibers, and detector electrode (DE) at various times is also shown

during discharging. Q_0 is the charge on the hair when fully charged.

The initial voltage V_0 induced on the detector electrode is not accurately recorded by the recorder pen because of inadequate response time. V_0 is therefore determined in a separate experiment in which no specimen is present. The half-life for charge induction τ^C is determined from the recorder trace as shown in Fig. 4.

To measure decay of charge from the fully charged hair, the charging electrode is disconnected from the high voltage source, and connected to ground. The charge on the detector electrode then becomes equal and opposite to that on the hair, since the total charge in the enclosure must remain zero. The half-life for charge decay τ^D is determined from the discharge curve of the detector electrode (Fig. 4). For all measurements, the electrometer output must be corrected for drift. Other experimental details and precautions are described in the ASTM procedure (14).

Four separate determinations of τ were made on each hair tress: both charging and discharging, each with both positive and negative charges induced on the hair. The half-life was calculated as a root mean square value, following general practice (9). With 3 replicate tresses, τ_{RMS} of the 4 determinations could be obtained with a 95 per cent confidence limit of ± 25 per cent.

THE MEASUREMENT OF CHARGE DISTRIBUTION ALONG THE HAIR FIBERS

An apparatus was devised to measure the variation of charge generated along the length of hair fibers as they are combed. The system is shown in Fig. 5. The hair tress is attached at the tab end to the cross-head of an Instron testing machine.* It is inserted in a lower test comb of hard rubber, and passes also through an upper metal comb which is grounded. A cylindrical brass detector electrode, on the inside of a glass cylinder, surrounds the specimen above the rubber comb. A brass shielding electrode which is connected to ground surrounds the outer surface of the glass cylinder. Grounded guard electrodes are placed adjacent to the inner detector electrode. The aluminum comb also acts as a guard electrode. The inner electrode is connected to an electrometer and chart recorder.

When the hair tress is pulled through the apparatus, charge is generated on the fibers as they pass through the lower comb. The charge on that part of the fibers which is immediately above this comb is sensed by the detector electrode. The guard electrodes and the upper metal comb serve to screen charges on the rest of the hair tress from the detector electrode. A fiber length of 1.9 cm is sensed by the detector electrode. By recording the electrometer output as a function of time as the hair is pulled through the combs, the variation of charge along the length of the hair is obtained.

The force required to pull the tress through the comb can also be recorded on the Instron. Because of interference from the metal comb which is present for measurements of charge distribution, however, force measurements were made in a separate experiment in which the metal comb was removed from the apparatus.

*Model 1125, Instron Corp., Canton, MA.

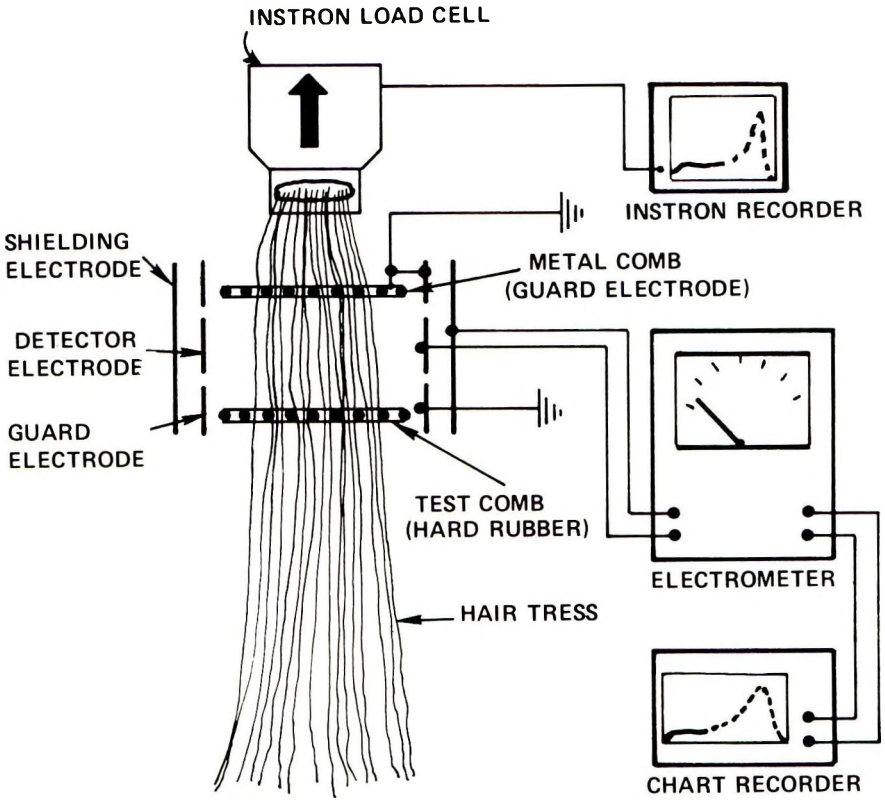


Figure 5. Apparatus used to measure distribution of charge density along length of hair as it is combed

RESULTS

CHARGE GENERATED BY COMBING

The charge generated on the hair by combing was found to be of positive sign, for typical hair treatments and for all comb materials examined. This finding is consistent with two factors. First, keratin is at or near the positive end of the tribolectric series (9), meaning that when it is rubbed against other materials which are lower than keratin in the series, a positive charge is developed on the keratin. (It is possible by certain treatments to alter the position of keratin in the tribolectric series (16)). Second, when 2 bodies are rubbed together under conditions where the bodies contribute unequal areas to the rubbing surface, the body which contributes the larger area tends to develop a positive charge (17). When hair is combed, it is the hair which contributes the larger area of contact.

The magnitude of charge generated Q varied with the comb material and with the number N of manual comb strokes applied to the tress, as shown in Fig. 6. The slope of the curve with nylon and hard rubber combs is consistent with the findings of Barber and Posner (6) who used a polystyrene comb. These comb materials are very poor conductors, and the results show an increase of charge with each successive comb stroke,

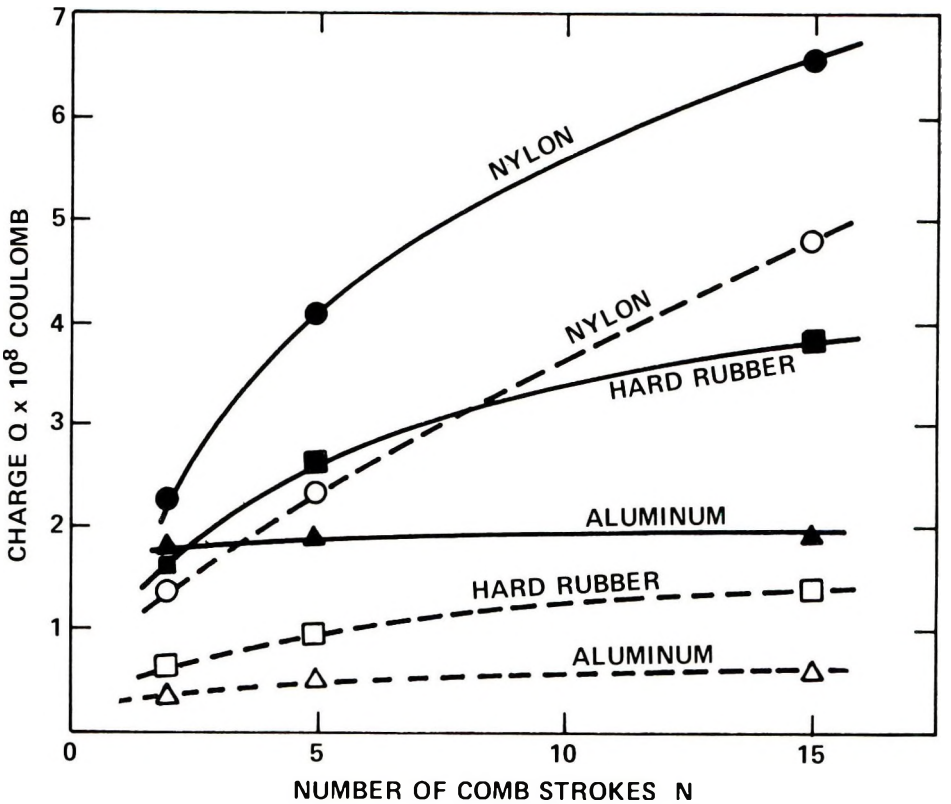


Figure 6. Charge Q generated by combing hair tresses with N manual comb strokes, with various comb materials, at 50 per cent RH (———) untreated hair; (- - - - -) hair treated with creme rinse A

with an eventual saturation level. When an aluminum comb is used, however, there is very little increase in charge on the hair with successive comb strokes.

We hypothesize that the conductive comb acts as a sink for charges. On the first comb pass, the comb becomes negatively charged; the hair positively charged. As the comb is passed again through successive increments of the charged hair, mobile charges on the conductive comb neutralize the charge on the hair, which then recharges to its original level when the comb leaves each increment of the hair. This does not occur with non-conducting combs because of their low charge mobility; in this case, charges on the hair are only partially neutralized on additional combing strokes, so that the total charge increases with each pass of the comb. Saturation is reached when the charge density on the comb reaches a certain level.

The magnitude of charge generated with various comb materials was found to increase in the order

$$\text{aluminum} \leqslant \text{hard rubber} < \text{nylon}$$

at all humidity levels examined (20 to 50 per cent RH) and with all hair treatments tested.

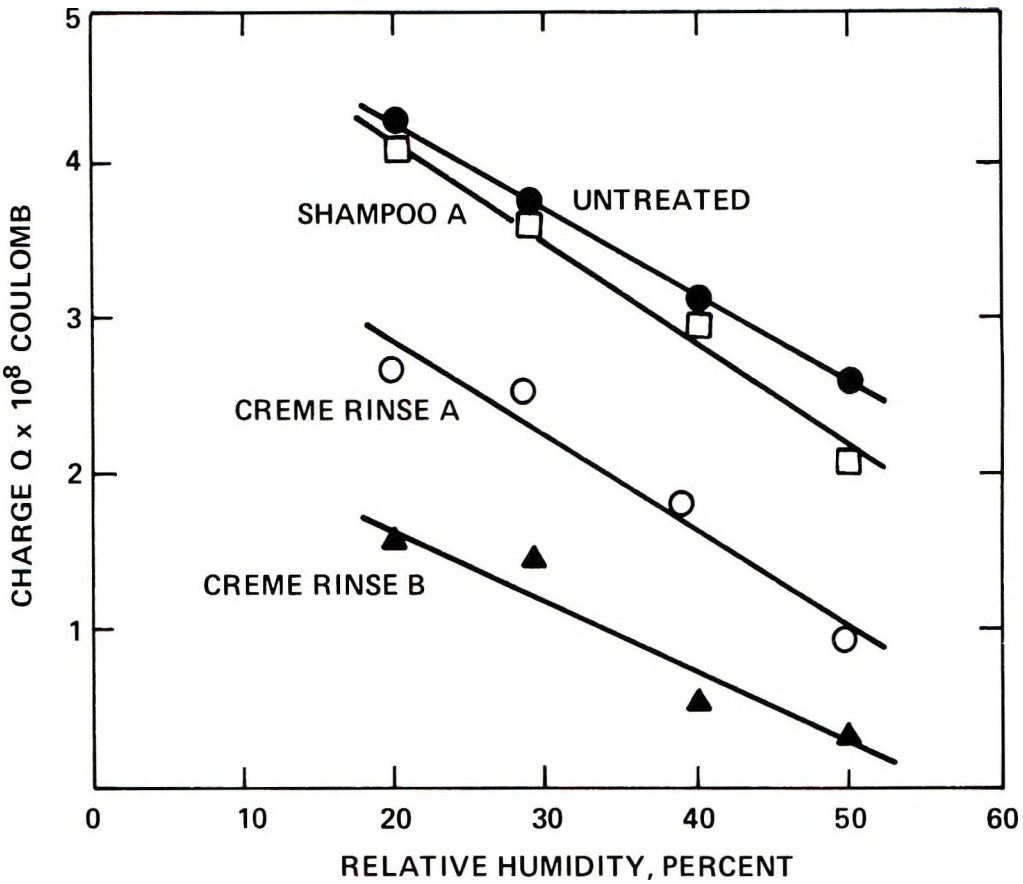


Figure 7. Variation of charge generated on hair tresses with relative humidity. Five comb strokes, hard rubber comb

Data for hair treated with a commercial creme rinse formulation containing a quaternary ammonium compound are shown in Fig. 6, as well as data for clean untreated hair. The formulation is particularly effective in reducing the value of Q when hard rubber and aluminum combs are used.

The magnitude of charge generated was unaffected by grounding the comb, even with the metal comb. This is, in fact, to be expected, since the charge arises from separation of the two objects (hair and comb). Grounding the comb merely dissipates the charge on the comb (if the comb is a conductor); the charge on the hair is unaffected. Grounding the hair, on the other hand, would cause the charge on the hair to dissipate at a rate related to its charge mobility half-life, so that the charge measured would vary with the elapsed time between combing and measurement of the charge. It is for this reason that the hair was always insulated from ground in these tests.

The charge generated varies greatly with the relative humidity. It was found to decrease linearly over the range 20 to 50 per cent RH, as shown in Fig. 7. A similar finding was reported by Barber and Posner (6) over the range 30 to 70 per cent RH.

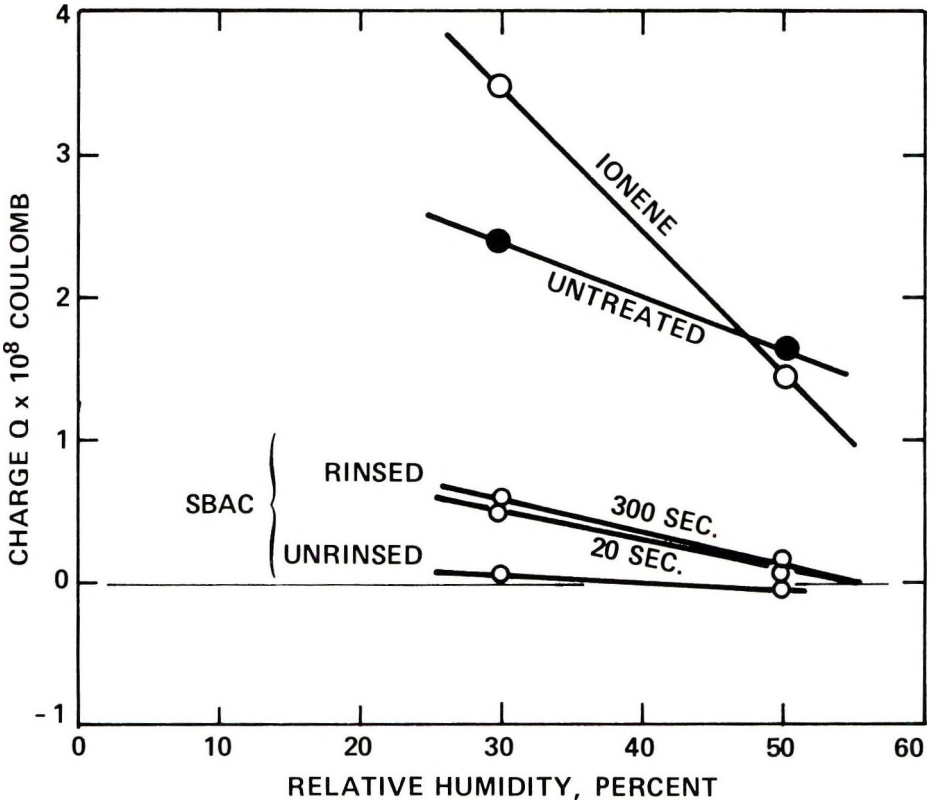


Figure 8. Variation of charge generated on hair tresses with relative humidity. Two comb strokes, hard rubber comb. SBAC: stearyl dimethyl benzyl ammonium chloride

We may write the empirical relationship valid over these ranges of humidity

$$Q(RH) = Q(0) - \alpha \cdot RH \tag{3}$$

where RH is the relative humidity, Q(0) is the charge generated at zero per cent RH, and $-\alpha$ is the slope of the plot of Q(RH) versus relative humidity. In routine testing, therefore, it was only necessary to make measurements at 2 humidity levels; 30 and 50 per cent RH were selected as convenient for this purpose.

It is essential to evaluate the effect of relative humidity in order to obtain an accurate measure of antistat performance. Although treatments which reduce the static charge generated on hair generally give results which are superior to untreated controls at all humidity levels, some materials were found to have an antistatic effect on hair at high humidities, but gave results worse than untreated hair at low humidities. An example is the ionene polymer $\left[N^+(CH_3)_2 \cdot CH_2 \cdot CHOH \cdot CH_2\right]_n$ n Cl^-, as shown in Fig. 8. This material has quaternary ammonium ions in the main chain of the polymer.

The amount of antistatic agent on the hair affects the magnitude of charge generated. Hair was treated with stearyl dimethyl benzyl ammonium chloride (SBAC) by immersion in a 3 per cent aqueous solution. When allowed to dry without being rinsed, so that a relatively large quantity of material remained on the hair, the charge generated

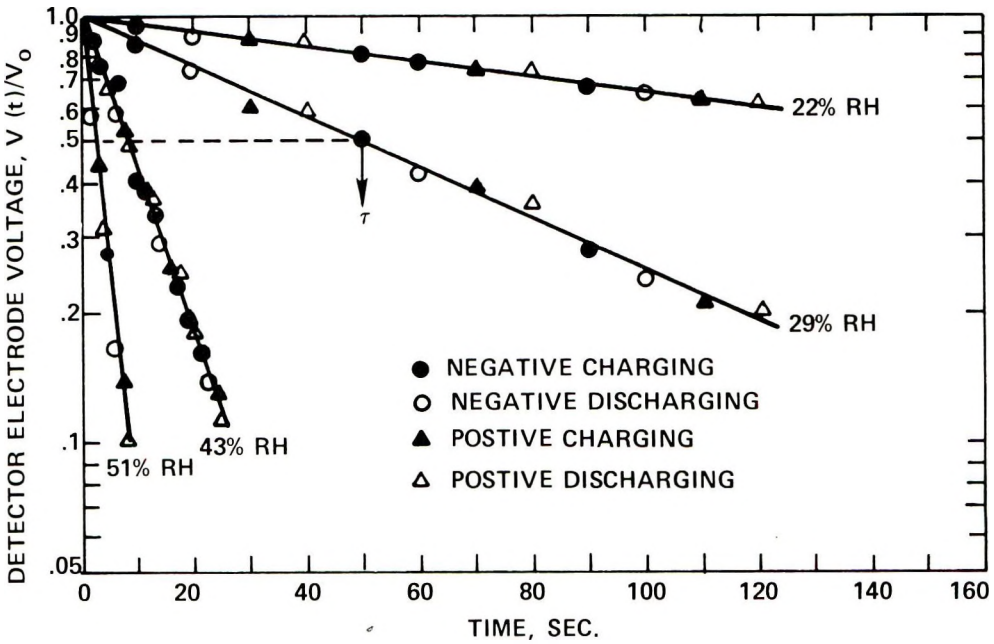


Figure 9. Charge on untreated hair during charging and discharging, as shown by relative voltage on the detector electrode. Charging potential: 2100 V

was essentially zero (Fig. 8). When rinsed under a running tap for 20 or 300 seconds before drying, however, the charge generated by combing increased to finite but still small values (Fig. 8).

CHARGE MOBILITY

When a tress of hair, which is insulated from electrical ground, is charged by combing, the charge will remain on the hair indefinitely. This was confirmed by an experiment in which a combed tress was suspended in a Faraday cage by a PTFE thread, with care taken to ensure that the tress did not touch the Faraday cage. The charge on the hair was found to remain constant with time. (Partial discharge by dielectric breakdown of the atmosphere may occur, if the charge density on the hair is such that the dielectric strength of air is exceeded. The loss of charge would occur instantaneously upon combing, and would not be detected by this experiment.)

When a charged tress is connected to electrical ground, the charge will decay. In the case of hair on the head, the scalp and body effectively act as a ground, because of their large capacitance relative to that of the hair. The rate of decay depends on the mobility of charges on the hair.

Charge mobility was measured by the Faraday shell apparatus described above, in which the hair tress was charged to and discharged from a potential of 2100 V. The charge Q(t) on the hair was monitored by the voltage V(t) on the detector electrode.

In Fig. 9, the detector electrode voltage is shown as a function of time, for untreated hair at various humidity levels. Charging and discharging data, for both positive and

negative applied potentials, are plotted.

The linear relationship between log V(t) and time in Fig. 9 confirms that the charge builds up and decays exponentially, as found by Wilson (8), Shashoua (9), and Ballou (10). We can characterize the process by the equations

$$Q(t) = Q_0 \left[1 - \exp\left\{-\frac{t \ln 2}{\tau^C}\right\}\right] \tag{4}$$

during charging, and

$$Q(t) = Q_0 \cdot \exp\left\{-\frac{t \ln 2}{\tau^D}\right\} \tag{5}$$

during discharging, where Q(t) is the charge on the hair at time t, Q_0 is the equilibrium charge, τ^C is the half-life of charge induction, and τ^D is the half-life of charge decay.

In this work, no systematic difference was found between values of τ for positive and negative charges, nor between values for charging and discharging. This is shown by the superposition of the four curves at each humidity level in Fig. 9, and a similar result was obtained for all hair samples examined, at all humidity levels, whether treated with antistatic agents or not. We, therefore, computed the root mean square half-life as follows:

$$\tau_{RMS} = 1/2\,[(\tau_+{}^C)^2 + (\tau_+{}^D)^2 + (\tau_-{}^C)^2 + (\tau_-{}^D)^2]^{1/2} \tag{6}$$

Our findings contrast with those of Shashoua (9), who found that τ_+ was generally not the same as τ_- in textile fabrics and films, and that τ^C and τ^D were also unequal when the voltage exceeded 2000 V. Shashoua attributed the inequality of τ^C and τ^D to ionization of the atmosphere. As discussed above, we found no such effect in this work.

The logarithm of τ_{RMS} varies linearly with relative humidity, over the range 20 to 50 per cent RH (Fig. 10). Shashoua (9) obtained a similar result for textile fibers and plastic films, over the range 15 to 65 per cent RH. Following this, we may write within these ranges

$$\tau_{RMS} = \tau_0 \exp[-\beta \cdot RH] \tag{7}$$

where $-\beta$ is the slope of the line, and τ_0 is the extrapolated half-life at zero per cent RH. Because of this linearity, experiments were routinely conducted at only two humidity levels (30 and 50 per cent) in this test also.

