J. Soc. Cosmet. Chem., 39, 93–105 (March/April 1988)

The chlorine-hair interaction. III. Effect of combining chlorination with cosmetic treatments on hair properties

N. B. FAIR and B. S. GUPTA, *University of Missouri-Columbia, Columbia, MO 65211 (N.B.F.), and North Carolina State University, Raleigh, NC 27695-8301 (B.S.G.)*

Received April 23, 1987. Presented in part at the Annual Scientific Meeting of the Society of Cosmetic Chemists, New York, December 1987.

Synopsis

The results of a study of the combined effect of chlorination and a cosmetic treatment on selected physical properties of human hair fibers are presented. The hair was either bleached, dyed, or permed as a pretreatment (before the chlorination procedure) or as a posttreatment (after the chlorination procedure). Cosmetic treatments given as pretreatments did not affect frictional properties and surface morphology as markedly as did the cosmetic treatments given as posttreatments. Bleaching and dyeing produced more pronounced effects on surface properties and weight loss of the hair fibers, while perming had the greater effect on tensile properties.

INTRODUCTION

In a previous paper (1), we described the results of a study of the effects of chlorine on various hair properties. It is clear, however, that the history of a given human hair may involve many more treatments than chlorination, but little information is available in the published literature on the effects of combining treatments with chlorination on the physical properties of this fiber. This paper reports the results of a study in which each of the treatments of hydrogen peroxide bleaching, oxidative dyeing, and permanent waving were combined with different durations of exposure to dilute concentrations of chlorine.

MATERIALS AND METHODS

SAMPLE PREPARATION/CHLORINATION PROCEDURE

Natural blond and dark brown Caucasian hair purchased from De Meo Brothers Company were used in this study, with samples prepared to suit the physical property being studied (1). Solutions with chlorine concentrations of 10 ppm were prepared by dilution of a sodium hypochlorite solution with deionized water.

Two chlorination procedures were used, one for the hair mounted on frames for friction, morphological, and knot strength tests, and the other for hair wound into loops or mounted onto tabs for weight loss or tensile tests, respectively. Treatments were carried

out at room temperature using a ratio of 2000 ml liquor to 1 g hair. The hair mounted onto frames was subjected to 5, 10, 15, and 30 cycles of chlorination. Each cycle consisted of soaking the hair for one hour in the chlorine solution, rinsing in water, and drying it for 15 minutes in an air-circulating oven at 40–50°C. The samples for weight loss and tensile tests were subjected to 10, 20, and 30 cycles of treatment. Each cycle consisted of soaking the samples for one hour in the chlorine solution. The samples were then transferred to fresh chlorine solution for the next cycle. After each 10 cycles of such treatment, the samples were rinsed in deionized water.

COSMETIC TREATMENTS

The hair was treated with either a bleach, dye, or perm treatment at one of two stages in the experiment, either as a pretreatment (before the chlorination procedure) or as a posttreatment (after the chlorination procedure). Control samples were subjected only to the chlorination procedure.

Bleach treatment. A 3% H_2O_2 solution adjusted to pH 9 was prepared by diluting 30% H_2O_2 reagent with 0.1 M ammonium hydroxide. The hair was soaked in the bleach solution for one hour at room temperature using a 2000-ml-liquor to 1-g-hair ratio. After soaking, the hair was rinsed in deionized water and air dried.

Dye treatment. A commercial oxidative dye (light auburn) was prepared following package directions. The hair samples were placed on polyethylene wrap and completely coated with the dye emulsion (150-ml to 1-g-hair ratio). The hair was treated with the dye for 30 minutes at room temperature, then rinsed with tap water until the water was clear. Immediately thereafter, the hair was soaked in a 5% sodium lauryl sulfate solution for 10 minutes, rinsed with deionized water, and air dried.

Perm treatment. A commercial permanent waving treatment (thioglycolate waving lotion and hydrogen peroxide neutralizer) was applied to hair samples lying on polyethylene wrap (150-ml to 1-g-hair ratio). The hair was soaked in the waving lotion for 30 minutes and rinsed with deionized water. The neutralizer was then applied to the hair and left on for 15 minutes. The hair was again rinsed with deionized water and air dried.