Conventional shampoos and some creme rinses do not change τ from its value for untreated hair; other creme rinses reduce τ significantly (Fig. 10). The level of agent remaining on the hair has a large effect on the half-life. The quaternary ammonium compound SBAC, when not rinsed off the hair before drying, reduces τ to very low values. When it is rinsed off before drying, however, the half-life of the hair is little different from that of untreated controls (Fig. 11). This is consistent with the findings of Sprokel (11) and Steiger (18), who showed that the surface conductivity of textile fabrics and yarns increases with the quantity of antistatic agents on the fibers. When the quaternary compound SBAC is rinsed off hair before drying, only small quantities remain on the fiber, so that the resistivity and hence the half-life are high.

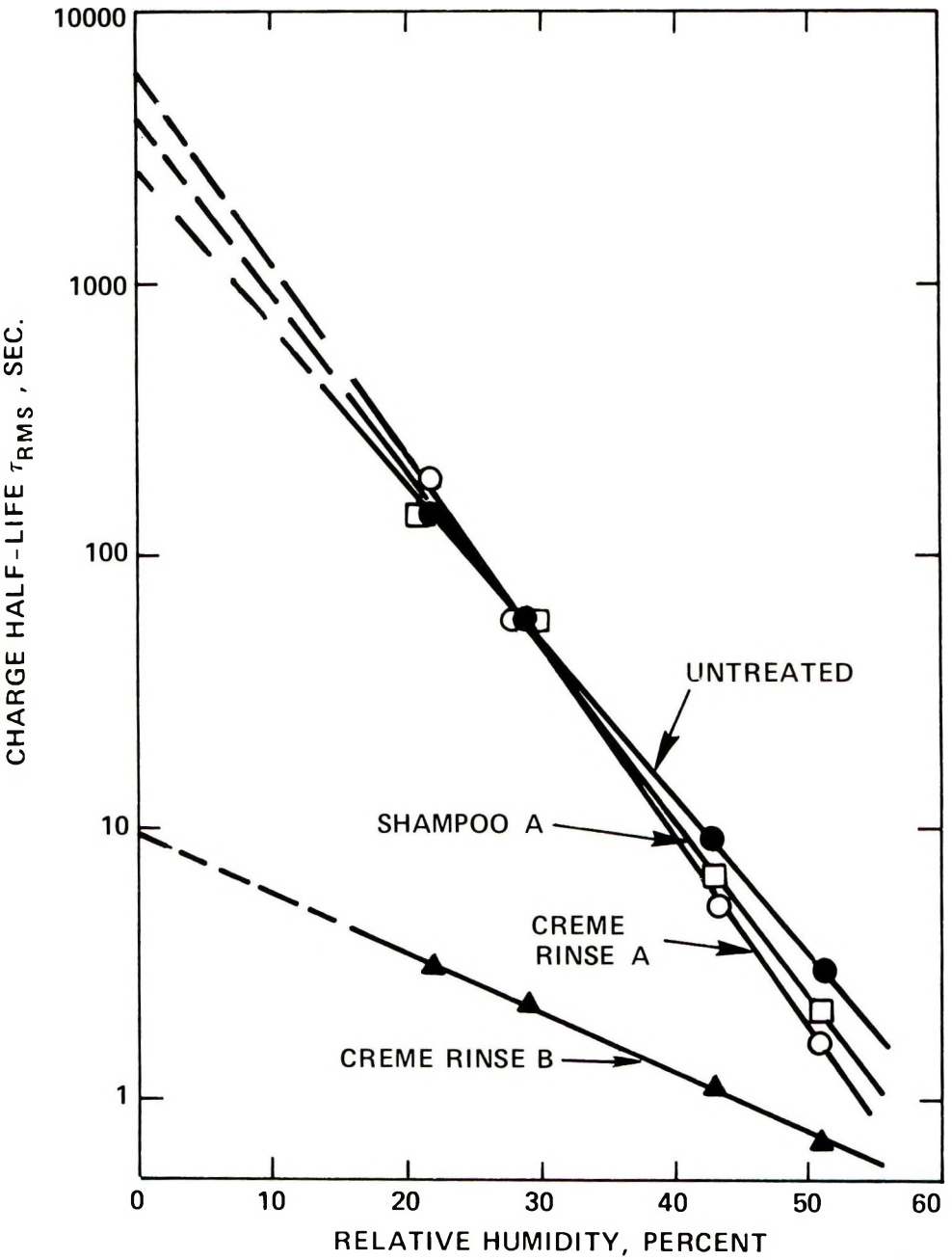


Figure 10. Variation of charge mobility half-life τ_{RMS} of hair tresses with relative humidity. Charging potential: 2100 V

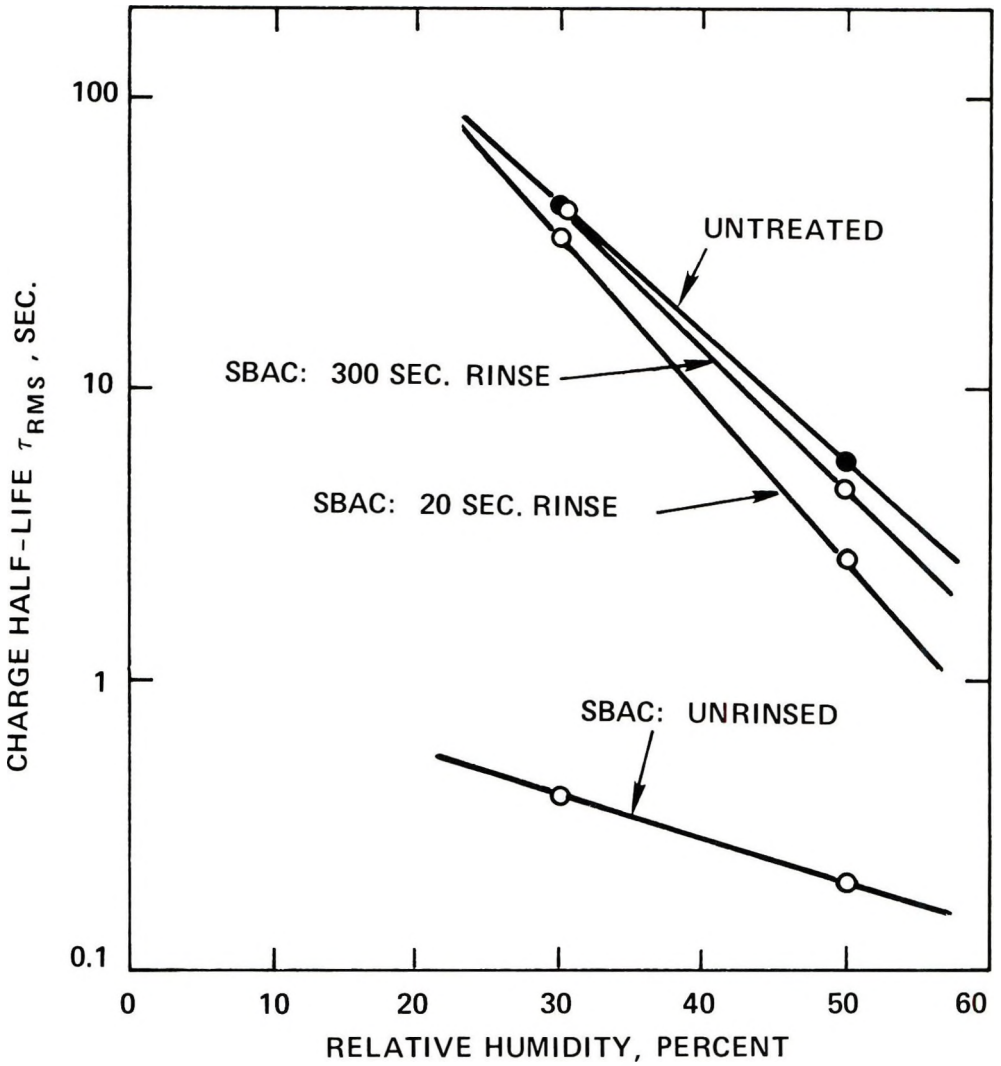


Figure 11. Charge mobility half-life τ_{RMS} of hair tresses. Charging potential: 2100 V

CHARGE DISTRIBUTION ALONG THE HAIR FIBERS

The variation of charge density q(x) along the length x of a dry hair tress as it is combed was measured with the apparatus shown in Fig. 5. Some results are shown in Fig. 12 (upper graph). A clean untreated tress develops some charge all along its length, but there is a substantial increase in charge generated as the comb passes through the final few centimeters of the hair fibers. Hair treated with a commercial creme rinse formulation which was rinsed 20 sec before drying shows a similar curve, but the end peak in q(x) is much lower in this case (note the different ordinate scale for this curve). When the creme rinse is not rinsed before drying, the charge generated is essentially zero.

The load p(x) required to pull the hard rubber comb through the dry tress shows a pronounced end peak force, which is likewise reduced substantially by the creme rinse

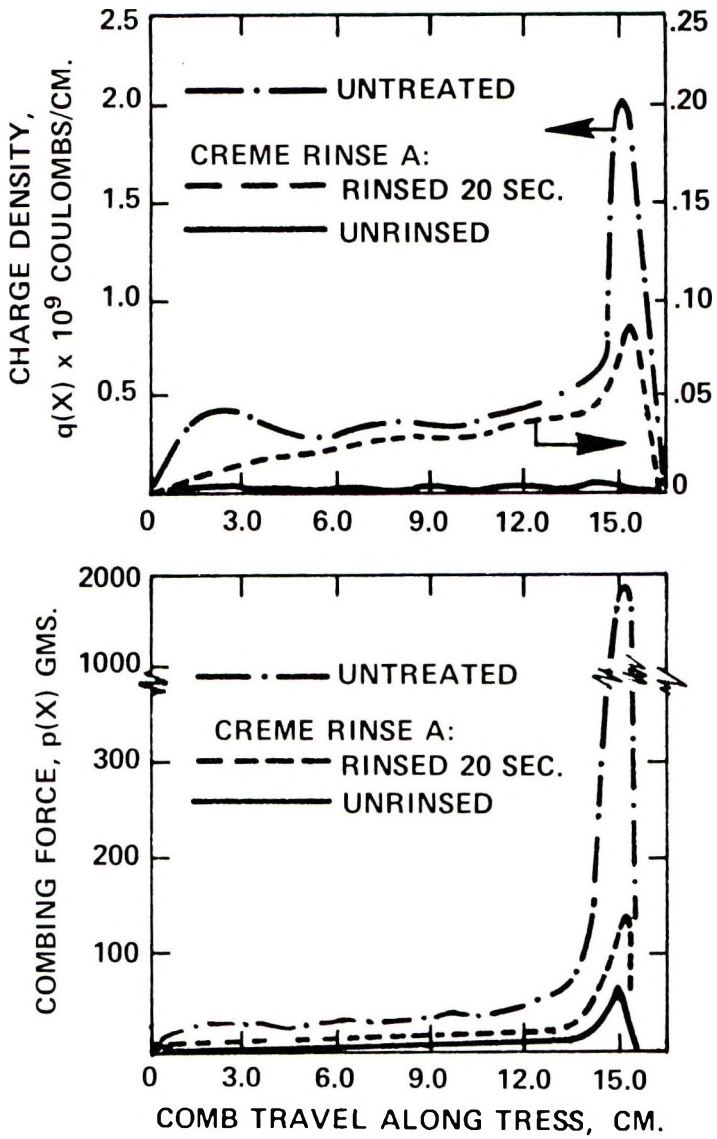


Figure 12. Variation of charge density q(x) (upper graph) and of combing force p(x) (lower graph) along the length x of a hair tress as it is combed. Relative humidity 50 per cent. Hard rubber comb. Combing velocity 1.7 cm/sec

treatments (Fig. 12, lower graph). The end-peak force has been described by Tolgyesi (19) and he has attributed this to an accumulation of tangling between the fibers near the free fiber ends. The effect is not eliminated by precombing or by parallelizing the fibers.

The explanation for the rise in generated charge in the final portion of the comb pass is not hard to find. It has been shown by many workers that the amount of charge generated when two bodies are rubbed together increases with the normal contact force between them (4,11,20,21,22). The effect arises from the increase in real area of

contact with normal force; the charge generated depends on the real area of contact. Now the combing force increases in the last few centimeters of the hair tress, because of tangling. The normal contact force between hair and comb is, therefore, increased, and so the amount of charge generated in this region of the hair fibers is increased.

THE MECHANISM OF ANTISTATIC AGENTS

By an examination of the available experimental evidence for the 3 properties measured—the magnitude of charge generated by combing, the mobility of charge on the fibers, and the distribution of charge along their length—we can now consider the mechanisms of static electrification of hair, and of the action of antistatic agents.

The charge generated by combing and the half-life of charge mobility both decrease with increasing relative humidity (Figs. 7, 8, 10, 11). The increased charge mobility is clearly a consequence of the greater water content at higher humidities, although the exact relationship is not well understood and other factors are also involved (23). Increased mobility of charges on the fiber leads to a decrease in the charge generated by combing, because of charge conduction along the fibers as they are rubbed, and this mechanism has been postulated to explain the decrease of generated charge with increasing relative humidity (3).

When a large concentration of a quaternary ammonium compound is present on the hair fiber, the surface conductivity is substantially increased, as evidenced by the very low half-life of charge (Fig. 11, SBAC, unrinsed). The negligible charge generated under such circumstances (Fig. 8) can be explained by this high conductivity, by the mechanism of charge conduction along the fibers. However, when the quaternary is rinsed off with water before drying, so that only small quantities remain on the fiber, the charge generated by combing remains relatively low (Fig. 8), even though the charge half-life increases substantially and is comparable to that of untreated fibers (Fig. 11). The commercial creme rinse A also has relatively low generated charge (Fig. 7) in spite of a high half-life (Fig. 10). The reduced charge generated with these materials, therefore, cannot be explained by a mechanism of enhanced surface conductivity. An alternative mechanism must be sought.

We hypothesize that the reduction of charge generated by combing, when hair is treated with quaternary ammonium compounds, is primarily due to the lubricating properties of these compounds on the dry hair, rather than to enhanced conductivity. The quaternary acts as a lubricant and reduces tangling, so that the force required to pull a comb through the hair is substantially reduced, especially the end peak force (work in these laboratories not reported here). A creme rinse containing the quaternary SBAC and other ingredients has a similar effect (Fig. 12, lower graph). The reduced normal contact force between hair and comb leads to a reduced charge on the hair (Fig. 12, upper graph) because of a smaller true area of contact between comb and hair.

Medley (20) has postulated that an antistatic agent need not be present as a continuous film in order to be effective. A discontinuous film would not give long-range conductivity and, therefore, the half-life of charge mobility would remain high. Medley proposed a mechanism requiring only localized conductivity at the contact site. This

mechanism could be acting as a secondary effect in the antistatic materials discussed here. Another secondary effect could be a change in the chemical nature of the fiber surface, which would alter the magnitude of charge generated. We believe, however, that the reduction of combing force by lubrication is the primary mechanism involved, as evidenced by the substantial effects on end-peak force and charge shown in Fig. 12.

The loss of charge by conduction to ground (the scalp) is not generally a significant contributor to reduced static in hair. Clean hair, and hair treated with most agents examined, has a charge half-life in excess of 10 sec, except at higher humidities (Figs. 10 and 11). This is too long for there to be a significant dissipation of charge in the few seconds between combing and the observation of troublesome static effects by the consumer. At higher humidities (above 60 per cent RH) the half-life drops to 1 sec or less. Here the dissipation of charge to electrical ground (the scalp) is rapid enough to be effective, but at these high humidities the charge generated (Figs. 7 and 8) is smaller in any case. The high charge mobility will also enable the concentration of charges near the fiber tips, produced by combing (Fig. 12), to be reduced by a redistribution of charge along the length of the fiber.

It is sometimes thought that difficulty in combing (high combing forces) is due to the generation of static charges on the hair. This is erroneous. The end peak force is observed even at high humidities or in the presence of static eliminators (19). Rather, the reverse is true; it is the normal force between comb and hair fibers which gives rise to static charges. A possible source of confusion is that there can be a secondary interaction between combing force and static charge, which can increase the combing force on further combing. Experiments in our laboratory have shown that the end peak force increases with successive passes of the comb. Charge is generated on the first comb pass, and the hair fibers will separate from one another and tangle so that an increased combing force is required on the next comb pass. When a static eliminator is used as the hair is combed, this increase in end peak force from pass to pass is eliminated.

CONCLUSIONS

Instrumentation has been developed to measure the magnitude of charge generated by combing, the mobility of charge and the distribution of charge along the length of hair fibers. Conventional antistatic agents for hair reduce the charge generated; the half-life of charge mobility varies with the quantity of antistat on the hair. The density of charge on a combed hair tress is shown to be at a maximum near the end of the fibers, and corresponds to the region where there is a peak in the combing force.

A theory of the mechanism of action of quaternary ammonium antistatic agents is proposed. These agents do not normally achieve their effect by mechanisms of increased conductivity or of charge dissipation. Their primary effect is a lubricating action, which reduces substantially the force required to comb hair, especially the end peak force. The reduced normal contact force between hair fibers and comb leads to a reduction of static charge generated on the hair.

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The optical properties of human hair I. Fundamental considerations and goniophotometer curves

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Synopsis

By using a GONIOPHOTOMETER and linearly polarized parallel white light incident obliquely on planar arrays of parallel oriented taut HAIR FIBERS, the light scattered and specularly reflected from the fibers has been recorded as a function of the angle of observation and direction of polarization in the exit beam. It can be categorized as being: (a) reflected from the air-cuticle interfaces on the near side (white light), from the cuticle-air interfaces on the far side (colored light), and from an interface probably consisting of a discontinous wedge-shaped sheath of air parallel to the axis of the fiber; or (b) scattered from optical imperfections which are principally on the surfaces of the fibers. Specular reflection from the front air-cuticle interfaces is independent of hair color and permits an evaluation of Θ ($\sim 3°$), the angle of inclination of the scales to the axis of the fiber.

INTRODUCTION

The optical properties of hair would include the refractive indices and birefringence of its various components, the color (hue, saturation, and brightness), diffuse reflectance, characteristic light-scattering patterns observed under various conditions of illumination, luster, spectroscopic properties (electronic and vibrational), and more specialized data on surface properties obtained *via* ellipsometry and internal reflection spectroscopy. Structural data obtained by means of X-ray diffraction, electron microscopy (EM), and NMR should be included, even though such techniques are nonoptical *per se*. In this paper, we are concerned primarily with studying the factors which determine the luster of hair. The topics to be discussed will be: scattering of light by infinite cylinders, reflection of light by dielectrics, and reflection and scattering of light by hair fibers.

SCATTERING OF LIGHT BY INFINITE CYLINDERS

An infinite cylinder is one whose length is infinite compared to its diameter. A discussion of solutions to some of the problems already studied will be found in the text

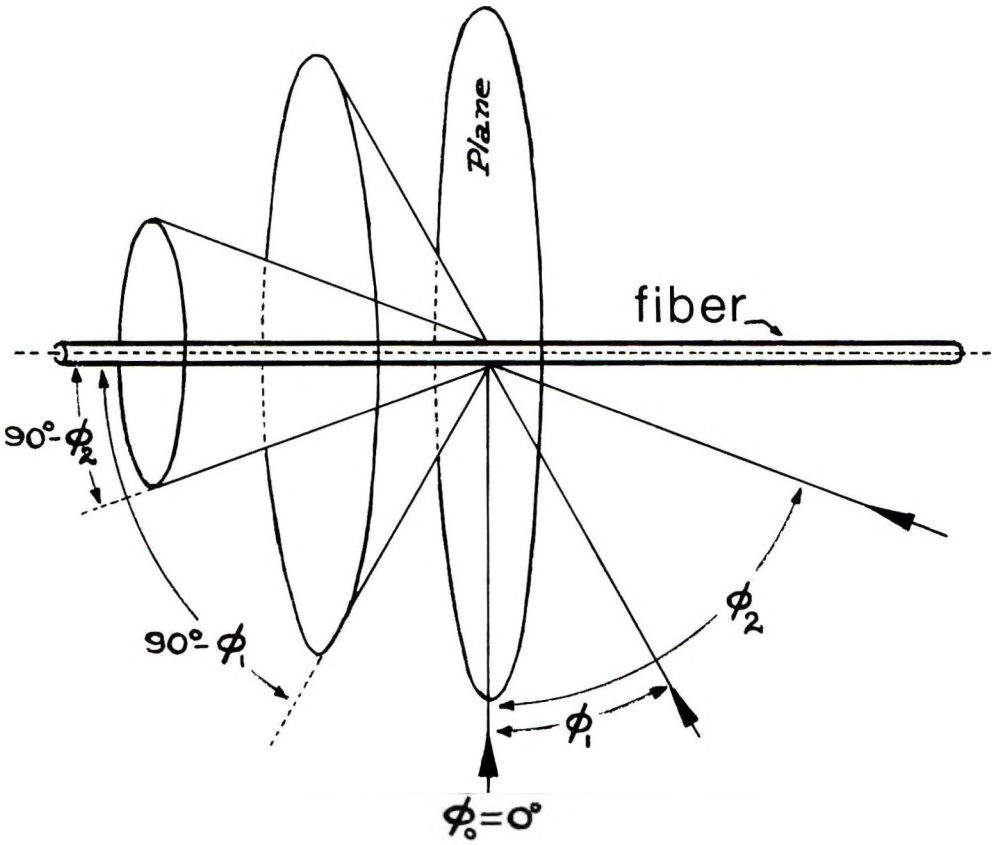

Figure 1. Diffraction of light by infinite cylinder (L/D equals ∞). Rays of light are shown which have angles of incidence (ϕ) of 0, 20, and 60°. In all cases, diffraction causes incident ray to fan out along surface which is plane normal to fiber for ϕ equals 0 or along conical surface for $\phi \neq 0$. To see diffracted light, eye must be in surface and looking at point of intersection of ray with fiber.

by Kerker (1). It is quite probable that the mathematical methods developed to date will not be capable of predicting the light-scattering patterns to be anticipated from hair fibers which are nonconducting, nonopaque, birefringent, provided with scales, and which possess elliptical cross-sections. Even so, theory is useful here because it explains the unique type of light-scattering pattern produced by infinite cylinders, and this should be understood by anyone involved in studying the optical properties of hair fibers.

NORMAL INCIDENCE

Imagine a narrow beam of monochromatic parallel rays from a small laser to impinge on a straight, nonopaque, dielectric fiber with an angle of incidence of 0° (normal incidence). (Please refer to Fig. 1.) The rays will be diffracted, reflected, refracted, and scattered. The diffraction of light consists of the bending of the rays any time they encounter the edge of an obstacle so that these rays are bent into the shadow of the obstacle. Thus, downstream from the filament, we can observe on a white card a series of spots consisting of a diffraction pattern generated by the constructive and destruc-

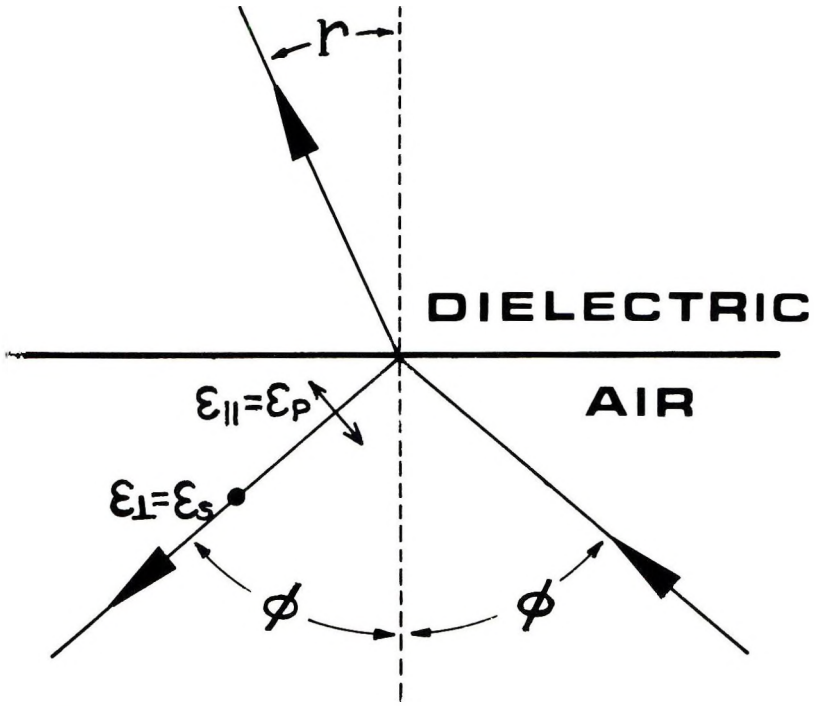

Figure 2. Reflection and refraction of light at air-dielectric interface. Incident ray comes from lower right with angle of incidence ϕ. It is partially reflected at equal and opposite angle and partially transmitted into optically more dense dielectric and suffers refraction at angle r. Plane of incidence is established by incident ray and perpendicular to interface. Direction of linear polarization is specified as being parallel to plane of incidence (ϵ_p equals ϵ) or perpendicular to that plane (ϵ_s equals ϵ) when electric vector (ϵ) of advancing wave front vibrates in direction so specified. Magnitudes of reflection and transmission coefficients must be calculated by Fresnel's equations (see text)

tive interference of the rays transmitted by the filament and those diffracted by the boundaries of the filament. These spots will be displaced symmetrically on each side of a very bright central spot formed by the rays directly transmitted by the filament. At normal incidence it will be observed that all the spots lie in a plane perpendicular to the axis of the filament. By direct viewing, it is possible to see the light diffracted by the filament only when the eye is in this plane and when it is looking at the point of intersection of the light beam and the fiber. This is 2-dimensional scattering, and the intensity decreases as $1/r$ instead of $1/r^2$, where r equals the distance from fiber to spot. In between the spots lies darkness; however, if scattering elements are placed inside the filament or on its surface, light will be stolen from the spots and converted to omnidirectional scattering whose intensity falls off as $1/r^2$.

The diffraction of light by fibers at normal incidence has been employed to determine the diameters of metal and dielectric fibers in the size range 10 to 80λ (2); the refractive indices and diameters of glass fibers to be used in fiber optic devices (3, 4, 5, 6, 7, 8) to measure and control the diameters of synthetic fibers in a production plant (9, 10), and to measure the diameters of fibers as a function of length in tests of uniformity (11, 12).

OBLIQUE INCIDENCE

If the same narrow beam of monochromatic light from a laser is incident obliquely on the filament, say at 20 or 60° as depicted in Fig. 1, and if a hollow cylinder with an inner white-wall surface is placed coaxially with the filament, a circular band of diffracted spots will be seen on the wall of the cylinder. Again, by placing a white screen at various distances downstream from the point of intersection it can be shown that these spots appear only on the surface of a cone whose half-angle is $(90\text{-}\phi_i)$ where ϕ_i is the angle of incidence (here shown as 20 or 60°). In making a direct visual examination of the diffracted light, it is found that it can be seen easily only when the eye is on the surface of the proper cone and is looking at the point of intersection of the beam with the filament. This also is 2-dimensional scattering (confined to a surface), and its intensity falls off as 1/r. If the cross-section of the filament is not a circle, the cross-section of the cone will be altered likewise. If we have a number of filaments parallel to one another and illuminated similarly, each filament will produce its cone and the sum of the light from all the cones will determine the resultant cone whose surface will now have a finite thickness.

REFLECTION OF LIGHT BY DIELECTRICS

Before discussing the reflection and scattering of light by hair fibers, it appears desirable to review certain fundamental laws which govern the reflection of light by dielectric materials. In Fig. 2 is depicted a ray of light incident at the angle ϕ on an air-dielectric interface. If the surface is optically polished, the scattering is negligible, and the ray is partly reflected at an angle ϕ and partly transmitted after refraction at an angle r. The angle of refraction is found from Snell's law

$$\sin r = (\sin \phi)/n \tag{1}$$

where n is the refractive index of the dielectric. Calculating the reflection and transmission coefficients is somewhat more lengthy, involves the use of Fresnel's equations, and requires a knowledge of the direction of polarization of the incident light generally taken to be linearly polarized with the electric vector ϵ vibrating parallel (ϵ_p) or perpendicular (ϵ_s) to the plane of incidence which is defined by the incident ray and the perpendicular to the interface. (In Fig. 2, the plane of incidence would be the plane of the paper.) Fresnel's equations enable us to calculate the amplitudes of the reflected (R_s, R_p) and transmitted (T_s, T_p) rays relative to the incident (E_s, E_p) amplitudes and have the form

$$R_s/E_s = \frac{-\sin\ (\phi - r)}{\sin\ (\phi + r)} \text{ and } R_p/E_p = \frac{\tan\ (\phi - r)}{\tan\ (\phi + r)} \tag{2}$$

$$T_s/E_s = \frac{2 \sin r \cos \phi}{\sin (\phi + r)} \text{ and } T_p/E_p = \frac{2 \sin r \cos \phi}{\sin (\phi + r) \cos (\phi - r)} \tag{3}$$

To obtain the intensities of the reflected rays relative to those of the incident rays, the amplitudes are squared; the reflection coefficients are given by

$$r_s = (R_s/E_s)^2 \text{ and } r_p = (R_p/E_p)^2 \tag{4}$$

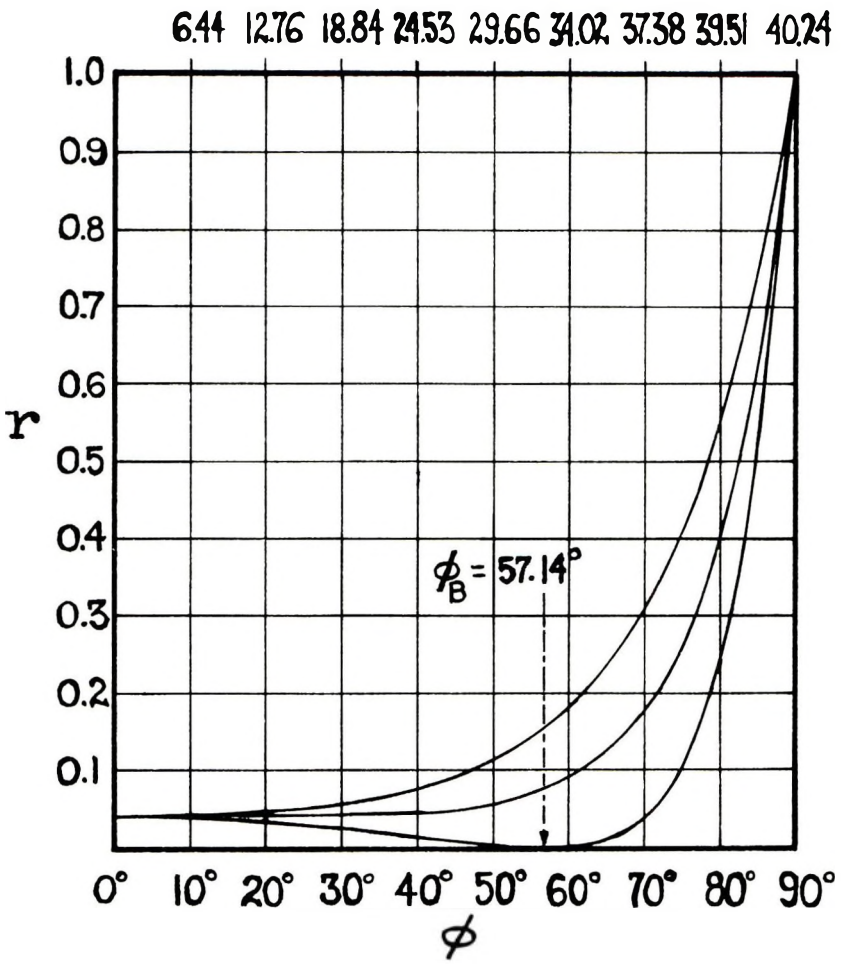

Figure 3. Reflection coefficients (r) vs. angle of incidence (ϕ) at air-dielectric (or dielectric-air) interface for dielectric having n = 1.548, value of n_μ for exocuticle of human hair. Upper curve is for ϵ_s. Lower curve for ϵ_p, and intermediate curve for natural (unpolarized) light. Angle values at bottom apply to ray approaching interface from air; those at top are angles of refraction which correspond to values of ϕ at bottom. Angle ϕ_B (equals $\tan^{-1}$ n) is Brewster's angle of incidence for which rays polarized ϵ_p suffer no reflection but are entirely transmitted. For ray inside dielectric trying to get out, Brewster's angle would be 32.86° for n = 1.548

The reflection coefficients for natural (unpolarized) light will be $(r_s + r_p)/2$. When ϕ equals 0° (normal incidence), we have

$$r_s = r_p = r_u = (n - 1)^2/(n + 1)^2 = 0.040 \text{ for } n = 1.50 \quad (5)$$

Letting n = 1.548, assigning various values to ϕ and calculating the corresponding values of r from Snell's law, Fresnel's equations are then used to derive the reflection curves shown in Fig. 3. Calculation of the reflection coefficients is straightforward, but calculating the value of a transmission coefficient at an interface for angles of incidence other than 0° is slightly more complicated because the relative areas of the beams on each side of the interface enter into the calculation. This arises since it is necessary to

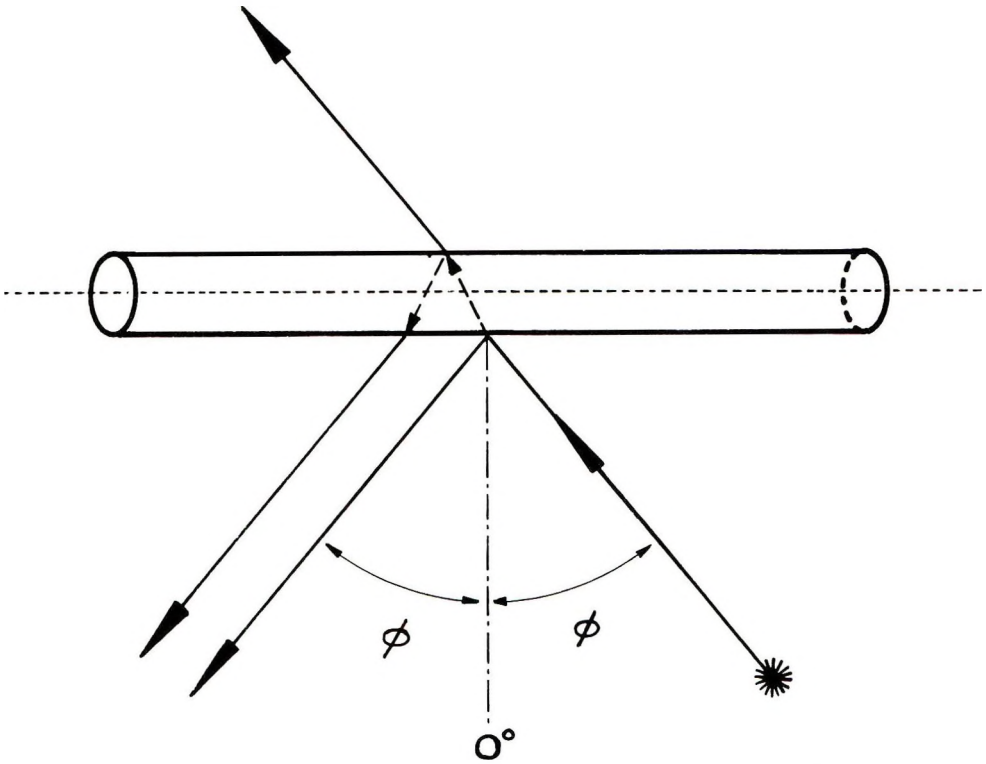

Figure 4. Reflection of light from near and far sides of idealized cylindrical fiber. Rays reflected from both sides are observed at same angle and are indistinguishable from one another. This is in marked contrast to case for fibers with scales (see Fig. 5.)

take cognizance of the energy flow, i.e., the energy reflected plus the energy refracted equals the energy incident. For details, it is recommended that the reader consult (13) (p. 392) or (14) (pages 40 and 41).

The following are noteworthy at this point: a. At the polarizing angle ϕ_B commonly known as Brewster's angle, the angle (ϕ + r) equals 90°, and since tan 90° equals ∞, the reflection coefficient, r_p equals 0, which means that at that angle of incidence, light linearly polarized parallel to the plane of incidence is totally transmitted into the dielectric. Determining ϕ_B experimentally also provides a means of measuring the refractive index of the dielectric since n equals tan ϕ_B. At grazing incidence (ϕ equals 90°), all the reflection coefficients are 1.00. And finally, for an optically polished surface, the reflection coefficient at the surface will be determined by the factors contained explicitly or implicitly in Fresnel's equations; thus the value of the refractive index is much more important than the color.

For light which is inside the dielectric and is incident on the dielectric-air interface, a similar set of curves can be used employing as abscissae integral values of r (inside the medium of higher optical density). This latter situation can involve the phenomenon of total internal reflection which arises (from Snell's law) when r has the value of the so-called critical angle r_c for which sinϕ equals 1,ϕ equals 90°; this is tantamount to "graz-

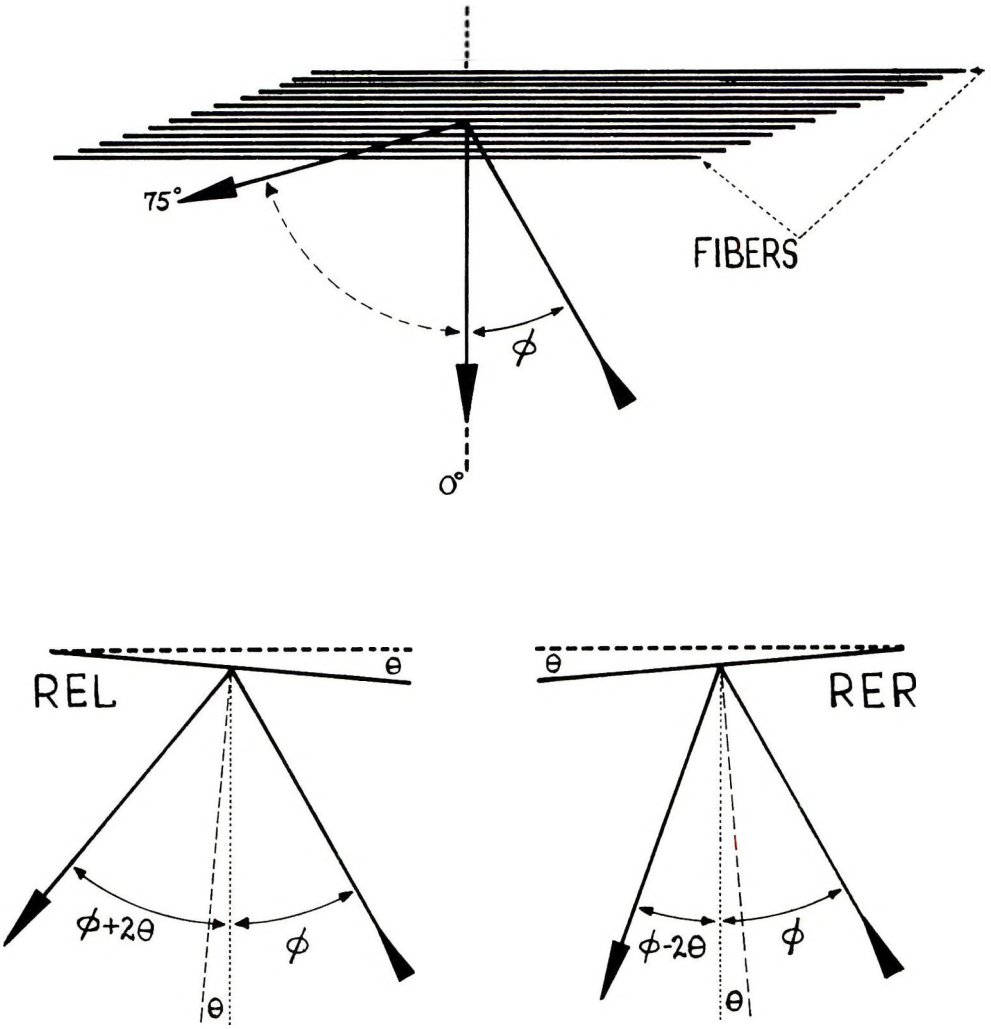

Figure 5. Method employed for illuminating planar array of parallel oriented hair fibers in obtaining goniophotometer curves. Angle of incidence is fixed (ϕ equals 30°), while mechanized arm which carries detector scans through interval (0 to −75°) on other side of normal to array. In lower portions of figure are shown inclinations of scales on near sides of fibers with orientations [root-ends-left (REL) or right (RER)], where θ is angle of inclination of scales relative to axis of fiber and is also angle between 2 perpendiculars, π_0 (dotted, perpendicular to axis) and π_1 (dashed, perpendicular to cuticle surface in plane of incidence). Light specularly reflected from front face of the cuticle is observed at angle $\pm 2\theta$ from position at which it would be observed for fiber having no scales. When oriented REL, incident light rays illuminate directly rough ends of scales; this generally increases amount of scattered light vs. the orientation RER

ing emergence" so the light cannot escape from the dielectric into air for internal angles of incidence $\geq r_c$. For n equals 1.548, sin r_c equals 1/n yields r_c equals 40.24°. Total internal reflection occurs with 100 per cent efficiency.

Using the foregoing material as a base, it will now be possible to discuss the optical properties of hair fibers.

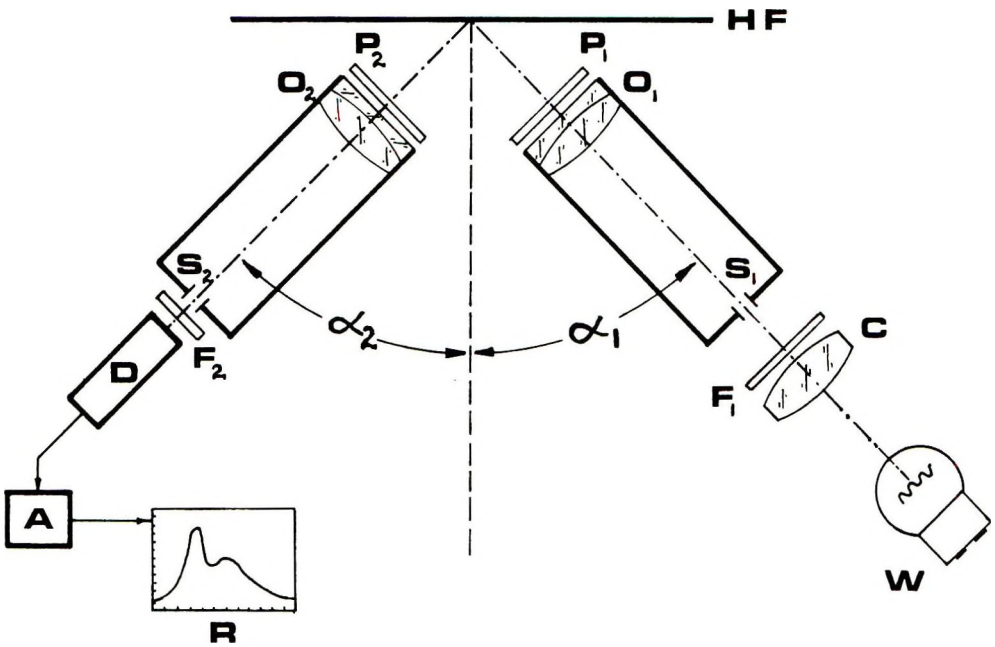

Figure 6. Recording goniophotometer. W is 30-W tungsten-filament bulb which sends light to condensing lens C. Dichroic heat filter F_1 reflects long wave radiation ($\lambda > 700$ nm) and transmits rays with $\lambda < 700$ nm. S_1 and S_2 are slits, O_1 and O_2 are achromatic doublet objective lenses of 2 collimators, P_1 and P_2 are rotatable Polaroid discs, and α_1 (equals ϕ, angle of incidence) and α_2 (angle of observation) are values for angles read off graduated arcs of instrument. HF designates planar array of hair fibers, F_2 consists of 1 or more neutral density filters employed to adjust magnitude of signal. D contains detector, A is amplifier, and R is strip chart recorder. Basic instrument was made by Zeiss (Model GP-2) while mechanization and other alterations were carried out by Clairol. Slits provided have angular widths of 0.25, 0.5, and 1.0°. Normally, we employ 1° slits in both telescopes and find angular resolution to be adequate for work we do with hair. With 0.25° slits and light specularly reflected from polished black glass, half-intensity width of peak is 0.25° and full width of base is 0.50°

REFLECTION AND SCATTERING OF LIGHT BY HAIR FIBERS GONIOPHOTOMETER CURVES

EFFECTS ATTRIBUTABLE TO THE SCALES AND REFLECTIONS FROM FRONT AND REAR SURFACES

In Figure 4 is depicted a ray of light incident obliquely on the surface of a taut horizontal fiber which is assumed to be ideal optically, i.e., it has a smooth external cylindrical surface, a circular cross-section, and is colorless, transparent, and optically isotropic. For rays incident in a principal plane which is vertical and bisects the fiber longitudinally, it can be seen that we would anticipate reflection from the front face (near side) and from the rear face (far side), that all the reflected rays in both sets (near side and far side) would be parallel to one another, and that the angle of reflection would be equal and opposite to the angle of incidence, both being measured relative to the perpendicular to the axis of the fiber. Such is found to be the case with glass or synthetic fibers which sometimes approach ideality.