ANALYSIS OF FIBER PROPERTIES

Fiber properties were determined by methods described earlier (1). The twist method of Lindberg and Gralen (2) for measuring friction was used. Parameters examined included coefficient of friction and "percent stick," the percentage of total time involved in the sticking (positive slope) portion of a stick-slip profile. Surface morphology was studied by the examination of fibers in the scanning electron microscope. Changes in the weight of samples were evaluated by determining dry weights before and after treatment. The force and the work required to extend wet fibers 20% of their original length were measured on a constant-rate-of-extension tensile tester using a crosshead speed of 5 mm/min. Fiber tenacity and knot-breaking tenacity were measured on a constant-rate-of-extension tensile tester, using a crosshead speed of 10 mm/min. The ratio of knot-breaking tenacity to fiber tenacity (K/T) was then determined for each hair fiber.

Table I
Effect of Cosmetic Treatment/Sequence and Cycles of Chlorination on the Coefficient of Friction and Percent Stick of Brown Hair

		Pretreated				Posttreated			
Cycles	Treatment	μ	s*	% Stick	s	μ	s	% Stick	s
0	Control	0.130	0.017	36.6	1.140				
	Bleach control	0.196	0.027	38.0	1.225				
	Dye control	0.166	0.015	36.8	1.095				
	Perm control	0.196	0.015	38.4	0.894				
5	Control	0.180	0.016	38.0	0.707				
	Bleach	0.230	0.031	42.0	1.871	0.300	0.035	45.4	2.408
	Dye	0.214	0.023	42.6	0.548	0.193	0.019	38.0	0.816
	Perm	0.218	0.013	42.2	1.643	0.244	0.009	42.6	1.342
10	Control	0.246	0.027	41.8	2.168				
	Bleach	0.218	0.028	41.6	2.881	0.306	0.025	47.8	2.490
	Dye	0.276	0.013	39.2	1.304	0.174	0.009	43.2	1.304
	Perm	0.234	0.018	42.4	1.140	0.276	0.011	47.8	4.324
15	Control	0.244	0.021	43.2	1.483				
	Bleach	0.290	0.023	41.4	2.191	0.326	0.056	49.6	4.393
	Dye	0.272	0.023	37.8	0.837	0.226	0.027	42.4	1.817
	Perm	0.254	0.018	43.0	2.828	0.292	0.019	51.4	4.506
30	Control	0.278	0.026	46.8	1.304				
	Bleach	0.326	0.015	52.2	3.421	0.262	0.025	44.6	2.608
	Dye	0.294	0.036	39.6	0.894	0.200	0.012	40.0	1.225
	Perm	0.280	0.025	54.6	3.782	0.268	0.017	45.3	2.500

* s = standard deviation for five observations.

STATISTICAL ANALYSIS

Statistical analysis computations were performed using various procedures of the statistical analysis system (SAS). The general linear model procedure and the analysis of variance procedure were used to analyze the sources of variation. Pairwise comparisons were used to determine differences between levels of a given source of variation. All tests of significance were made at the 95 percent level.

RESULTS AND DISCUSSION

The effect of cosmetic treatment sequence and number of one-hour cycles of chlorination on average values of the coefficient of friction are given in Tables I and II. Treatment and cycle effects are evident, with the blond and brown hair showing similar trends. The cosmetic treatments alone significantly increased the coefficients of friction beyond that of the untreated controls (0 cycles). When the cosmetic treatments preceded chlorination, coefficients of friction generally increased with increased cycles of chlorination. This continual increase was similar to that of the control samples. These results indicated a gradual softening of the surface of the fibers, first with the cosmetic treatments and then with continual chlorination.

Table II
Effect of Cosmetic Treatment/Sequence and Cycles of Chlorination on the Coefficient of Friction and Percent Stick of Blond Hair

		Pretreated				Posttreated			
Cycles	Treatment	μ	s*	% Stick	s	μ	s	% Stick	s
0	Control	0.132	0.013	36.8	0.837				
	Bleach control	0.194	0.015	39.2	0.837				
	Dye control	0.184	0.040	36.8	1.304				
	Perm control	0.202	0.023	40.0	1.581				
5	Control	0.180	0.014	38.6	0.548				
	Bleach	0.266	0.026	43.2	2.280	0.254	0.019	44.0	0.236
	Dye	0.222	0.008	39.6	1.140	0.184	0.015	43.4	0.894
	Perm	0.194	0.013	38.2	1.304	0.248	0.013	44.0	1.732
10	Control	0.222	0.031	42.8	3.033				
	Bleach	0.268	0.024	40.2	2.387	0.256	0.025	43.6	2.702
	Dye	0.280	0.065	39.0	1.581	0.220	0.022	42.0	2.236
	Perm	0.214	0.021	43.2	1.095	0.264	0.013	49.2	5.263
15	Control	0.220	0.014	43.6	1.140				
	Bleach	0.310	0.027	41.8	1.924	0.294	0.032	47.2	2.683
	Dye	0.254	0.019	37.0	1.225	0.206	0.029	40.6	3.362
	Perm	0.246	0.013	44.6	1.673	0.306	0.025	50.0	3.162
30	Control	0.302	0.023	51.4	5.597				
	Bleach	0.312	0.008	51.4	2.074	0.248	0.026	41.2	1.483
	Dye	0.358	0.035	39.6	1.673	0.208	0.033	39.8	2.168
	Perm	0.312	0.023	46.2	3.701	0.272	0.016	48.2	3.114