Human hairs depart considerably from the ideal, and one principal point of departure is the existence of up to 10 layers of scales (cuticle) which cover the fiber, each layer

possessing a radial thickness of ~0.5 μm. It is the presence of the scales which enhances the difficulty in measuring the light reflected by the external surfaces of hair fibers. In Fig. 5 is shown in elementary fashion a parallel beam of white light, coming from the lower right, illuminating a planar array of hair fibers held under slight tension, parallel to one another and oriented with all their root ends either to the right or to the left. The intensity of the light, which is specularly reflected and scattered by the hair fibers, is detected by suitable means at various angles in the plane of incidence, and recorded on a strip chart recorder. Such a device is known as a goniophotometer; a rudimentary diagram of the instrument appears in Fig. 6 whose caption contains the necessary explanatory material. While maintaining the angle of incidence constant at, say, +30° relative to the perpendicular to the plane of the sample, the other collimator (provided with a detector) was scanned from 0 to −75° from the perpendicular reference line, and the intensity of the light detected was recorded as a function of the angle of observation. The array of fibers was 25 cm long × 25 mm wide, and the central fiber of the array was in the plane occupied by the optic axes of the two collimators. (Details regarding the instrumentation will be found in Appendix I.)

In Fig. 7 we see, much reduced in size, goniophotometer (GP) curves typical of those obtained with root ends left (REL) or root ends right (RER) according to the diagram in Fig. 5. To emphasize specular reflection, Polaroids were used in front of each collimator lens in the configuration we designate $\epsilon_s\ \epsilon_s$ with ϵ, the electric vector, vibrating perpendicular to the plane of incidence. There are 2 prominent features in each curve. In the case REL, there is a sharp peak at 35.2° and a weaker broader peak at ~23°. The curve for the case RER is essentially the mirror image of the case REL except that the intensities are different. (The apparent discrepancy in intensities will be explained subsequently.) Den Beste and Moyer (15) published a curve of this type obtained using a goniophotometer with a "hair tress mounted in a special jig so that a straight flat surface was presented to an incident light beam at an angle of 30°." (The angle of incidence relative to the normal to the plane of the sample was 60°.) The resolution manifested by their curve was low because of the multiplicity of fibers employed. The brief statements made by them on page 600 of their paper were correct, but they did not go further into the optical aspects of the case because they were interested primarily in using the areas under the diffuse peaks to measure the X, Y, and Z chromaticity values for various samples of hair.

Returning to Fig. 7, if we replace the detector in the GP by the human eye, we find that the strong sharp peak is white light, whereas the light associated with the diffuse peak is the color of the hair. If the fibers had no scales, we would anticipate finding a single peak at 30° but there is none there. For the cases REL and RER, we calculate the displacements of the strong sharp peaks from the 30° position and find each of them to be 5.2°, which we divide by 2 to get 2.6°. This angle we shall designate as θ and shall assume it to be the angle of inclination of the scales to the axes of the fibers. In addition, because this is white light, we assume the sharp peak is attributable to direct specular reflection from the air-cuticle interfaces on the front faces or near sides of the fibers, i.e., the faces initially encountered by the incident light.

Next, using optically flat black paint (3M Nextel Brand Velvet Coating, 101-C10 Black) the far sides of the same set of mounted fibers were spray painted using a technique which avoided getting paint on the near sides. After running the GP curves of the blackened fibers, it was found that the weak diffuse peak had disappeared, and only

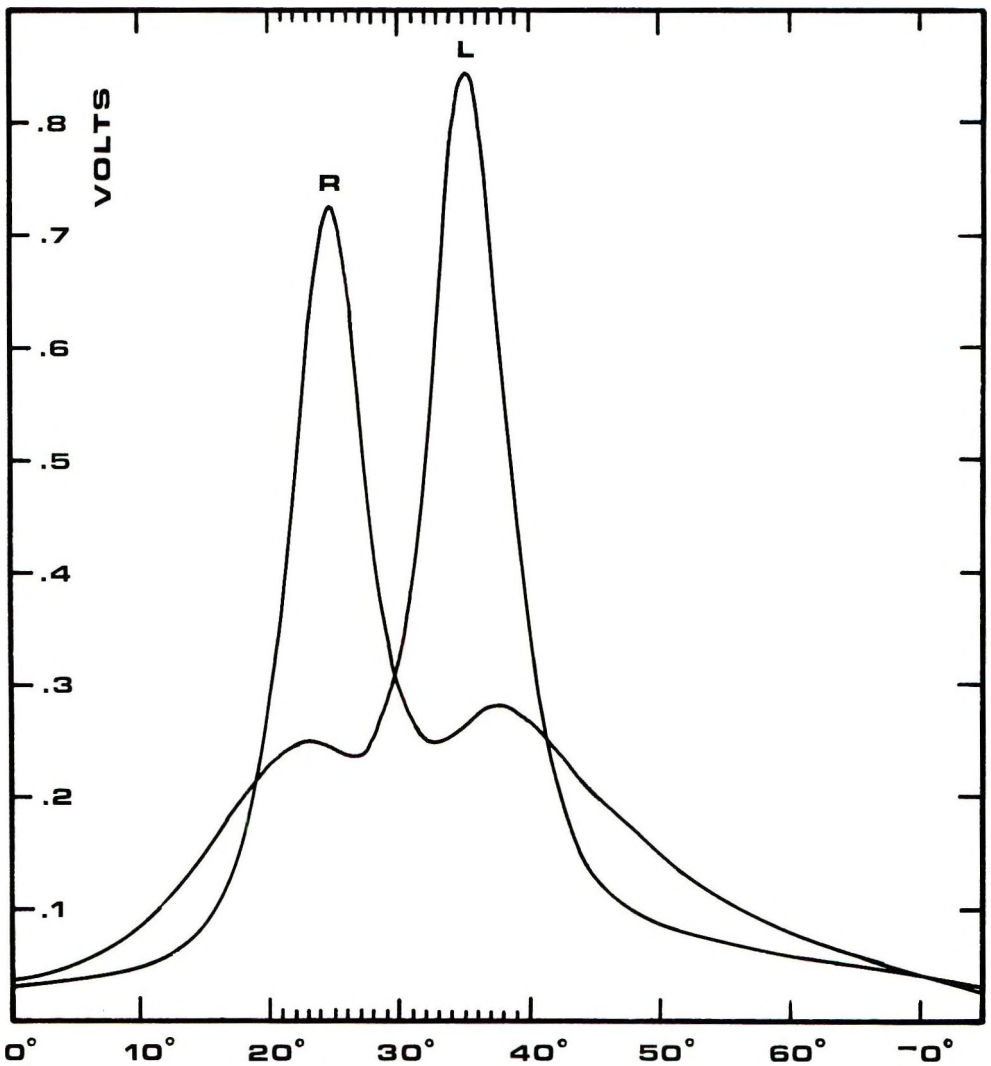

Figure 7. GP curves obtained from dark brown hair; $\epsilon_s\epsilon_s$, REL and RER, 21 fibers, ϕ equals 30 °, 1 ° slits, T equals 0.5 (transmission of filter F_2 in Fig. 5(b), center strung (which means that centermost slots of spacer screws were occupied by fibers which had center to center separation of 1/60 in. = 0.423 mm; this provides signal 28 per cent greater than that from "wide strung" arrangement which involves full width of 25.4 mm for 21 fibers; however, center-strung arrangement enhances possibility of detecting multiple fiber to fiber scattering effects when studying lightcolored fibers or fibers having diameters larger than normal)

the sharp peak remained; this was true for both REL and RER. This experiment provided convincing evidence that the diffuse peak was attributable to specular reflection from the cuticle-air interfaces at the far sides of the fibers.

SCATTERING FROM THE INTERIOR AND FROM THE SURFACE AND THE EFFECT PRODUCED BY COLOR IN THE HAIR

Omnidirectional scattering of light is caused by optical imperfections. These include voids, inclusions, the rough ends of the scales, the medulla, and particles of pigmentation. The presence of such scattering manifests itself by genuine signals above the baseline at 0 and 75° when the specular peaks are approximately halfway between these 2 extreme positions. With white light, the scattering appears to be devoid of structure when GP curves are obtained at a wide varity of angles of incidence. In addition, since the scattering in the forward direction (75°) is greater than that at lower angles (0°), it can be estimated that the geometrical dimensions of the scattering centers are comparable to or greater than λ, the wavelength of the light. Also, one-half to two-thirds of the scattering is attributable to the rough ends of the scales. Quantitative data will be given in Part II of this paper, which is devoted to the subject of luster. When the hair is colored, the reflection of light from the far sides of the fibers is diminished; the diffuse peak essentially vanishes in the case of black hair.

THE EQUAL-ANGLE PEAK (EAP)

Since the angles of inclination of the scales (relative to the axis of the fiber) on the near and far sides of a fiber are equal numerically and opposite in sign, in a GP curve, one would not anticipate the appearance of a sharp peak at an angle equal and opposite to the angle of incidence. When such a peak was first observed, it was considered an artifact and was attributed to reflection from the under side of the sample plate. However, the peak persisted even when a GP curve was obtained from a single fiber using no sample plate. It is observed when using incident light, which is unpolarized or polarized (ϵ_s or ϵ_p), and becomes more prominent at angles of incidence of 50° or more. In some hair it is not seen at angles of incidence as low as 30° when using the configuration $\epsilon_s\epsilon_s$ (as shown in Fig. 7 for example), but for the same hair, it will appear for an angle of incidence of $\phi \geq \sim 50°$. Also, with ϕ as low as 30°, it will appear when using $\epsilon_s\epsilon_p$ as shown in Fig. 8. In this configuration ($\epsilon_s\epsilon_p$), the light which retained the original direction of polarization (ϵ_s) of the incident light was blocked by the second Polaroid disc thereby permitting weaker peaks to be seen which were partially obliterated in Fig. 7. (The signals in Fig. 8 are about one-fifth of those in Fig. 7.) An explanation for the origin of the EAP will be given in the section on Optical Models for Hair.

LIGHT COLORED HAIR

In order to gain an idea of the relative degrees of importance of the different types of reflection and scattering which occur in hair, it is advisable to employ hair which is essentially devoid of color. Thus we made a study of the following types of hair; Piedmont (medullated and nonmedullated), blond, and gray. The GP curves were obtained REL and RER using the Polaroid configurations $\epsilon_s\epsilon_s$ and $\epsilon_s\epsilon_p$. Also, in all cases, GP

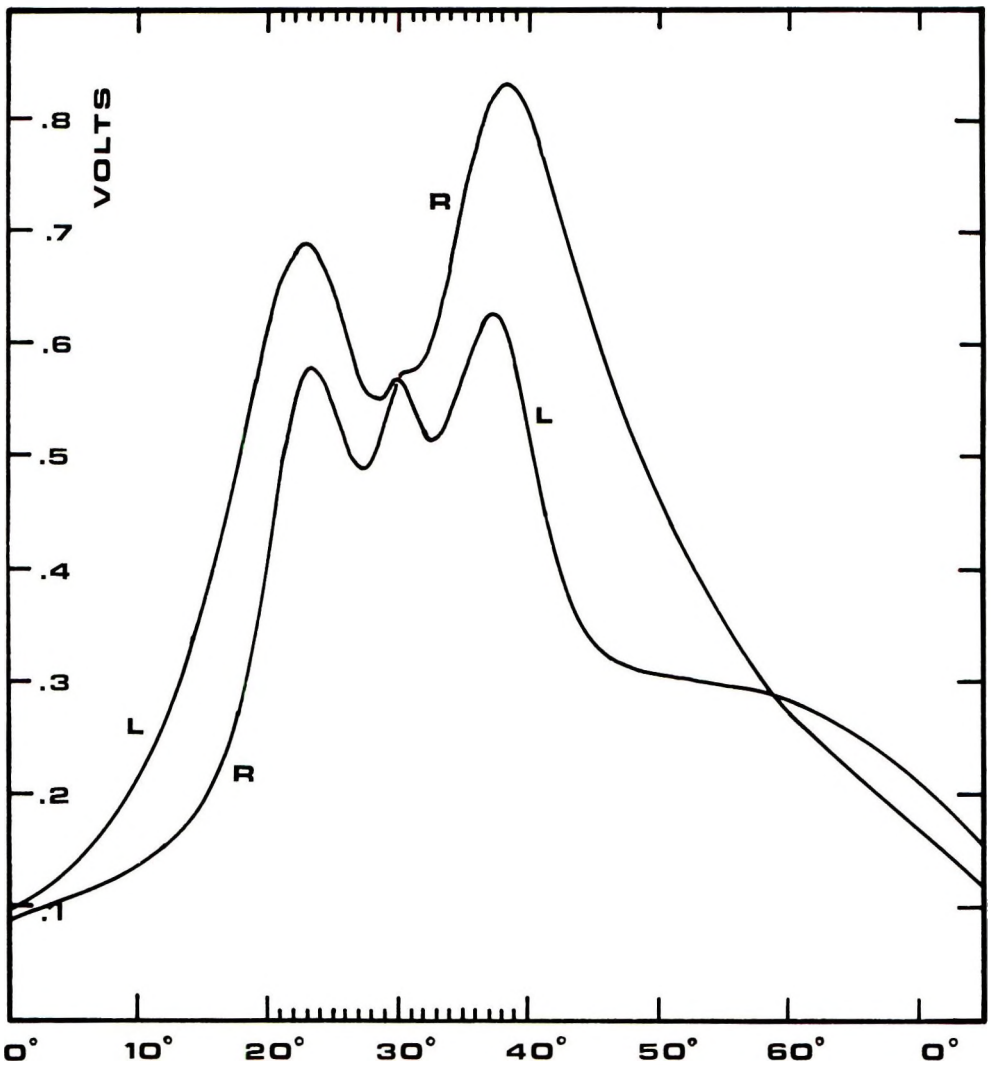

Figure 8. GP curves obtained from dark brown hair; $\epsilon_s\epsilon_p$, REL, and RER, 21 fibers, ϕ equals 30°, 1° slits, T equals 1 (air alone in place of F_2 of Fig. 5(b), center strung. Note EAP at 30°

curves were obtained after coating the fibers with a colorless transparent layer of hair spray resin which, in some cases, was sufficiently thick to negate the optical effects of the scales. For the sake of brevity, the curves are omitted and we present only a synopsis of the results here.

In comparing GP curves for dark brown hair with those for Piedmont hair we note the following: (1) the diffuse (farside) peaks are weaker for the colored hair; (2) the resolution is much better for the dark hair because of less scattering; and (3) the continuous background from diffuse scattering is ~4 fold greater for the Piedmont hair.

When comparing medullated (m) and nonmedullated (nm) Piedmont hair we find: (1) the resolution for nm is better than for m because of less scattered light; (2) the ratio of

the intensities of the specular peaks (far side/near side) is ~50 per cent greater for nm than for m because a relatively large fraction of the inward and outward bound rays in question suffer omnidirectional scattering by the medulla; (3) the asymmetry of scattering (75/0°) is about 30 per cent greater for the nm fibers probably because the medulla diminishes the scattering from the scales on the far side; and (4) the ratio of the scattering (0 and 75°) relative to the signal for the front specular peak is larger for the m fiber, ~15 per cent at 0°, and ~15 per cent at 75°. This extra scattering is ascribed to the medulla.

With regard to resolution, the order is blond (highest), gray, piedmont (nm), and piedmont (m). The progressive loss is attributed to a progressive increase in scattering from the interiors of the fibers since a considerable degree of scattering persists even after the fibers are coated. It had been anticipated that the experiments performed with uncoated versus coated fibers would permit an evaluation of the relative amounts of scattering from the scales and from the interior. Unfortunately, only in the case of the gray fibers was the degree of encapsulation good enough to make such a determination. In the case of gray hair (ϕ equals 30°, $\epsilon_s\epsilon_s$), 30 per cent of the scattering observed at 0° came from the scales (RER) and 44 per cent from the scales (REL). Thus, with gray hair fibers, more than 50 per cent of the scattering comes from the interiors of the fibers, and the same thing is true of blond hair and nonmedullated Piedmont hair. In the case of medullated Piedmont hair, it is estimated semi-quantitatively that ~90 per cent of the diffusely scattered light comes from the interiors of the fibers! As will be seen in Part II of this paper, all fibers which have this large amount of diffuse scattering from the interior have lower values of luster.

BLACK NAVAJO HAIR

GP curves obtained from the hair of a young Navajo female (age 21) appear in Figs. 9 and 10. These fibers have an average diameter of 94 μm, ~50 per cent greater than any of the other fibers studied; many of them are medullated; some have a deep reddish/brown color; the scales are quite tight to the cortex, but the value of θ is 4.75°, the largest we have ever measured. In the configuration $\epsilon_s\epsilon_s$ (Fig. 9), only the front face peaks are seen because the deep color and greater path length essentially obliterate the rear-face peaks which do appear weakly in Fig. 10 ($\epsilon_s\epsilon_p$). For fibers this dark, the magnitude of the diffuse scattering is high; it was estimated that this arose from damage to the cuticle, and this was confirmed by SEM photographs. This diffuse scattering also lowered the luster value (see Table I, Part II) from the value (~0.9) which would be anticipated for hair of this color if the cuticle were in excellent condition.

θ VALUES

It is sometimes desirable to measure small changes in θ (the angle of the scales relative to the axis of the fiber) produced by various hair treatments. As yet we have not attempted to make such measurements while the treatments were in progress but have been content to measure $\Delta\theta$, the change in θ before and after treatment with the hair being in equilibrium with our room conditions, 70(±1)°F, 65(±1) per cent RH. Because of the hysteresis effect encountered in the wetting and drying of hair, it is not possible to have the hair taut during treatment since the tension values before and after

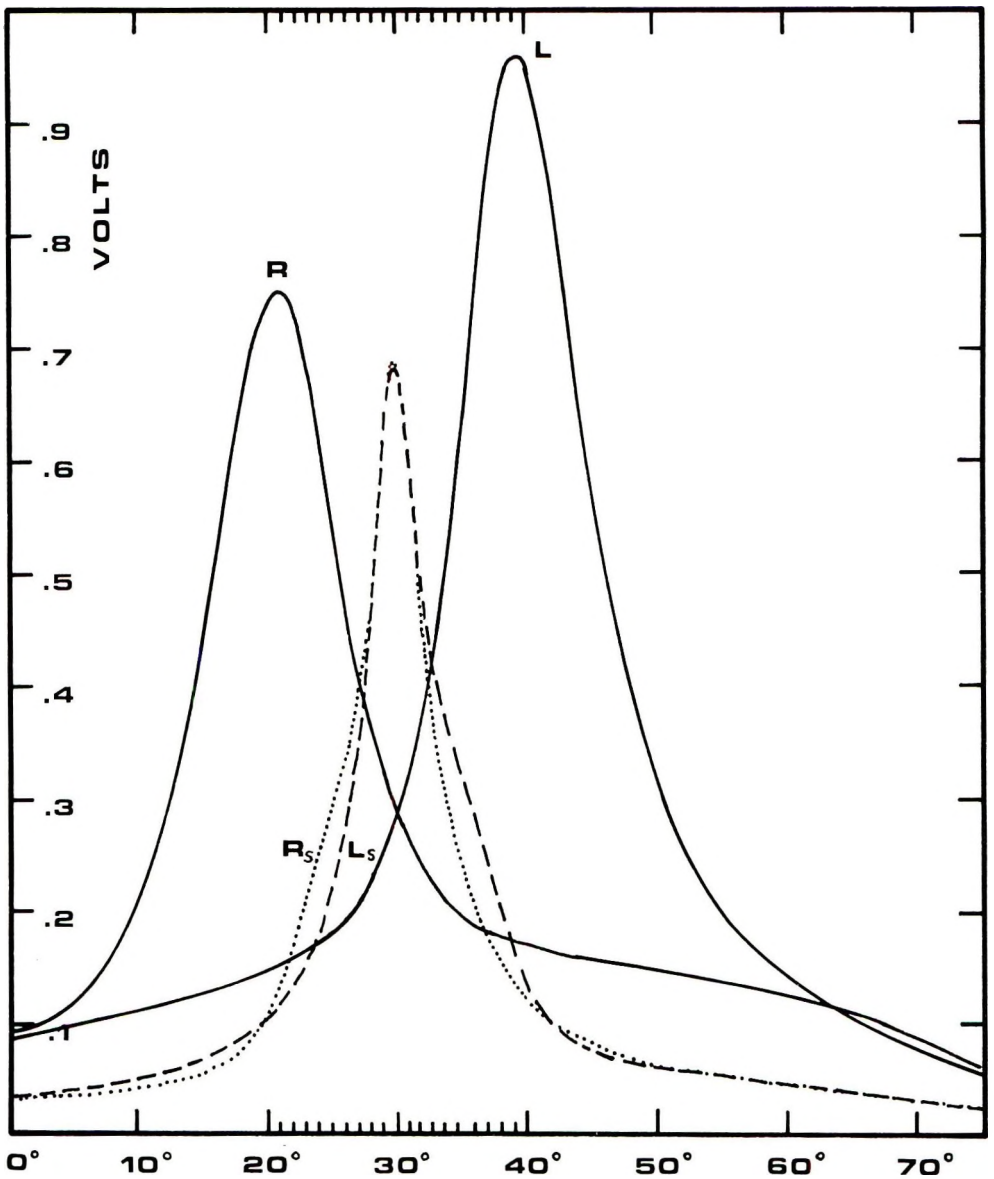

Figure 9. GP curves obtained from black Navajo hair, $\epsilon_s\epsilon_s$; REL, and RER, unsprayed (solid lines) and sprayed (dashed and dotted lines, n_D of resin equals 1.503) 21 fibers ϕ equals 30°, 1° slits, T equals 0.276 (unsprayed), T equals 0.138 (sprayed), wide strung, average diameter of fibers = 94 μm. Each fiber is almost completely sheathed with resin after spraying with solution of resin. Peak values for EAP Peaks would be >1.3 Vs if plotted on same scale as curves for unsprayed fibers. Note absence of far side peaks because of color and diameter of fibers

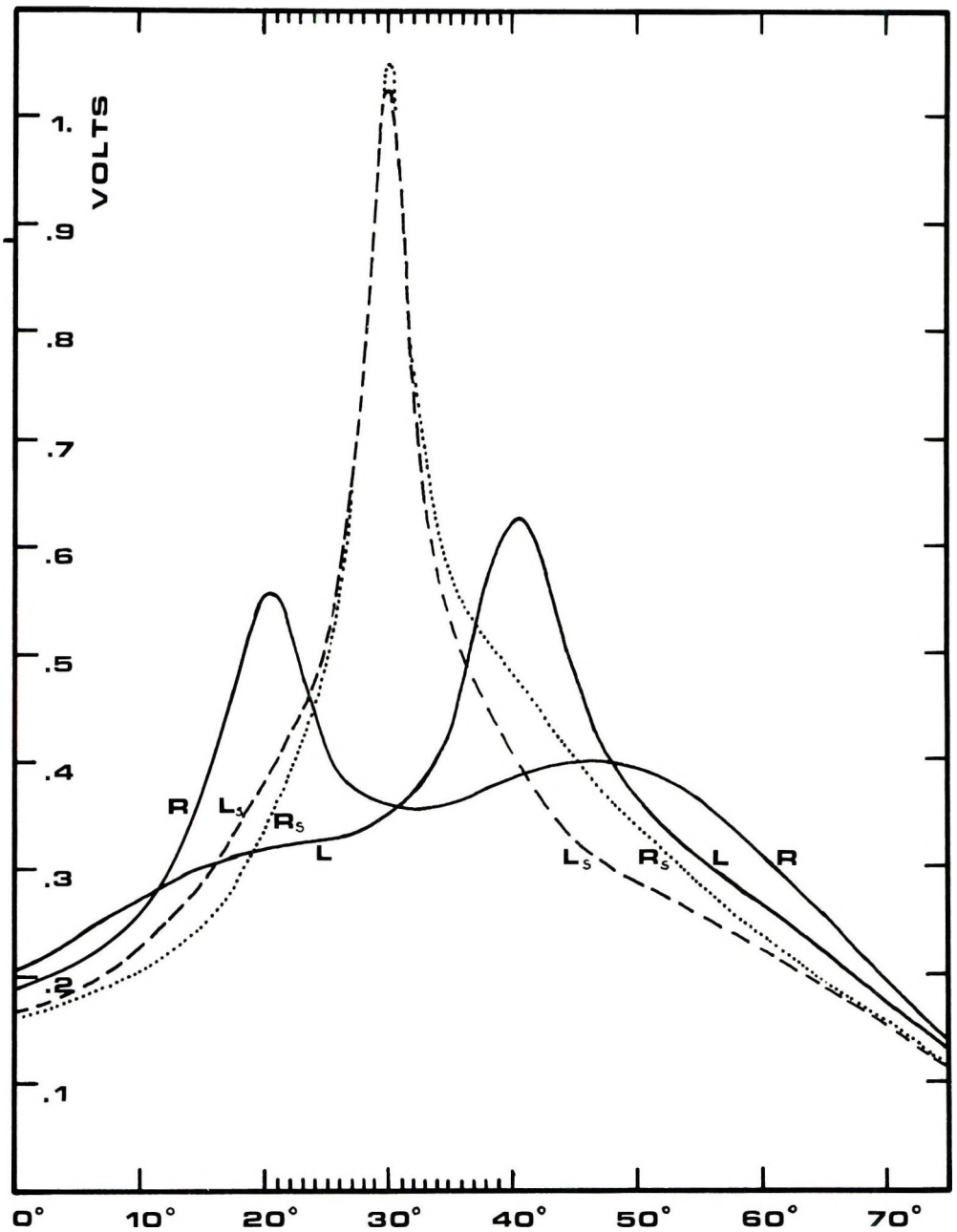

Figure 10. GP curves obtained from black Navajo hair, $\epsilon_s\epsilon_p$, REL, and RER, unsprayed (solid lines) and sprayed (dashed and dotted lines, n_l of resin equals 1.503), 21 fibers, ϕ equals 30°, 1° slits, T equals 1 (no filter), wide strung, average diameter of fibers equals 94μm. Each fiber is almost completely sheathed with resin after spraying with solution of resin. In curves for unsprayed fibers, far side peaks appear weakly

treatment generally will be different, and this will alter θ. (Increasing the tension lowers θ.) Consequently, we string the fibers, record the GP curves, measure the θ values by hand cranking the detector telescope instead of using the motor drive, unstring all the fibers at one end leaving the root ends still mounted, carry out the treatment with the fibers between glass and a plastic film, wash the fibers, dry them for 30 min with room air using only a blower and no heat, restring the tip ends, record the GP curves, and measure the θ values by hand cranking. From the chart paper, values of angles are good only to $\pm 0.1°$ because of the uncertainty in coordinating the zero points of the GP and the recorder. However, by hand cranking the GP and reading the scale with a 4 X eyepiece, we can find values of $\Delta\theta$ good to $\pm 0.02°$ at a 90 per cent confidence level if we perform 5 repetitive experiments. Instead of reading the angle at the peak, it is better to read the angles corresponding to equal signal values each side of the peak but still close to the peak so that any effects from the asymmetry of the peak will not be important. When typical, mild treatments are applied to the hair, values of $\Delta\theta$ ranging from 0.1 to 0.2° are obtained, but 0.2° would be considered a large change.

AN OPTICAL MODEL FOR HAIR; THE REFRACTIVE INDEX AND BIREFRINGENCE

In attempting to understand the significance of the experimental results described in the foregoing material it is necessary to resort to ray tracing to verify that the light should emerge at the angle where it is observed. The act of ray tracing requires an optical model plus knowledge of the refractive indices and birefringence of the exocuticle and of the cortex. Employing a microscope, light from a sodium vapor lamp, and the Becke line method, we have measured the value of n equals 1.548 (±.001) using several different types of human hair (whole hair fibers) as well as cuticle scraped from hair and free from the cortex. We find the cuticle in this condition to be free from birefringence. With regard to the birefringence for human hair, we have noted the value of $(n_p - n_s)$ equals 0.007 reported by Fraser (16). When the fibers have a low moisture content, this is believed to be the so-called intrinsic birefringence, and is attributed to the helical molecules in the cortex. For wool fibers, a value of $(n_p - n_s)$ equals 0.0114 at 65 per cent RH (12. 7 per cent regain), corrected for swelling, can be interpolated from Fig. 2 of the paper by Haly and Swanepoel (17). (The uncorrected value would be ~0.0103.)

Using a fiber of Navajo hair which was devoid of cuticle over a short length, but was not split or damaged, the birefringence Γ_D equals 0.0068 (±1.5 per cent) was measured directly at 22°C. For the same fiber which had cuticle closer to the root end, the value Γ_D equals 0.0076 (± 1 per cent) was measured for cortex plus cuticle at the same temperature. From these data, we infer that, *in situ*, the cuticle has a weak birefringence of ~0.001. In all probability, this is attributable to the strain imposed on the scales during growth. When devoid of cuticle, the hair was swollen by the immersion liquid which surrounded it. The diameter increased 6 per cent in ~2 h at 22°C; this was 10 times the rate of swelling observed for the same fiber with cuticle. For the sheath of the cortex, the values n_p equals 1.548 and n_s equals 1.541 were measured. The difference $(n_p - n_s)$ yields an inferred value of $\Gamma_D = 0.007$ to be compared with 0.0068, the one measured directly. (The relative humidity was 65 per cent which produces ~12.7 per cent regain in wool; see (17)). The low value of birefringence, approximately that of crystalline quartz, should not produce significant effects except in

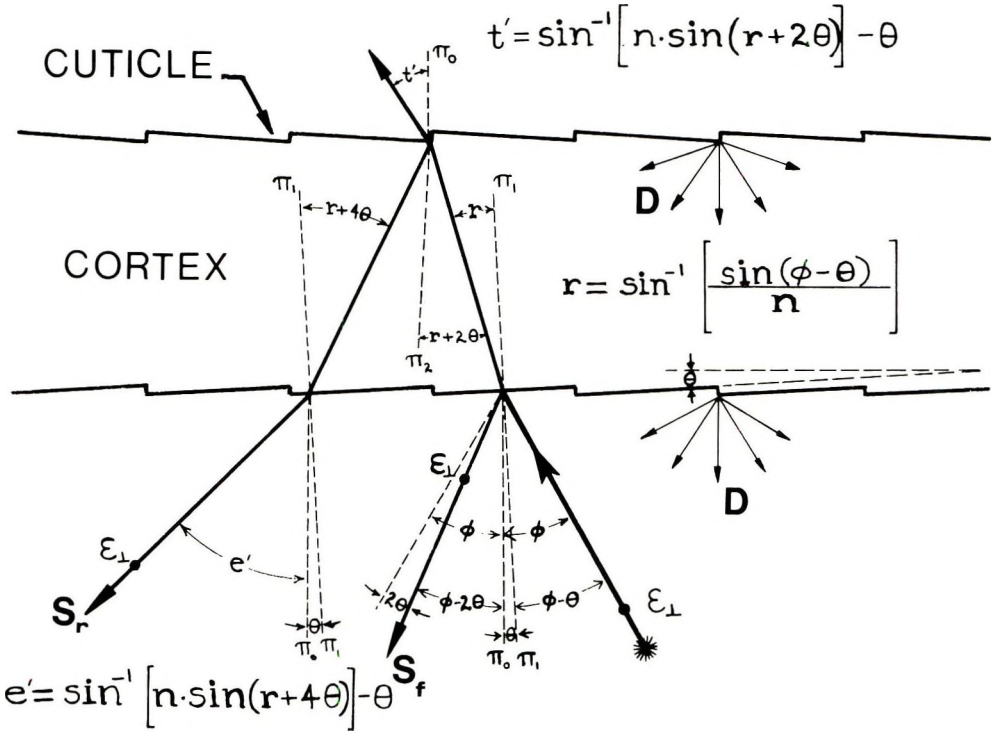

Figure 11. Optical model for hair: number 1. For orientation RER and angle of incidence of θ vs. π_0 or $(\phi - \theta)$ vs. π_1, rays have been traced in principal plane which bisects fiber longitudinally. Indices of cuticle and cortex have been assumed to be equal. Specularly reflected rays (S_f, front face, and S_r, rear face) do not appear at equal and opposite angles vs. $(-\phi)$. At far side, the internal angle of incidence is $(r + 2\theta)$ vs. π_2, and angle of emergence would be $\{\sin^{-1}[n \sin (r + 2\theta)] - \theta\}$ vs. π_0 which is not equal to ϕ. Thus, either for oblique incidence, or for normal incidence ($\phi = 0°$), the ray which emerges on far side would be deviated relative to incident ray because of prism effect of hair fiber in this model (cf. model 2 in Fig. 12.). Rays denoted by D on both near and far sides represent diffuse scattering from ends of scales. For orientation REL, angles become: ϕ, $(\phi + \theta)$, r equals $\sin^{-1}$ $[\sin (\phi + \theta)/n]$, $(r - 2\theta)$, $(r - 4\theta)$, e' equals $\{\sin^{-1}[n \sin (r - 4\theta)] + \theta\}$, and $\{\sin^{-1}[n \sin (r - 2\theta)] + \theta\}$ vs. π_0 for angle of emergence on far side

experiments conducted with crossed Polaroids, and even in that case, other effects will probably be of greater significance.

OPTICAL MODEL NUMBER ONE

This model is shown in Fig. 11 in the configuration RER. An explanation is presented in the caption. This model can predict the angular location of the light specularly reflected from the air-cuticle interface on the front face but not that from the rear face. Thus, with ϕ equals 30°, θ equals 2.5°, n equals 1.548, and with no Polaroids or with $\epsilon_s\epsilon_s$, for the orientation REL, we calculate r equals 20.3° and from this e equals 18.6° versus 22° observed; the calculated value is low by 3.4° (15 per cent). For the orientation RER, we calculate r equals 17.4° and from this e equals 42.8° versus 39° observed; the calculated value is high by 3.8° (10 per cent). Making reasonable adjustments of θ and n did not permit agreement to be achieved. In addition, this model is incapable of explaining the EAP, *vide supra*.

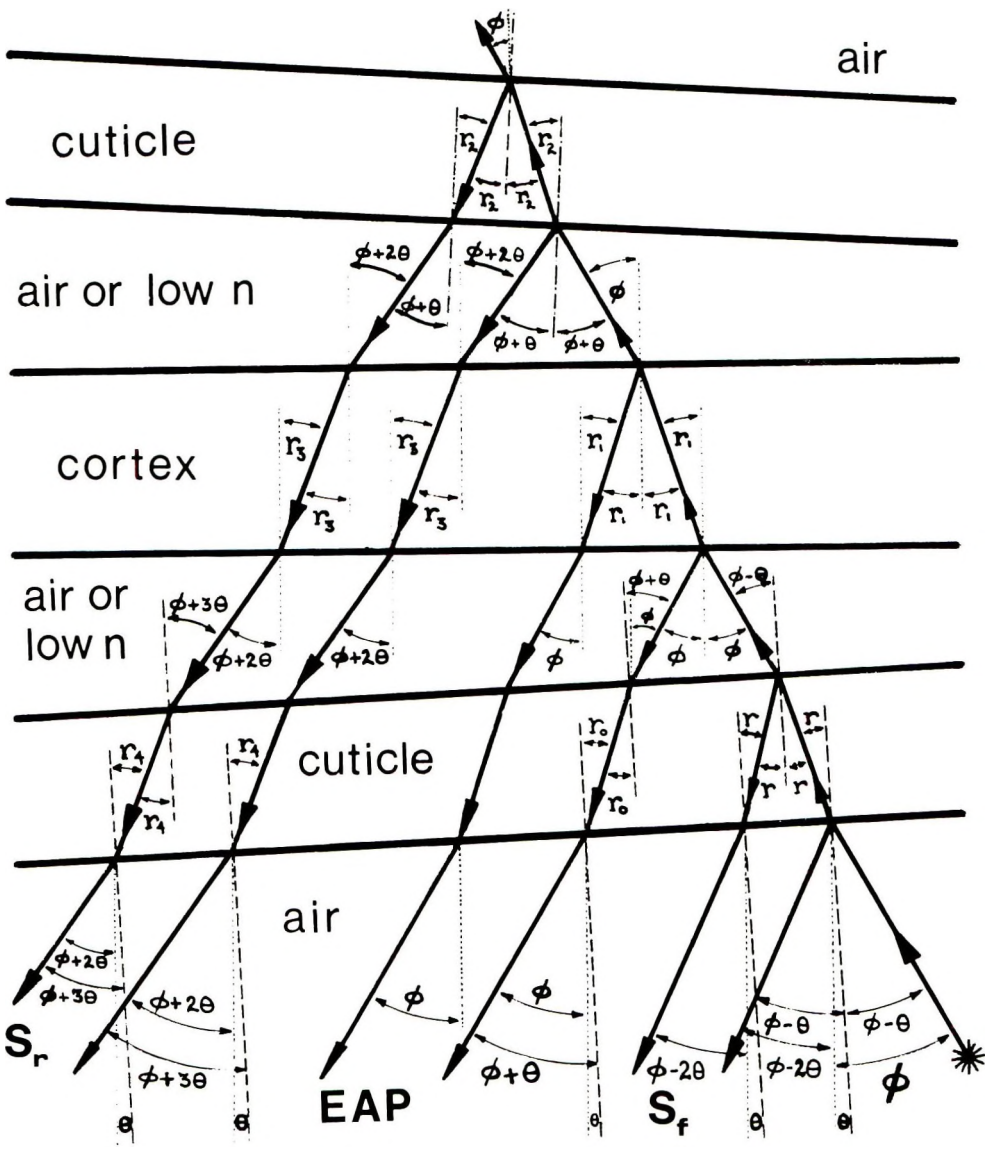

Figure 12. Optical model for hair: number 2. For orientation RER and angle of incidence ϕ vs. π_0, rays have been traced in principal plane which bisects fiber longitudinally. In this model we postulate existence of discontinuous wedge-shaped sheath of air between cuticle and cortex in order to be able to explain EAP. Specular reflections S_f and S_r are symmetrically disposed relative to $(-\phi)$. (The perpendiculars are represented by: a dotted line (π_0, for axis of fiber), dashed line (π_1, for near side scales), and dashed-dotted line (π_2, for far side scales).) At far side, angle of emergence into air would be ϕ vs. π_0 meaning that ray would remain undeviated after passing through hair (cf. model 1 in Fig. 11.). Experiment was performed using single hair fiber and horizontal He–Ne laser beam. With fiber vertical and root end Up, many of rays were deviated DOWN; with root end Down, many of rays were deviated UP. However, in both cases, a number of rays were undeviated thus indicating that true model might be Composite of models 1 and 2

OPTICAL MODEL NUMBER 2

This model is relatively more complex and is shown in Fig. 12; the caption explains the ray tracing depicted. In order to explain the EAP, it appears necessary to postulate the existence of a discontinuous wedge-shaped sheath of air (or material of low index) between the cortex and the cuticle. In addition it is necessary that θ, the angle of inclination of the scales to the axis of the fiber should be retained all the way to the inner end of each scale. In order to ascertain whether or not this was so, fibers were placed under slight tension along the axis of a tube, potted, and then sliced longitudinally until a section was obtained which indicted that the section exposed was a slice which very nearly bisected the fiber longitudinally and parallel to the axis of the fiber. From SEM pictures (4700 X) it was possible to measure the angle of inclination of the cuticle relative to the axis as $\sim 3°$ and to see that this angle was retained throughout the entire length of each scale. In Fig. 12 we indulge in artistic license and show the air films and cuticle layers having radial thicknesses comparable to the diameter of the cortex. This was done in order to trace the rays. (The radial thickness of the air film need be only $\sim 1\ \mu$m.)

In this model it is postulated that the near and far side reflections may occur from both the inner and outer layers of the cuticle. With the orientation RER, the specular reflections nearside $(\phi - 2\theta)$ and far-side $(\phi + 2\theta)$ are predicted to be disposed symmetrically relative to $(-\phi)$. For the orientation REL, they would be $(\phi + 2\theta)$ and $(\phi - 2\theta)$, respectively. The angles of emergence for rays reflected from the cuticle-air interfaces at the far side would be predicted to occur at 35° (REL) which is low by 4 from 39°, observed and at 25° (RER) which is high by 3 from 22°, observed. Thus, the errors made by the 2 models in predicting the locations of the farside peaks are comparable and opposite in direction (high versus low and vice-versa) but, of the 2 models, only the second one predicts the EAP. Since these optical parameters of hair are variable, we encounter samples where the locations of the maxima for the farside peaks are predicted to within 0.5 to 1° by optical model 2, and occasionally we run a sample where this is true for optical model 1.

THE EXTREME BREADTHS OF THE FAR-SIDE PEAKS

Without taking note of the extent of medullation, 21 Piedmont hair fibers were selected at random and strung on the sample rack after which GP curves were obtained $(\epsilon_s\epsilon_s)$ using the orientations REL and RER. The background lines were drawn in from 0 to 75° for each curve, and the peak signals above background noted. After this, the full widths of each peak at half-peak height $(\Delta W_{1/2})$ were calculated, and the ratios of the $\Delta W_{1/2}$ values (rear/front) were computed. The values found were 17.4/10.5° equals 1.66 (REL) and 24.6°/9.4° equals 2.62 (RER). These ratios change from sample to sample but, on the average, the half-width of the far side peak is about twice that of the near-side peak for noncolored hair. Also, since the maximum signals for the far side peaks are more than one-half those for their rear-side companions, this means that the integrated intensity values (far side) are somewhat greater. (In this treatment, we did not correct the intensity of each peak for the contribution of the underlying shoulder of its companion.)

In seeking an explanation for these observations, the most obvious reasons are as follows:

1. The rays which make 2 traversals through the fiber are subjected to optical disturbances from numerous interfaces and from the cortex (as well as from the medulla, if present) and have to traverse a much more tortuous path than do the rays reflected from the front face.
2. Since the rays are incident obliquely, the optical paths employed by the rays for the incoming and return trips are different. For the same reason, the scales on the near side, from which the rays emerge, are not the same as those through which they entered initially.
3. The rays reflected from the front face diverge, whereas those which enter the fiber are caused to converge by the cylindrical-lens effect of the fiber and by the focusing action of the concave far side for the rays reflected internally. Thus, other than losses suffered from scattering and absorption, the light which enters the fiber is "conserved," and this may explain why the integrated intensity of the rear face peak is greater than that of the front face peak in the case of "colorless" hair which is nonmedullated.

TOTAL INTERNAL REFLECTION

The refractive index of the cuticle is 1.548. The mean value for n_p and n_s for the cortex is very close to the index of the cuticle. As was discussed previously, total internal reflection will occur when r_c equals $\sin^{-1}(1/n)$ which for hair would yield r_c equals 40.24°, where r_c is the critical angle. Using Fig. 12 we attempt to find the angle of incidence required to produce total internal reflection at an interface leading to a ray which could emerge and be observed. In the case of the Zeiss GP-2, the maximum value for the angle of incidence achievable is 75°, and it can be shown that for rays traveling in the principal plane of Fig. 12, this could not lead to total internal reflection for orientations REL or RER. In the case of model 1 in Fig. 11, the internal angle of incidence relative to π_2 (the perpendicular to the scales on the far side) is $(r + 2\theta)$ for RER and $(r - 2\theta)$ for REL. For the orientation RER and with θ equals 2.5°, $(r + 2\theta)$ equals r_c for r equals 35.24°, and this would be achieved with an angle of incidence versus π_1 of $(\phi - \theta)$ equals $\sin^{-1}(n \sin 35.24°) = 63.3°$ or with $\phi = 65.8°$ versus π_0. Thus, for rays traveling in a principal plane, total internal reflection at the far side could occur with $\phi \neq 65.8°$ for the orientation RER. It could not be achieved for the orientation REL. In 1973 we performed some experiments employing the configuration $\epsilon_p\epsilon_p$ with the angle of incidence near Brewster's angle so as to negate specular reflection from the front face. At that time we observed very large reflected intensities which could be attributed only to total internal reflection at values of $\phi \geq 61°$. However, this light emerged as an EAP. A similar experiment was performed in 1975 with improved apparatus ($\epsilon_p\epsilon_p$, RER, ϕ = 50 to 70° by 1° steps), and the EAP was the principal component for values of $\phi \geq 55°$. As ϕ was increased above 55°, the EAP signal increased from 0.74 V (ϕ equals 55°) to 5.1 V (ϕ equals 70°); meanwhile, the peak value of the far side peak decreased steadily for values of $\phi \geq 58°$. These results indicate that the EAP orginates from internal reflection which probably does not involve the external faces of the far side scales, since the far side peak became progressively weaker as the EAP became stronger. This occurred because the incoming rays encountered the interface which produces the EAP before they reached the scales on the far side, i.e., the EAP got its hand in the till first.