* s = standard deviation or five observations.

When the cosmetic treatments followed chlorination, however, different trends were obtained. For the bleached and the permed samples, the average values of coefficient of friction increased with chlorination up to 15 cycles of treatment. These values were generally significantly higher than those of the control samples and either similar to or significantly higher than the values of the corresponding pretreated samples. For the postdyed samples, the values of coefficient of friction did not change much with increased chlorination and were consistently significantly lower than the corresponding values of the postbleached and postpermed samples.

Similar results were seen for the percent stick parameter (Tables I and II). There was little difference between the percent stick values of the control samples and the prebleached and prepermed samples. Values generally increased with increased cycles of chlorination. In the postbleached and postpermed samples, percent stick increased up to 15 cycles of chlorination and then either decreased significantly (postbleached; brown, postpermed) or remained relatively unchanged (blond, postpermed). In the dyed samples, the results of percent stick were inconclusive; generally, there was little effect of cycles of chlorination or of treatment sequence.

Examination of fibers in the scanning electron microscope showed little definite differences in the morphology of the cosmetically pretreated and control fibers. The cosmetic

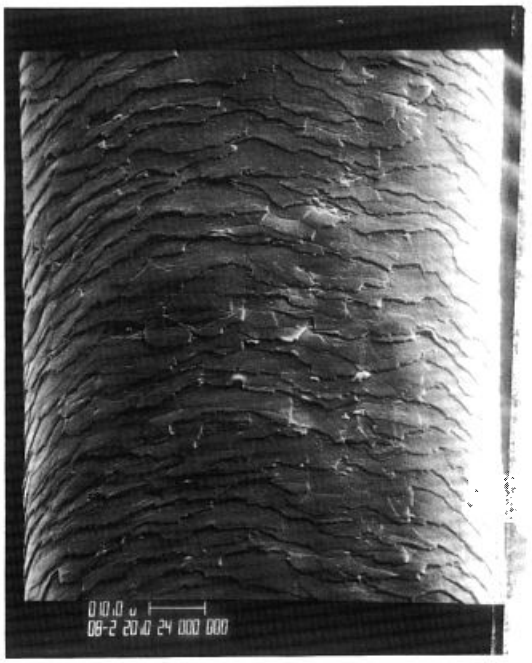

Figure 1a. Blond hair, untreated control.

Figure 1b. Blond hair, bleached only.

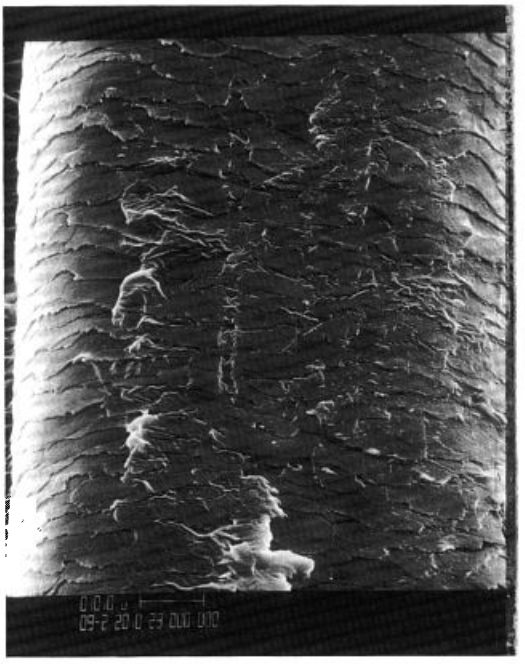

Figure 1c. Blond hair, dyed only.