It would appear that the interpretation of such experiments and the determination of an acceptable optical model for hair will not be gained until we employ a single fiber (preselected) with a circular cross-section, and a low power laser as a source of monochromatic light.

ELLIPTICAL POLARIZATION FROM INTERNAL REFLECTION AND THE EFFECTS OF SKEW RAYS

It has been shown that when the incident light is linearly polarized (ϵ_s) perpendicular to the plane of incidence we obtain signals from specular reflections when the second Polaroid disc is crossed (ϵ_p) with the first one. (It was demonstrated in a separate experiment that this could not be attributed to defects in the discs.) This means that changes in the direction of linear polarization have occurred either on reflection or on entering and leaving the fibers. These effects are caused by: elliptical polarization produced by internal reflection, and by changes in the direction of orientation (azimuthal angle) of the electric vector (ϵ_s) of the incident light on entering and leaving the fibers when the rays are not in the principal plane depicted in Figs. 11 and 12. (Details on these two items can be found in Sects. 18.3 (p. 394) and 18.4 (p.396) of (13). The effect from elliptical polarization will occur even for rays in the principal plane regardless of the diameters of the fibers. Thus, incident rays polarized ϵ_s enter the fiber in the principal plane and undergo internal reflection at the cuticle-air interface on the far side. After the internal reflection occurs, the light is not longer linearly polarized and now has a sizeable component ϵ_p at right angles to ϵ_s.

Next we consider those rays (parallel to the principal plane) which encounter the curved sides of the fibers. The plane of incidence is defined by the ray and the perpendicular to the interface. Once the ray moves out of the principal plane, the perpendicular to the interface is no longer in the principal plane. Thus, as the incoming rays move farther and farther out of the principal plane, the plane of incidence is shifted more and more, and this alters the direction of linear polarization of the incident light. The extent to which the azimuthal angle is altered by a given departure from the principal plane will be governed by the radius of curvature of the fiber. Thus, the smaller the fiber, the greater the change.

Skew rays are those which enter the fiber out of the principal plane and, by some means, get back into the principal plane (or nearly so) after multiple internal reflections. Ray tracing for such rays is possible only when the fibers have circular cross-sections and known diameters.

REFLECTION COEFFICIENTS

Using Fresnel's equations, values of the reflection coefficients were calculated for each of the interfaces encountered by the rays depicted in Fig. 12. With ϕ equals 30°, θ equals 2.5°, and n equals 1.548, the following ranges of values were calculated: for r_s, 0.062 to 0.081; for r_p, 0.021 to 0.032, and for r_u, 0.047 to 0.051. Thus, in the case of the light which is intercepted by the fibers, a relatively small amount is reflected, whereas the major portion of it is transmitted for angles of incidence as small as 30°. For larger angles of incidence, the amount reflected increases as shown in Fig. 3.

From the GP curves shown in this paper can be seen that for the front face peaks, the intensity for REL (front) exceeds that for RER (front) and that just the reverse is true

Table I
Reflection Coefficients Calculated for the cases REL Versus RER (ϕ equals 30 °, θ equals 2.5 °, n equals 1.548, incident light linearly polarized ϵ_s); Intensity Ratios, REL versus RER

				Intensity Ratios					
		r_s Values		REL(F)/RER(F)			RER(R)/REL(R)		
Orientation	Face	Model 1	Model 2	Model 1	Model 2	Experimental	Model 1	Model 2	Experimental
REL	Front	0.0703	0.0703	1.127	1.127	1.205	1.330	1.127	1.109
RER	Front	0.0624	0.0624						
REL	Rear	0.0582	0.0624						
RER	Rear	0.0774	0.0703						

for the rear-face peaks. Let us now compare the calculated and experimental values for these intensity ratios. In the case of the calculated values we again use ϕ equals 30°, θ equals 2.5°, and n equals 1.548 (for cuticle and cortex); we assume that the light losses suffered at the extra internal interfaces encountered in optical model 2 are comparable for the round trip routes in cases REL and RER so that for the rear face cases, the important reflection coefficients are those pertaining to the cuticle-air interface at the far side; we also assume that the rays lie in the principal plane, and that the incident rays are linearly polarized ϵ_s. The calculated and experimental values appear in Table I. The following items are worthy of note at this point.

1. The front face reflection coefficients are the same for both models and are within 10 per cent of the value observed.
2. In model 2, the r_s values for REL (F) and RER (R) are equal as are those for RER (F) and REL (R).
3. In model 1, the internal angles of incidence versus π_2 on the rear face are $(r - 2\theta)$ for REL, and $(r + 2\theta)$ for RER, respectively.
4. Model 2 gives good agreement with the value observed for the intensity ratio of the rear face peaks, whereas model 1 does not and is high by 20 per cent.
5. These results combined with the fact that model 2 explains the EAP incline us to favor Optical model 2 over model 1. (Please refer to the caption of Fig. 12 regarding a possible composite model.)

APPENDIX I

APPARATUS AND EXPERIMENTAL PROCEDURES

The apparatus consists of mechanical, optical, and electronic components and accessories and will be described briefly in that order after which an outline of the procedures employed will be presented.

MECHANICAL, OPTICAL, AND ELECTRONIC COMPONENTS

All the curves presented in the paper were obtained by means of a Zeiss Model GP-2

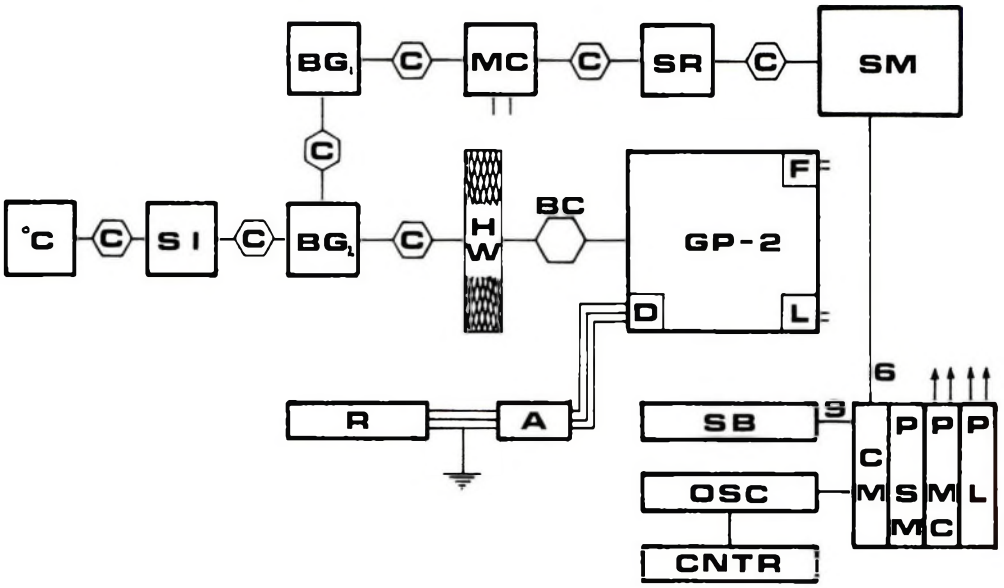

Figure 13. Electronic, mechanical, and optical components associated with mechanized goniophotometer. SM, stepping motor (Superior Electric, Model M063-FC09 with STM1800CV Translator Module); numerous components from PIC (Ridgefield, Conn. 06877), namely: C, various couplings; SR, speed reducer (400:1); MC, magnetic clutch; BG_1 and BG_2, bevel gear boxes; SI, speed increaser (1:23.3); HW, hand wheel; and BC, bellows coupling; °C, degree counter (Durant); P-L, P-MC, and P-SM, DC power supplies for lamp, MC and SM; OSC, Wave Tek DC Square Wave Pulse Generator (Model 131A with 10 turn [potentiometer] for fine tuning); CNTR, Hewlitt-Packard Digital Electronic Counter (Model 5223L); SB, switch box for control of SM and MC; GP-2, Zeiss goniophotometer; F, exhaust fan; L, GP lamp (6 V/5 amp.); D, UDT diffused SI photodiode detector (see text); A, UDT amplifier (see text); R, Houston series 5,000 strip chart recorder (see text). Numbers 6 and 9 alongside 2 cables refer to number of conductors in cables

Goniophotometer. As received from Zeiss, the instrument had to be operated manually; the detector was a selenium barrier-layer cell (photovoltaic device), and the read-out was accomplished by means of a galvanometer. A description of the Zeiss instrument was published in an article by Heinz Loof (18). A rudimentary diagram of the principal optical components is given in Fig. 6. In order to make this instrument useful in the present application, it was necessary to mechanize the drive of one of the collimators (the detector side was selected); to provide a dichroic heat filter* (placed just downstream from the condensing lens in Fig. 6) in order to reflect back to the source radiation having $\lambda > 700$ nm and thereby reduce the heating of the fibers by the incident radiation; to provide polarizing discs† (Polaroid film,‡ type HN-32, cemented between plane, parallel, colorless glass discs) in fabricated metal holders capable of producing either ϵ_s or ϵ_p in each side; to provide an assortment of neutral density

*Fish-Schurman Corp., 70 Portman Rd., New Rochelle, NY 10801.
†Obtained from Wakefield Precision Optics, 247 Water St., Wakefield, MA 01880.
‡Polaroid Corp., Cambridge, MA.

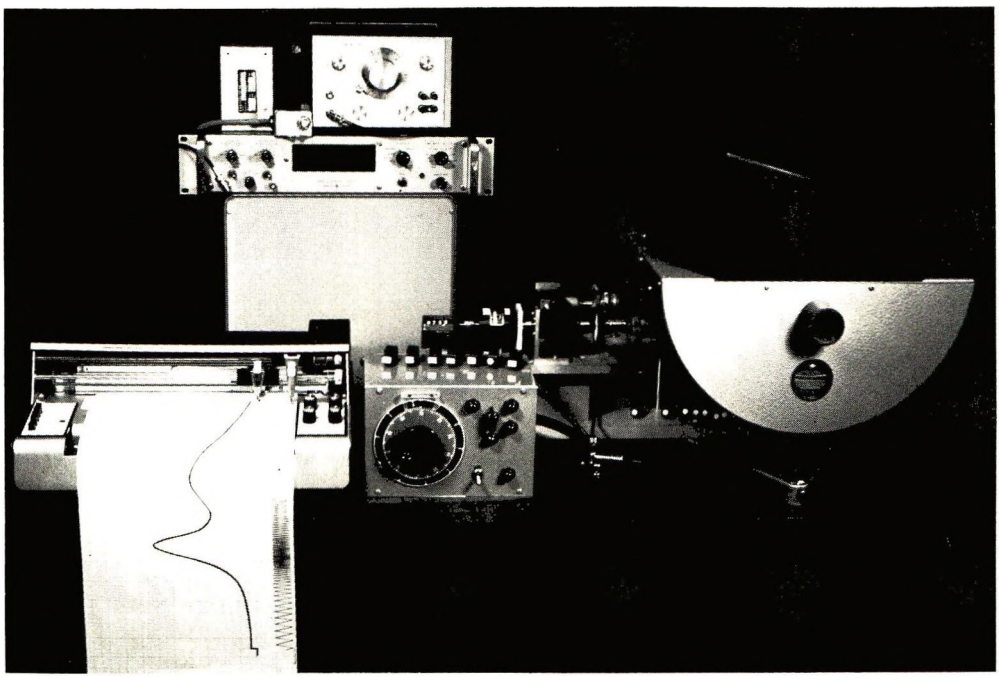

Figure 14. Recording goniophotometer assembly. In front, reading from left to right, are recorder, switch box, amplifier, and GP-2; in rear are lamp power supply, the Wave Tek Generator, HP Counter, and large box which houses power supplies for magnetic clutch and stepping motor and also translator module. Stepping motor and exhaust fan are behind GP-2. Black box on top of GP-2 is large light trap or "black hole" which traps light transmitted by sample and also excludes room light from cavity of GP

filters* with a wide variety of transmission values (T equals 0.01 to 0.5) to supplement those provided by Zeiss (T equals 0.001, 0.01, and 0.1) so that the strongest signals can generally be made to provide a full-scale deflection on the chart paper; to provide a stable light-detecting device possessing adequate sensitivity (UDT† PIN-3008 (Special PIN-10DF) Diffused Si Photodiode with flat (±7 per cent) response 400 to 700 nm), an amplifier (UDT† 101B) with a low-noise level; and a 2-pen recorder (Houston Omniscribe Recorder‡ Model 5213-15) provided with an integrating circuit so that a number (called counts) proportional to the area between the curve and the baseline can be obtained directly from the integrator trace on the chart paper without having to use a planimeter; to provide a light-tight air inlet, an air outlet, and an exhaust fan for the cavity of the GP-2 in order to maintain constant temperature and RH inside the cavity for the sake of the hair samples and to prevent overheating of the Si photodiode detector which is temperature sensitive.

*Neutral density glass filters from Fish-Shurman Corp., 70 Portman Rd., New Rochelle, NY 10801. Perforated metal screens from Perforated Products, Inc., 68 Harvard St., Brookline, MA 02146.

†United Detector Technology, Inc., 2644 30th St., Santa Monica, CA, *via* Scientific Devices, Inc., 60 Connolly Pkwy., Bldg. 11, Hamden, CT 06514.

‡Houston Instrument, One Houston Square, Austin, TX 78753, *via* Scientific Devices, Inc., 60 Connolly Pkwy., Bldg. 11, Hamden, CT 06514.

The elements employed in the mechanization of the scanning arm (LH side of Fig. 6) are shown in Fig. 13, and are listed in the caption of that figure. In mechanizing an exisiting piece of equipment, difficulties are generally encountered in coordinating the numbers on the existing instrument (in this case degree marks on the scale of the Zeiss GP-2) with the time-scale lines on the chart paper of an existing recorder. The recorder selected (Houston Series 5000) has a variety of fixed paper speeds (1, 2, 4, or 10 in./min, ÷ 1, 10, or 60). One revolution of the hand wheel on the GP-2 alters the scale reading by 23.3° so it appeared sensible to drive the gear train with a stepping motor (DC square-wave pulses) in order to be able to fine tune the speed of the GP-2 in a reproducible manner and achieve essentially perfect coordination of the degree marks with the time scale on the chart paper. It was decided to allow 15 mins for scanning the interval 0 to 75° at 5°/min which translates into a chart speed of 1 in./min with 1°/0.2 in. of chart paper and 286.2 pulses/sec to the stepping motor whose shaft rotates at 1.8°/pulse.

Silver-tipped set screws were employed for all couplings to avoid scoring the shafts. Because the motor has high torque and also because its speed has been stepped down

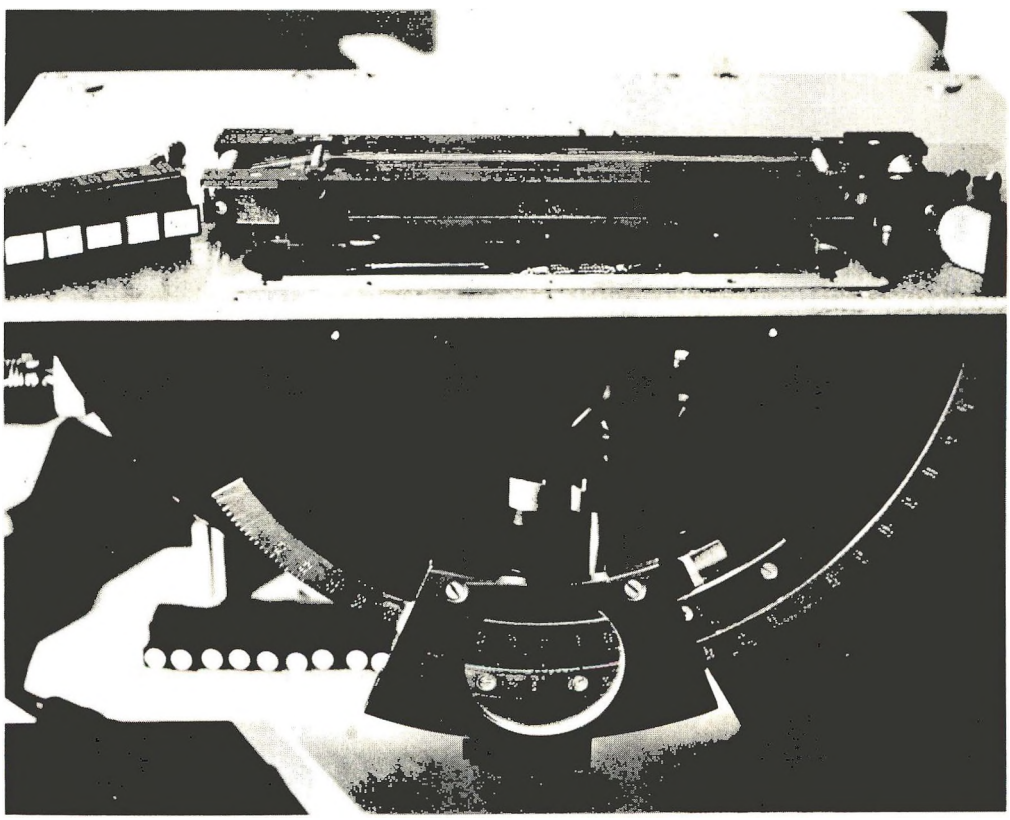

Figure 15. Interior of GP-2. Illuminating system is to right in 30° position; telescope which is mechanized and carries detector is in center at 0° position. Nonblackened brass parts at end of each tube hold rotatable Polaroid discs. On top plate can be seen long slot over which sample is placed; when in use, fibers are in plane defined by this slotted SS plate. Rack on which fibers are strung is upside down and to rear of slot. Filter holders are shown at each end of slot

400:1, the torque downstream is measured in foot × pounds rather than in ounce × inches. This means that if we energize the magnetic clutch with the motor running at, say, 2 × 286.2 pps, 1 or more of the set screws will slip, and it is not prudent to use pins instead of set screws because of the possible failure of a micro-limit-switch at the 0 or 75° positions. Thus for the present we are content to use 15 min per scan.

Photographs of the instrument are shown in Figs. 14 through 17, inclusive; elements of interest are pointed out in the captions.

THE SAMPLE HOLDER

GP curves of tresses of hair do not provide results as precise as those obtained from monolayers of parallel oriented fibers, and once a decision was made to use that approach, it was necessary to design and fabricate a versatile reliable rack on which a number of fibers sufficient for obtaining a GP curve could be strung, unstrung, and restrung in a reasonable time, e.g., 15 min or less per stringing. A photograph of most of the elements involved can be seen in Fig. 18; the caption provides further explanation.