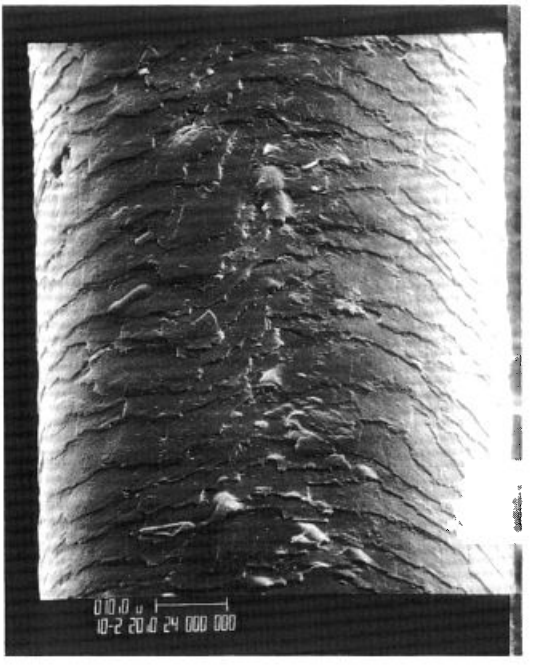

Figure 1d. Brown hair, permed only.

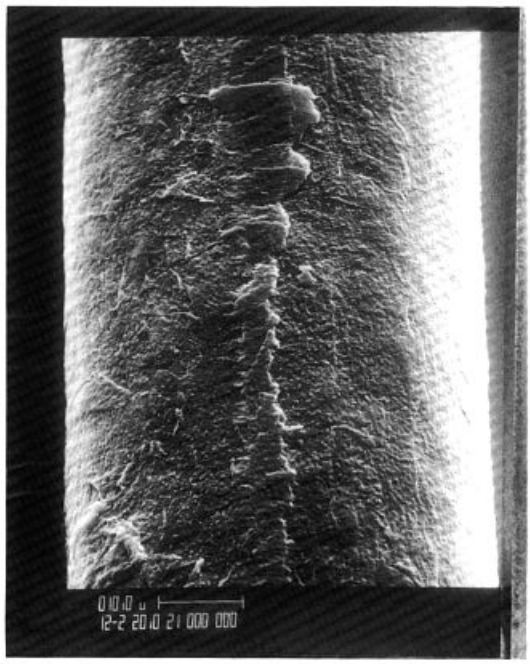

Figure 2a. Blond hair, control, 30 cycles of chlorination.

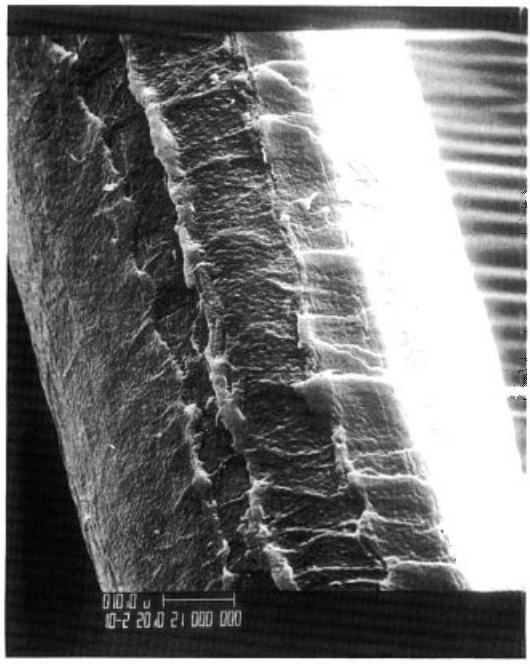

Figure 2b. Blond hair, prebleached, then 30 cycles of chlorination.

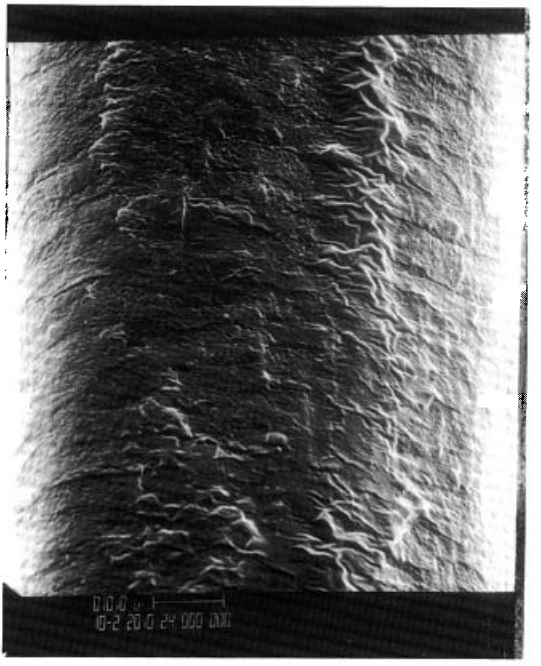

Figure 2c. Blond hair, predyed, then 30 cycles of chlorination.