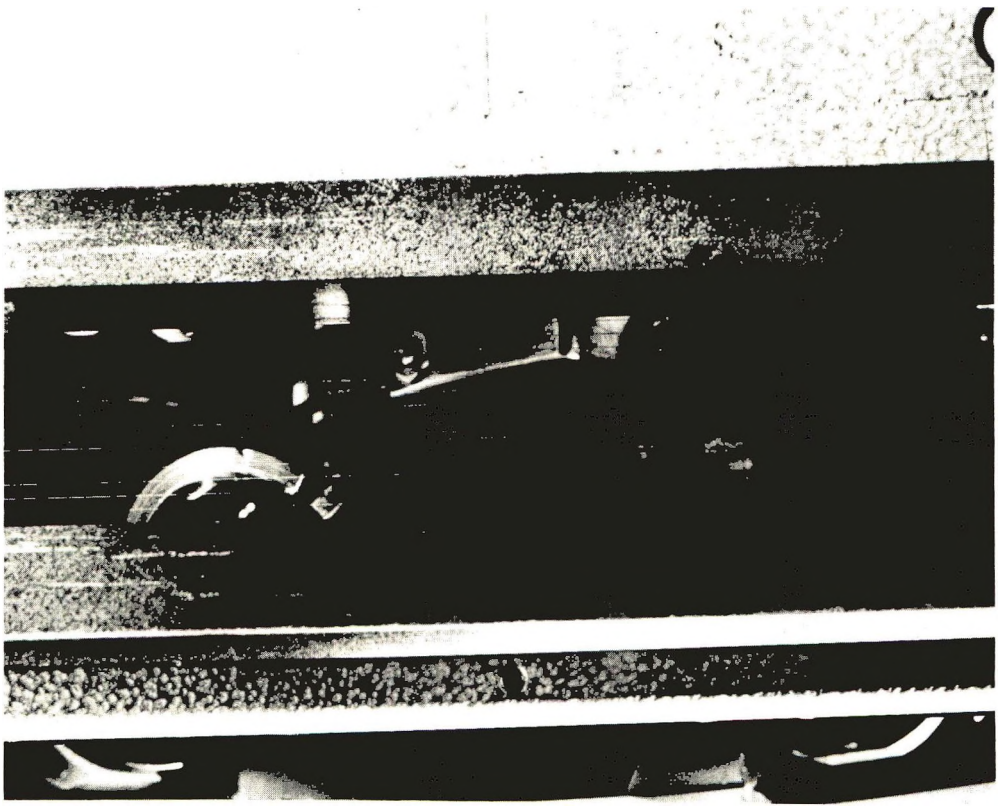

Figure 16. Cavity of GP-2 with fiber rack in place

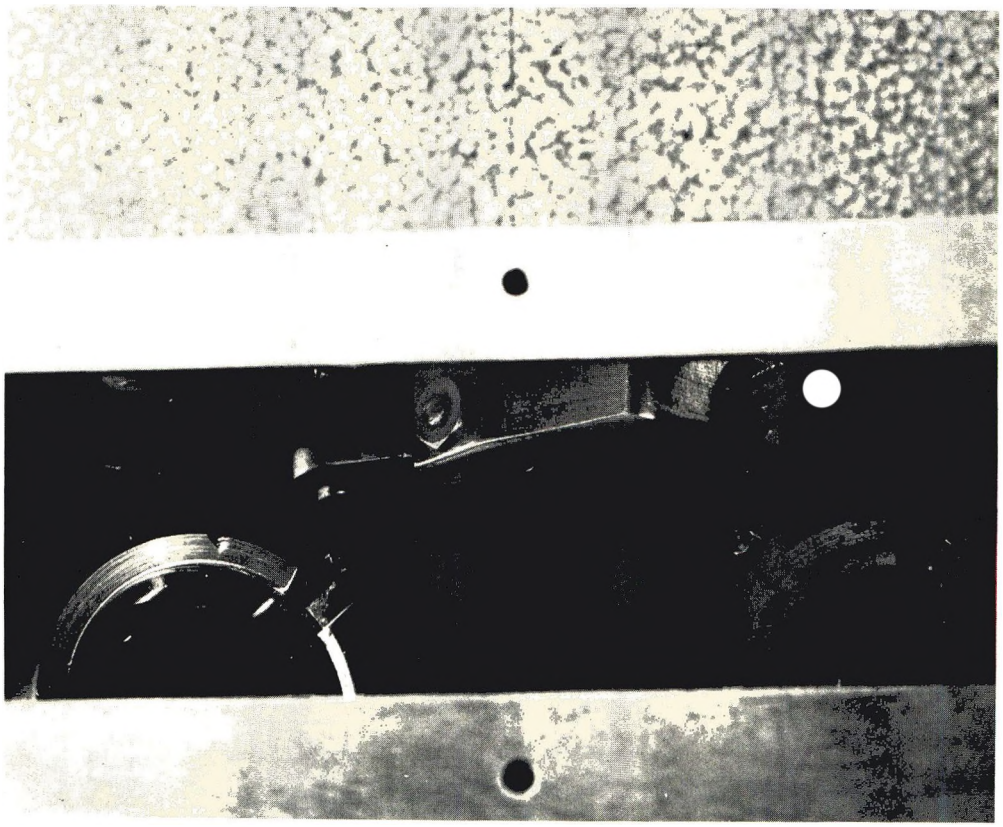

Figure 17. Same as Fig. 16 but with fiber rack removed. Both rotatable Polaroid discs are in ϵ_s position with levers against pin stops. Item in upper portion of picture moves with mechanized (detector) telescope and actuates microlimit switches at 0° (moving down scale) and 75° (moving up scale)

EXPERIMENTAL PROCEDURES

The fibers are strung using as a visual aid a "swing-away" monocular (focal lenth ~3.5 in.) placed on a spectacle frame; the distance from lens to eye should be adjusted so as to provide a working distance of ~4 in. In order to be able to use angles of incidence and observation as large as 75° from the normal and illuminate or "see" only the fibers, it is necessary to separate the 2 screws on the sample rack by 7 in. and the keyed shafts on which the washers are mounted by 9½ in.; this means that the fibers have to be ~12 in. long. If hair that long cannot be obtained, it is lengthened by glueing it to a similar hair fiber with cyanoacrylate glue. Fine-bore hypodermic syringe needles are used in pairs to guide the ends of the fibers close together before making the joint. The joints have to be positioned so thay they will not be illuminated or observed. From the traces ($\epsilon_s\epsilon_s$, RER, ϕ equals 30°) we record on our data sheets the counts for the area (S + D), the peak voltage value s_1 for the front-face peak, and the voltage values of diffuse scattering $d_{0°}$, and $d_{75°}$. In a separate experiment, by means of the zero-adjust potentiometer of the recorder, the baseline is moved, say, 0.2 V up scale and the integrator pen allowed to provide the number of counts equivalent to the area (0.2 V × 15 min). The area (D) between the baseline and the ordinate values at 0 and 75° will be 15/2 ×

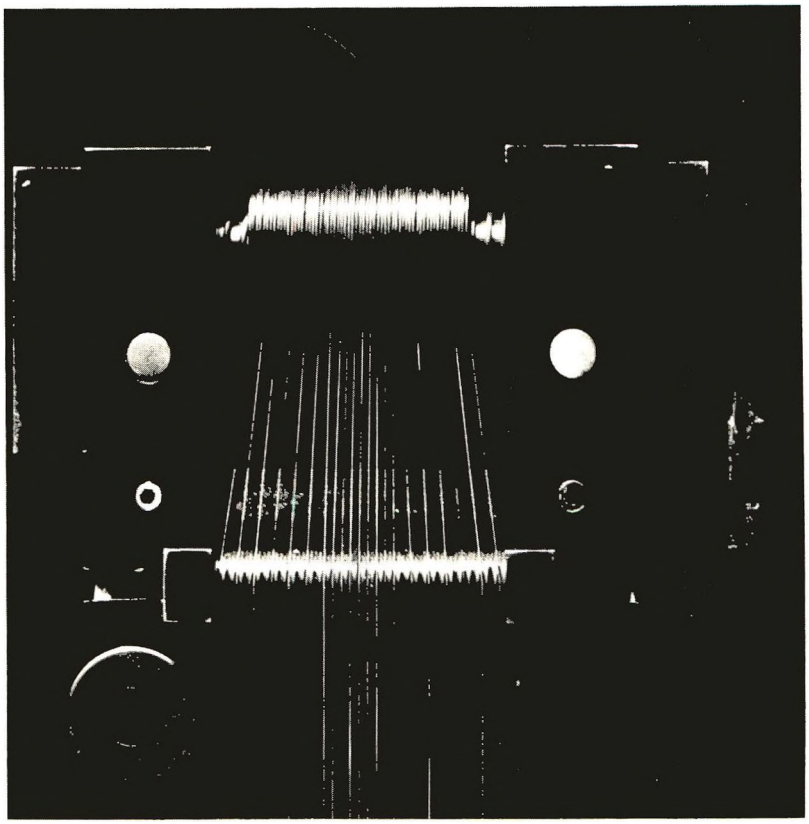

Figure 18. One end of rack on which fibers are strung. While stringing fibers, this side is up; when mounted on GP-2 it is down. Grooves in brass screw (foreground) establish spacing of fibers which are shown "wide strung." With 60 threads/in., rack can accommodate 63 fibers, although, we normally string only 21. In "wide strung" array shown, 9 central fibers are in every other groove (0.033 in. center-to-center) while 6 fibers on each side are in every fourth groove (0.067 in. center to center). When fibers are "center strung" they are placed in the 21 centermost grooves (0.0167 in. center to center). By placing fibers close together near center of the beam, signal strength is increased but diffuse scattering (from fiber to fiber) is increased more than specular reflection. Thus, we use "wide strung" array when obtaining luster values. The horizontal 3/16 in. shaft to rear has key-way slot over its entire length so that washers, having a 1/16 × 1/16 in. key, cannot rotate on shaft. One of washers is shown in foreground to left; they are made of full hard no. 302 stainless steel (0.0125 in. thick) and have been ground on both faces at periphery and then tumbled so that when they are mounted on shaft, assembly has saw-tooth edge. Polycarbonate knife edge tool at right is used to separate adjacent washers prior to inserting fiber. Weak compression springs of equal strength on each end of each washer assembly provide sufficient friction to prevent fibers from slipping once they are mounted. Should it be desirable to relieve tension, each end piece can be moved inward to provide relief of 1 per cent of length

$(d_{0°} + d_{75°})$ in units of (volts × minutes) which can be converted to counts by means of the factor obtained in the separate experiment described above.

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The optical properties of human hair II. The luster of hair fibers

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Synopsis

Part I of this paper contains the results obtained with regard to the SPECULAR REFLECTION and DIFFUSE SCATTERING of LIGHT by HUMAN HAIR FIBERS as studied by means of GONIOPHOTOMETRY. Such data provide a means of measuring the luster of hair fibers. For evaluating the LUSTER of HAIR, the method chosen employs white light polarized perpendicular to the plane of incidence and incident at 30° with observations being made from 0° to − 75° through an analyzer which is aligned with the polarizer. The integral of the trace of intensity versus the angle of observation yields the specular reflection (S) and diffuse scattering (D). The luster (contrast gloss) value is (S−D)/S. Numerical values extend from zero for bleached hair in very poor condition to ~ 0.85 for dark hair in excellent condition. Using 3 evaluations per sample, luster values have a 90 per cent confidence limit of ±2.5 per cent of the mean value.

THE LUSTER OF HAIR FIBERS

DEFINITION AND TERMINOLOGY

The word luster (or lustre) is defined as: "a glow from reflected light," or as "natural or artificial brilliancy or sheen;" synonyms are gloss, refulgence, or sheen. Artists, novelists, and poets have used and misused the word for describing optical effects, sensations, and human character so that most people are confused about its meaning because of the mystique surrounding it. A book by Harrison (1) gives a survey of the literature on gloss and related subjects published prior to 1945. Today, this book is of value mostly in an historical sense, but it does contain references to articles, which would be very difficult to find otherwise. A paper (2) (by J. S. Christie of the Hunterlabs) contains a useful appendix, which gives accepted definitions of terms related to geometric attributes of reflectance, i.e., those attributes related to the geometrical distribution of reflected light rather than to its color characteristics. From (2) we quote the definitions for gloss and luster. "*Specular gloss (shininess):* The appearance attribute corresponding to the intensity with which lights are seen to be specularly reflected." *Luster:* The appearance characteristic of a specimen associated with a change in intensity of reflected light when the angle of view is changed."

In order to reduce experimental evaluations to numbers, terms such as gloss and luster need to be defined in terms of measurable parameters. This was done by R. S. Hunter (3), and a useful synopsis of his recommendations appeared in a paper (4) by Dorothy Nickerson. Referring to Figure 2, in Part I of this paper, if I_0 is the incident intensity and if we assume that the intensity(s) of the light specularly reflected at the interface is

measured at an angle equal to that of the angle of incidence and on the other side of the normal to the interface, the specular gloss would be

$$G_S = s/I_0 \tag{1}$$

For low-gloss surfaces, the sheen would be given by the same ratio when the beams are used at grazing incidence and grazing reflection.

The term contrast gloss applies to the contrast existing between the intensity of the specularly reflected light (s), measured at the angle of direct specular reflection, and that of the diffusely scattered light (d), measured at an angle of emergence of 0°, i.e., along the normal to the interface. Thus, for Hunter's contrast gloss, we have

$$G_c = s/d \tag{2}$$

However, as pointed out by Nickerson (4), this function goes to infinity as d approaches zero. For this reason, she suggested, and put into use, an alternative form of this expression, namely

$$G_c = (s - d)/s \text{ or } (1 - d/s) \tag{3}$$

which has limiting values of 0 when d equals s, and 1 when d equals 0. (The value of G_c could be negative if $d > s$ but such cases are excluded from consideration.) The function in eq. (3) was employed (4) to evaluate the luster of cotton fibers and fabrics and was found to correlate well with estimates of relative luster values made visually.

A similar type of expression, used in an inverse sense, was employed by Jeffries (5) who made a relatively thorough analysis of the optical elements involved in making measurements of the extent of delustering of textile fibers and fabrics by means of goniophotometry. In the third paper, noted in (5) , he stressed the advantages of employing polarized light in making such measurements.

Both Nickerson and Jeffries employed white light and measured spot values of s and d at their respective individual angles. In evaluating the luster values of single fibers, Holboke and Berriman (6) oriented the fiber vertically, illuminated it with an horizontal beam of monochromatic light linearly polarized vertically and, using a Polaroid®* also in the exit beam, made two scans from 0 to 180°, one with the Polaroids aligned, the other with the Polaroids crossed. Letting α be the degree of coherency of the scattered light (i.e., the degree to which the original direction of polarization of the incident beam was retained after scattering by the fiber) they obtained an expression for α

$$\alpha = (I_A - I_c)/(I_A + I_c) \tag{4}$$

where I_A and I_c are the integrated intensities for the angular interval 0 to 180° when the Polaroids were aligned and crossed, respectively. They demonstrated that values of α correlated well with relative values of luster estimated visually. (The limits for α would be 0 and 1.) We attempted to use this method employing oblique incidence with a planar array of oriented, parallel hair fibers (as depicted in Fig. 5 of Part I). The range of values obtained for α was very small, and the method was deemed to be unreliable when using oblique incidence because the direction of polarization of the incident light is altered by the curved walls of the fibers, whereas this problem is not en-

*Polaroid Corporation, Cambridge, MA.

countered when using normal incidence and incident light linearly polarized with ϵ parallel to the axis of the fiber. For human hair, there are large variations in color and size among fibers even when obtained from 1 head, so measurements of the luster of single fibers would not have the statistical significance required. For these reasons, the method was abandoned.

THE METHODS EMPLOYED FOR MEASURING THE LUSTER OF HAIR

Starting with the qualitative definition of luster given in (2), we make it quantitative by saying that luster is given by the rate of change of the intensity of specularly reflected light with the angle of observation when employing a fixed angle of incidence. This concept was investigated using unpolarized incident light as well as the configuration ϵ_s ϵ_s (see Fig. 2, Part I for notations used). The slopes measured on the goniophotometer (GP) curves were those on each side of the specular peak from the front face. It was found that the method did not provide a large spread in values among different kinds of hair, and that the precision was not good enough. Thus, at present, we use this approach only when other methods are not appropriate (which happens occasionally).

For hair, the spot values for s (specular reflection) and d (diffuse scattering) are obtained from GP curves at the top of the front-face specular peak and from the background value at 0°. These are tabulated as well as values of $g_c = (s-d)/s$ where we employ lower case letters to designate spot values versus capital letters for integrated values. We find for various kinds of hair that the function g_c has high precision, but has only a narrow range of values.

From the recorded GP curve, we obtain directly the integrated area between the curve and the baseline. This area we take to be (S + D) the sum of the specular reflection and diffuse scattering. We "draw" an imaginary line between the ordinate values at 0° and 75°, the extreme limits of the angular region scanned, and assume that the area between this line and the baseline is D, the diffuse scattering. Knowing (S + D) and D, we obtain S by taking the difference and can then evaluate the function for luster

$$\text{Luster} = G_c = (S\text{-}D)/S \tag{5}$$

For the angular interval scanned (0° to −75°), we find the highest precision to be obtained when the slope of this imaginary line is a minimum, i.e., when the spot values at 0° and −75° are most nearly equal, and this condition obtains when we employ the configuration $\epsilon_S\epsilon_s$, the orientation root ends right (RER), and ϕ equals 30°. For hair fibers possessing the wide variety of colors and diameters encountered in nature, this function yields values ranging from as low as 0 for damaged bleached hair to as high as 0.85 for very dark brown hair in excellent condition. Twenty-one fibers are used per ringing, and 3 stringings are used per evaluation. This procedure yields luster values ith a precision of ± 2.5 per cent of the mean value at a 90 per cent confidence level. (This is equivalent to a σ value of ± 1.5 per cent of the mean value.) The time required to check the orientation (finger tip test) and to mount 21 fibers is 15 min after which the GP curves can be obtained immediately. The time required to run 1 GP curve is 15 min, and duplicate curves are obtained for each stringing. Processing the data from 2 curves requires an additional 20 min so the total elapsed time needed at present for a luster measurement involving 3 stringings and 6 curves is ~ 3.25 h. (The instrument does not have to be tended while the curves are being traced.) We get enough light from 15 fibers but actually string 21 fibers to achieve results having greater statistical

Table I

Values Found for 3 Different Luster Functions Pertaining to Various Types of Hair and Precision Achieved at the 90 Per Cent Confidence Level Expressed as a Per Cent of the Mean Value. (All Luster Measurements made from Wide Strung Fibers.)

	(S − D)/S	(s − d)/s	S/D
Very dark brown	0.85	0.97	6.7
Medium brown	0.80	0.96	5.0
Light brown	0.74	0.93	3.8
Blond	0.73	0.94	3.7
Nonmedullated piedmont	0.70	0.90	3.4
Ash blond	0.68	0.91	3.1
Gray	0.60	0.89	2.5
Navajo, black[a]	0.56	0.89	2.3
Medullated piedmont	0.25	0.76	1.3
Excessively bleached[b]	~0	~0.75	~1.0
L(90)	±2.5%	±0.7%	±7.5%

[a]Hair fibers had diameters ~90μm and were damaged; if in good condition (S − D)/S should be ~0.90 (estimated).
[b]Also damaged.

significance. Also, the GP curves could be obtained in half the time, but there are certain mechanical problems which preclude this at present.

In addition to the functions (S−D)/S and (s−d)/s, we also tabulate values for the ratio S/D from integrated values and find this to be of interest. The range of values for these functions found for several different colors of hair are given in Table I.

The values in Table I show that (s−d)/s has high precision but poor sensitivity; S/D has a fairly good range of values but poor precision; (S−D)/S has a good range of values and a precision that is high enough for the method to be valuable in making assessments of the luster of hair by an objective instrumental method.

VISUAL ESTIMATES OF LUSTER

It is both desirable and necessary to demonstrate that significant changes in luster, which are detectable instrumentally, can also be detected visually even by unskilled observers. For making visual estimates of luster we employ a 150 W xenon arc* in a lamp house provided with condensing lenses having apertures of 3 in. The lamp is placed near the ceiling on a shelf on 1 wall so that the optic axis is about 12 in. below the ceiling. The beam is slightly divergent, and after traveling horizontally a distance of ~ 12 feet is intercepted by a flat mirror, which directs the beam downward vertically. At a distance of 2.5 ft below the center of the mirror, the beam encounters the sample which is at eye level for an individual (5 ft-10 in.) who is standing. (The vertical height of the sample can be adjusted to suit the height of the viewer.) The angle of incidence relative to the perpendicular to the plane of the sample is adjustable and normally is set at 60°. Samples are mounted in pairs side-by-side separated only by a narrow strip of dull black paper, and are viewed from a distance of 10 ft. The fibers are mounted with their root ends up, and at the viewing distance employed, only diffuse scattering is visi-

*Type X150S-2008. Illumination Industries, Sunnyvale, CA.

ble from the hair. To provide specular reflection, an artificial high-light is created near the top of the sample over the entire horizontal width by means of a 10° angular wedge fastened to the sample holder and placed underneath the hair. The act of mounting the samples on the holder creates slight tension and alignment; this enhances the possibility of making a judgment. The light on the hair approximates sunlight in spectral composition and, at the surface of the hair, provides an illumination level about one-eighth that of bright noonday sunlight. Samples are viewed with the room lights out. The observer is asked to make a judgment on the relative degrees of contrast existing between the highlight and the diffuse scattering on each side. If they are unable to make this judgment they are asked to judge which side has the lesser amount of light coming from the dark area below the highlight. The latter type of judgment can be made by unskilled observers (clerical workers, shop mechanics, visitors, and administrators) so that it can be said that the enhanced luster of hair treated with an agent that increases the luster by 20-per cent versus the control can be detected quite easily, whereas the effect of an agent that enhances the luster by only 5 per cent can also be detected visually but with greater difficulty.

FACTORS WHICH INFLUENCE THE LUSTER OF HAIR

Optically, it would appear that the physical and geometrical factors which have the greatest effect in determining the luster rating of unmodified human hair are as follows: high specular reflectivity, straightness, low diffuse scattering, alignment and color. These factors will be discussed in the order listed above.

SPECULAR REFLECTIVITY

The specular reflectivity depends on the refractive index of the exocuticle, the cleanliness, on the absence of surface defects of the exocuticle, and to a lesser extent on the color of the hair. Due to the extensive cross-linking of the exocuticle, it is dense, and the refractive index is high. It might be difficult to find a substance possessing all the compatabilities required, having an index higher than that of the cuticle, yet capable of forming a very thin film ($\lesssim 0.1\ \mu$m thick) on the hair so as to increase the specular reflectivity and still retain the optical effect of the scales.

The cleanliness of the hair can be controlled by the owner, and, as stated earlier, it is difficult to increase the specular reflectivity of clean hair. Defects in the surface of the cuticle would lower the reflectivity and increase the diffuse scattering. Such defects could be produced by using a metal comb with burrs on the teeth or by "teasing" the hair (combing it against the grain).

The color of the hair has very little effect on the specular reflectivity because the principal specular reflection is a surface phenomenon which occurs at the air-cuticle interface on the near side of the fibers (the side initially encountered by the incident rays) and because the cuticle is not pigmented. Thus, if white light is incident on the fibers, the front-face peak consists of white light, while the rear-face peak is the color of the hair. The near equality of the front-face specular reflectivities of blond hair and very dark brown hair is shown in Fig. 1. However, in the treatment we employ for evaluating luster by means of the function $L = (S-D)/S$, the integrated value S is the sum of the near-side and far-side specular reflectivities, and the contribution of the far-side

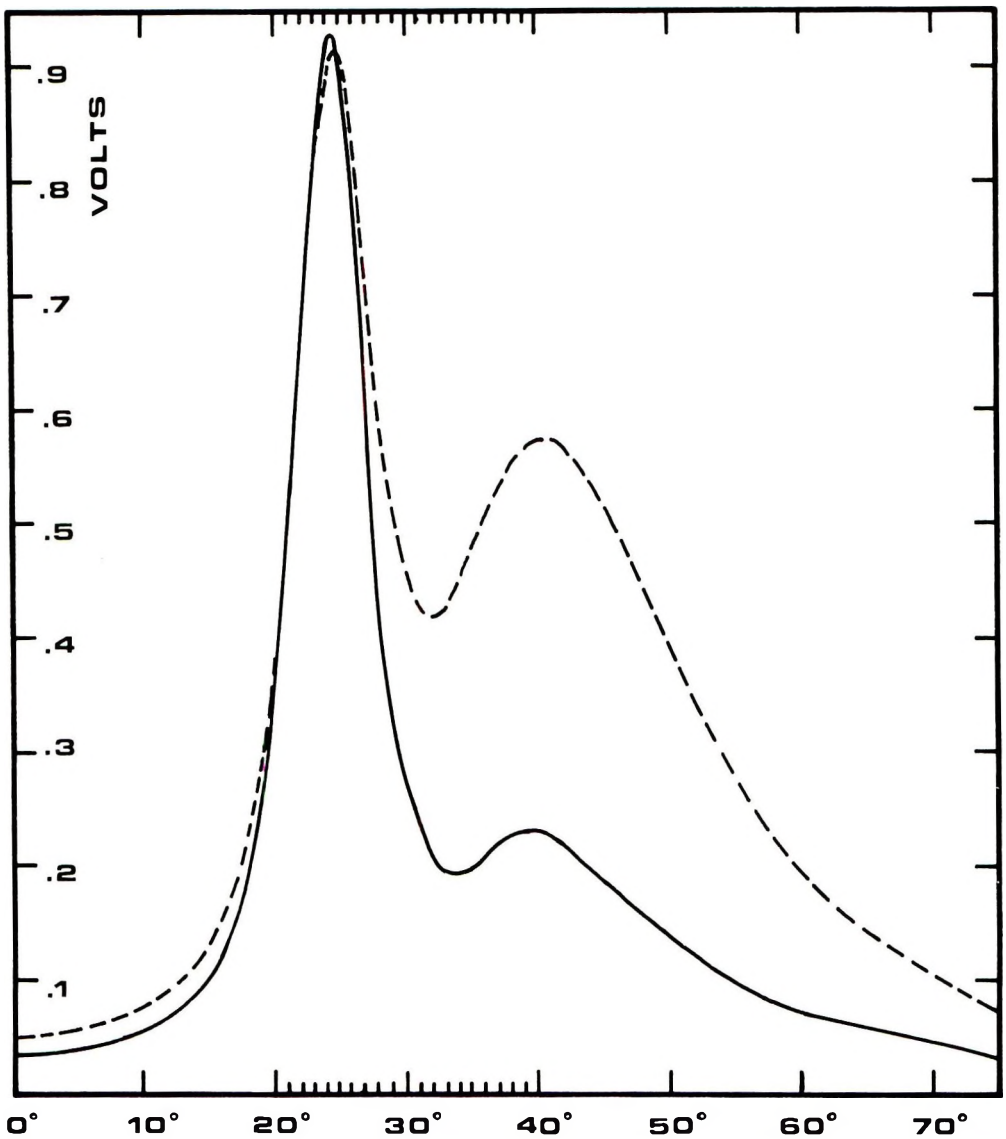

Figure 1. Comparison of specular reflectivities of blond hair and very dark brown hair. $\epsilon_s\epsilon_s$, RER, 21 fibers, ϕ equals 30°, 1° slits, T equals 0.168, center strung; dashed curve: blond hair, average diameter of fibers equals 64.0 μm, spread equals 47.2 to 87.6 μm; solid curve: very dark brown hair, average diameter of fibers equals 65.8 μm, spread equals 49.9 to 89.4 μm. The most important thing shown by these 2 curves is that specular reflectivities for the front-face air-cuticle interfaces (peaks at ~ 24.5°) are very nearly same, proving that refractive index of cuticle governs specular reflectivity. Other things shown are large differences in intensities of rear-face peaks in diffusely scattered light, and in asymmetry of scattering. From front-face peaks, θ value is slightly larger for solid curve, while for rear-face peaks, reverse is true indicating that θ values must be measured from locations of front-face peaks. From light incident on fibers, we ascertained percentage detected by using light reflected from polished black glass (n equals 1.515, reflection coefficient equals 0.06035 for ϵ_s) as reference. With ϕ equals 30°, pattern of light at fibers was ellipse (axes equal 29.16 mm and 25.53 mm, area equals 584.7 mm^2). 21 fibers captured 6.6 per cent (blond) and 6.8 per cent (dark brown) of incident light. Integrated intensities were obtained from GP curves in terms of counts; these provided following: front specular/incident captured equals 1/2,564 (blond) versus 1/2,500 (dark brown); (S + D)/incident captured equals 1/923 (blond) versus 1/1,544 (dark brown); and front specular/(S + D) equals 1/2.78 (blond) versus 1/1.62 (dark brown)

peak decreases as the extent of the color increases. Thus, the specular reflectivity of the near-side peak is altered very little by the color of the hair, whereas the apparent specular reflectivity of the far-side peak, judged by its intensity on the GP curve, actually vanishes for black hair (see Fig. 9 in Part I). The inclusion of both specular reflections in S simplifies the evaluation of S and will not affect the values of L so long as $S >> D$, which is generally the case. In unusual cases, where $D \approx S$, the values of L actually will be kept from going negative by including the far-side specular reflections in S. In the textile field, S always includes the near-side and far-side reflections because, except in the case of oriented wool fibers (a remote possibility), both peaks will be observed at the same angle. This probably is the reason why the specular reflectivities of textile fibers change markedly with the color of the fibers.

DIFFUSE SCATTERING FROM THE SURFACE AND FROM THE INTERIOR

Scattering of light can be anticipated from optical discontinuities which are on the surface or in the interior. In the case of the outer surface, such discontinuities would include the edges of the scales themselves, dust particles and the like, damaged scales, scalp secretions and debris, and split hairs. In the case of the interior, scattering would occur because of the medulla, granules of melanin, fibrillar polymer molecules, any naturally occurring glue or pasty material used for maintaining the integrities of the fibers or filling in the interstices, and from voids or inclusions; very marked scattering would occur from certain kinds of gray hair fibers in which gray pigment particles or voids are situated in a chain along the axis of the fiber.

In general, for particles which are spherical and whose diameters are less than one-tenth the wavelength of the light employed, the intensity of scattering is proportional to the third power of the diameter of the particle and to the inverse fourth power of the wavelength. Thus, if we halve the wavelength, the intensity of scattering is increased by 2^4 equals 16 fold. Likewise the scattering is proportional to the number of particles per cubic centimeter and to the volume of the individual particle. If unpolarized incident light is used, the angular dependence of the scattering is symmetrically disposed relative to the 90° direction and is twice as great in the forward and backward directions as it is at 90°. In addition, for purposes of orientation, it is well to recall that the scattering is proportional to $(\Delta n/\Delta c)^2$ for a solution of polymer particles in a liquid medium or to $(N_1/N_0)^2$ for a suspension of particles in a matrix.

If a change is made in the shape of the particles from spherical to ellipsoidal, if the volume of each individual particle remains the same as the spherical particle, and if the volume concentration remains the same, then the total amount of light scattered for the ellipsoids will be greater than that of the spheres.

As the particles increase in size so that they have gross dimensions equal to or greater than the wavelength, the intensity of the light scattered in the forward direction increases at the expense of the backward scattering, and the scattering envelopes become progressively more unsymmetrical as the size increases. For melanin granules, it would be anticipated that the light-scattering envelope would be unsymmetrical. The same would hold for the roughness on the surfaces of the hair fibers attributable to the ends of the scales.

Table II
Effects Produced on Luster Parameters by Touching Strung Hair Fibers with the Fingers. Single Source, Light Brown Virgin Hair; $\phi = 30°$, $\epsilon_i\epsilon_s$, RER, Slits = 1°, 21 Fibers

	Counts			Luster Functions		Spot Readings		(Volts)
	(S+D)	S	D	S/D	(S−D)/S	s	d	(s−d)/s
b	8677	6796	1881	3.613	0.7232	3.537	0.206	0.9418
a	8703	6759	1944	3.477	0.7124	2.858	0.218	0.9237
Per Cent Change	+0.30	−0.54	+7.34	−3.76	−1.45	−19.2	+5.83	−1.92

b = before touching hair.
a = after touching hair.

DECREASE OF LUSTER PRODUCED BY HANDLING HAIR

Handling clean hair with the fingers and palms of the hands soils the surfaces of the cuticle and decreases the luster. People who wear glasses should grasp one lens on opposite sides of the lens with thumb and middle finger and then look at the soil left on the surfaces of the lens. The specular reflectivity is diminished, and the light scattered at the surfaces is increased. The same thing happens to hair, and this decreases the luster by a measurable amount. A sample of single-source light brown virgin hair was strung and a curve run after which the fibers, while still strung, were touched from opposite sides in the manner described above over the length of sample involved in making the measurements. The curve was then rerun, and the results obtained are shown in Table II.

Thus, it appears quite likely that handling hair fibers without using rubber gloves can decrease the luster by an amount which is both measurable and significant. In anticipation of this finding, we have been using either rubber gloves or rubber finger cots when handling hair prior to making luster measurements. In addition, in the case of hair samples submitted for evaluation we have to assume that the hair has been soiled by handling and execute the required cleansing treatments ourselves whenever possible. Probably there is no other measurement made in these laboratories as sensitive to surface contamination as measurements of luster, and the staff members of any similar laboratory need to be alerted to this if they are interested in subtle distinctions requiring luster measurements of high precision. By the time a swatch of hair has been handled by 5 observers, the luster of the hair will have been altered undeniably, but most people treat is as though it could not possibly be soiled by their hands.

EFFECT OF COLOR ON LUSTER

With regard to color, other conditions being equal, the darker the color, the higher the luster. This arises from the fact that the light which has entered the hair and has reemerged at an angle different from that of the direct specular reflection (but still close to it) will be much less for dark hair than for light hair. Thus, since the specular reflection depends more on the refractive index than the color, a greater contrast exists between the specular reflection and the diffuse scattering for dark hair than for light hair, and the luster of the dark hair is judged to be higher. In the case of the sample of

black Navajo hair, there was some cuticle damage which enhanced the diffuse scattering and decreased the luster (see Figs. 9 and 10 of Part I).

EFFECTS OF STRAIGHTNESS AND ALIGNMENT ON LUSTER

Two other important factors which will affect the luster are the degree of straightness of the fibers and the degree of alignment. The straighter the fibers and the higher the degree of alignment, the greater will be the level of illumination at the eye of the observer when the eye is situated at an angle of observation such as to see the specularly-reflected light either in a plane (perpendicular incidence) or on the surface of a cone (oblique incidence) according to the principles enunciated in the material describing Fig. 1 in Part I. For hair that is kinky as in an Afro hair style, the luster will be low because of the complete lack of straightness and alignment. The light that is reflected goes in all directions and thus virtually approaches the condition of being scattered diffusely rather than specularly-reflected.

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Letters to the Editor

Sir:

Yin et al. (1) have provided an interesting and useful contribution describing the role of fiber diameter in various "use" properties of hair masses. This letter suggests that certain morphological or physical considerations, also diameter related, might help to extend the understanding of their results.

The authors assume their hair fibers to be uniformly circular in cross-section having "no reason to assume that the sized fiber groups separated from a homogeneous hair mass had widely different cross-sectional shapes." It is possible to explain the unexpected combing test results—coarser hair being found harder to comb than finer—if it is assumed that the coarser fibers are more elliptical and the finer ones rounder. With this picture, the thicker elliptical fibers pack more densely into the spaces between the comb teeth, since the preferred orientation of the hairs would be with the major axis parallel to the comb teeth. Accordingly, the frictional forces would be greater, consistent with the reported combing data. That cross-sectional ellipticity increases with hair diameter is supported by the observations of Fourt (2) who found coarse hairs to exhibit major:minor axis ratios roughly 20 per cent smaller than fine fibers from the same head.

Additionally, one of the authors suggests (3) that with the ellipticity pattern suggested above, the bending moment of the hair would depend on the minor-axis dimension, rather than on the average diameter. Thus, the expected differences in the facility of separation of crossed-over entangled fibers ahead of the comb would be minimized as between coarse and fine hair.

The superior set holding reported for coarse hair versus fine hair shows a diameter relationship, although, not one comfortably in the range of a fourth power dependency with diameter, as implied. The ratio of set retentions of the coarsest to finest tresses (at 100 min) is approximately 1.6, while the fourth power diameter ratios are approximately 3.5. Furthermore, while bending and torsional forces are involved in set-holding, implying a fourth power dependency with diameter is not appropriate, since the deformations are not elastic in character. For viscous behavior in a time-dependent process like set relaxation, creep compliance is more likely the relevant kind of physical deformation. Interestingly, the rate of creep in torsion has been shown (4) to be roughly twice as great in fine hair fibers as in coarse hairs from the same head.

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Editors Note: The authors of this article have indicated that they are in general agreement with the findings of Mr. Bogaty.

Dr. John J. Sciarra
Editor

Book Reviews

FOAM CONTROL AGENTS, by Henry T. Kerner, Noyes Data Corporation, Park Ridge, New Jersey, 1976. xii + 372 pages, 10 Figures, 25 Tables. Price $39.00.

This is another volume (Number 75) in the series of chemical technology review books published by the Noyes Data Corporation on a wide range of technical subjects. Like other volumes in this series, this book supplies detailed information based entirely (and exclusively) on the U.S. patent literature.

This volume reviews and gives examples in the field of foam control agents from 206 U.S. patents that were issued between 1960 and 1976. The book is well indexed by company, names of the inventors, and by patent number.

The book is divided into chapters categorizing applications where foam control agents are used. These comprise the following fields: detergents and cleansers; pulp and paper; lubricants, fuels, and organic liquids; textiles; phosphoric acid processes; latex, coating, and photographic application; fermentation, pharmaceuticals, and foodstuffs; polymerization and distillation; antifreeze, drilling fluids, acid gas separation, and other applications; and foam control—general processes.

There also is a short introduction and a foreword; the latter is written in a somewhat promotional style and suggests "fifteen reasons why the U.S. Patent Office literature is important to you," and presumably, why you should buy this book.

As the titles of the chapters indicate, few applications are covered that are of concern to cosmetic chemists. Only one example of some relevance is cited, namely, U.S. Patent 3,853,989 which describes a technique for controlling or suppressing internal foaming in aerosol containers. There are only a few pharmaceutical examples and are limited to the use of simethicone in a well-known antacid product and to formulations of calcium novobiocin suspensions with lauryl sulfates.

This volume will probably be of practical use to workers in many of the fields listed in the chapter headings. For libraries servicing primarily the cosmetic or pharmaceutical industry, there is little reason to add this volume to their collection.—ERIC JUNGERMANN—Helene Curtis Industries, Inc.

ENCYCLOPEDIA OF CHEMICAL PROCESSING AND DESIGN, Vol. 3, Edited by John J. McKetta, Marcel Dekker, Inc., New York, 1977, 493 Pages, Price $95.00.

This is the third volume in what should be a long and detailed series on the developments in the field of chemical processing. Volume 3 covers the topics that lie between Aluminum and Asphalt, design. This volume has been prepared by 23 renowned individuals and organizations.

Each chapter contains sections on chemical and physical properties, economics, the manufacturing process, shipping, storage and handling, in addition to a reference section.

usly, the cosmetic chemist is robably not going to find many topics of interest in this volume, but he will find that the material cited in the Amine and Amino Acid chapters is excellent. A perusal of these chapters by the comestic chemist will lead to a better understanding of the problems associated with their synthesis and some of the reactions that these compounds undergo.

The chemical engineer will find much material relating to plant design, operating parameters and economics, which is not usually found in a book of this nature.

The aniline design problem is a step by step analysis of how to design a plant for chemical production. This chapter should be a useful refresher for the chemical engineer who has faced the problem of obtaining cost estimates for a new plant or process design.

The only drawback is the lack of an index for Volume 3, but I hope that the editors will prepare an index once this encyclopedia has been completed.

In summary, this book should serve the needs of the cosmetic chemist and the chemical engineer and would be an excellent addition to the Research Library.—GERALD ROYE—Chesebrough-Pond's.

INTERFACIAL SYNTHESIS, Vol. 1, Fundamentals, Edited by F. Millich and C. E. Carraher, Jr., Marcel Dekker, Inc., New York, 312 pages, illustrated. Price $34.50.

Volume 1 of a two-volume series deals with the present day exercise of interfacial synthesis, which is a new technology that has seen limited application in the preparation of some condensation polymers. Volume 1 is introductory in nature and is intended as a means of stimulating further study in this field.

The book consists of various chapters contributed by well-known scientists from the United States and overseas. One chapter discusses the principles of mixing and fluid mechanics and their application to chemical processing. Another is on the effect of high speed stirring and the effects of that on chemical reactions such as alkylation, gas/liquid hydrogenation, emulsion, suspension, and solution polymerization. The book also discusses the kinetics of interfacial synthesis and reports on some preliminary studies conducted.

The chapter on liquid/vapor interfacial polycondensation discusses the synthesis of various polymers and copolymers and the importance of macroscopic kinetics in copolycondensation in two-phase systems and the various experimental parameters involved.

The book also discusses biomembrane organization and areas where biological polymers and interfaces are of key

significance such as in the area of surfaces of collagen and keratin; surgical and dental adhesives, etc.

This book will prove to be of value to students and researchers interested in new avenues of synthesis and mechanistic exploration as well as being a good source for the published literature in this field.—HOSNY Y. SAAD—

ADVANCES IN MODERN TOXICOLOGY, Vol. 4, Dermato—Toxicology and Pharmacology, P. N. Margulli and H. Maibach, Halsted Press, Div., John Wiley and Sons, Inc., New York, 1977. XVIII + 567 pages. Price $37.50.

This book marks another useful volume in the *Advances in Modern Toxicology* series. Dermatotoxicology is the science of adverse skin effects and the substances that produce them. An international list of authors has been brought together to produce one of the few definitive books on a broad range of related topics, including: effects of topical agents on sweat and sebaceous glands, cutaneous absorption and metabolism, eye and skin irritation, contact sensitization, photoallergy, human patch testing, chemically induced alopecia, cutaneous carcinogenesis, and the effect of drugs on skin microbiology. Each chapter is written by an authority in that field and includes many useful charts, tables, and illustrations. An adequate list of references is included after each chapter. The book is well indexed and should prove to be a useful reference work for researchers interested in the toxicology and physiology of the eye and skin.—CHARLES O. WARD—Huntingdon Research Center. (Present address: Gulf Science and Technology Co.)

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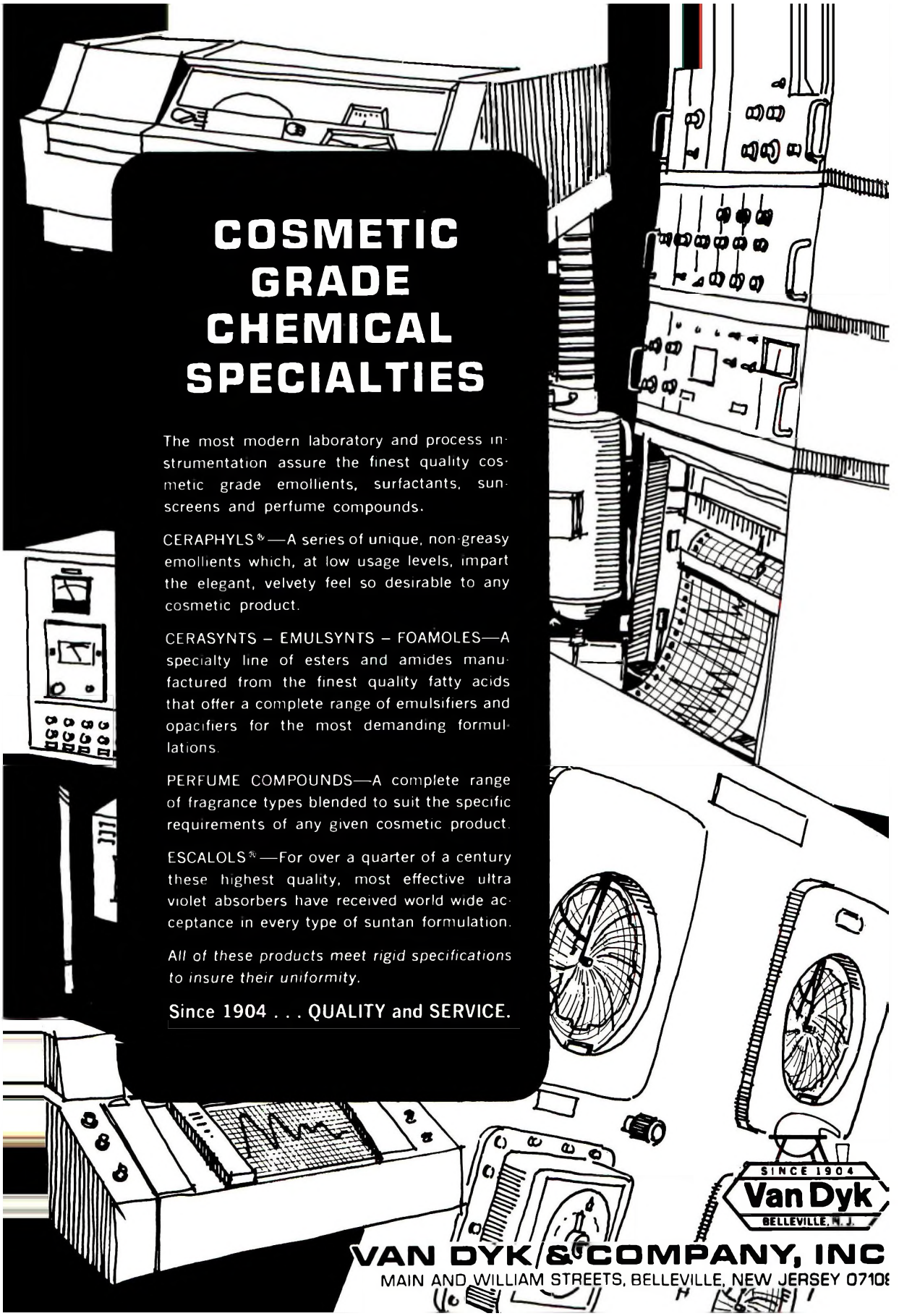

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SOCIETY OF COSMETIC CHEMISTS

ANNUAL SCIENTIFIC MEETING

December 1–2, 1977

Mr. Stephen Sichak and Mr. Leonard Appelle, Program Co-chairmen, have announced plans for this forthcoming SCC Annual Meeting.

The theme will be "Cosmetic Chemistry and Technology in 1977." Topics that will be presented cover research on hair, skin, nails, cosmetic technology and ingredients, information retrieval and an in-depth look at surfactants.

Participation by noted experts in each of these fields is anticipated. The four moderators will be: Gail P. Bucher, Dr. Stephen M. Greenberg, Dr. E. J. Karolyi, and Harry F. Hess, Jr.

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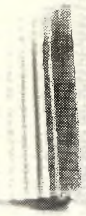

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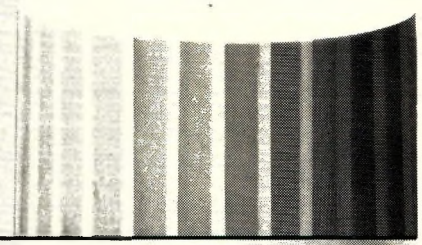

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