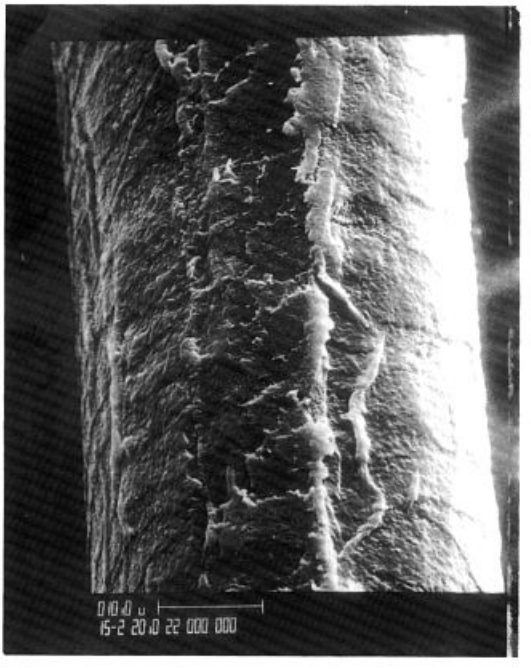

Figure 2d. Brown hair, prepermed, then 30 cycles of chlorination.

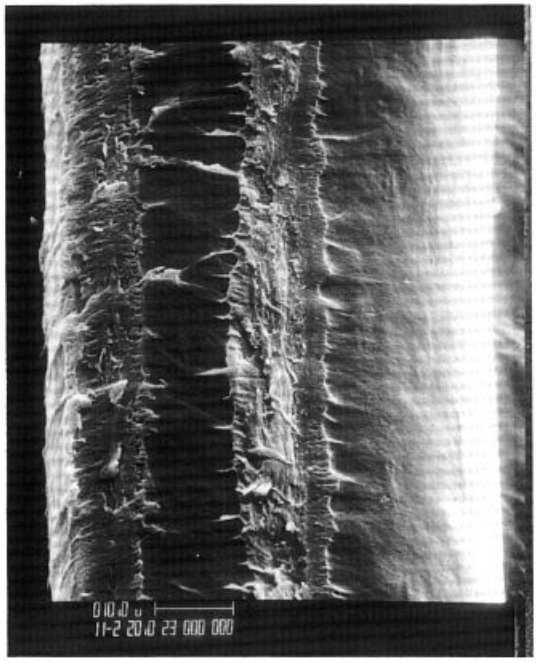

Figure 3a. Blond hair, postbleached after 30 cycles of chlorination.

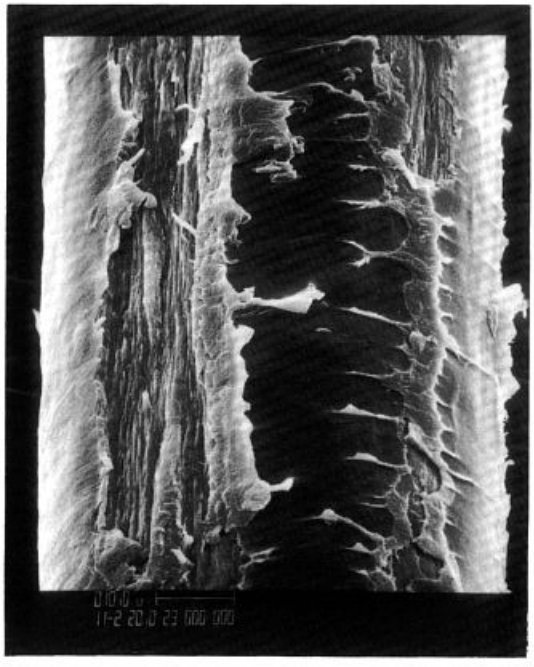

Figure 3b. Blond hair, postdyed after 30 cycles of chlorination.

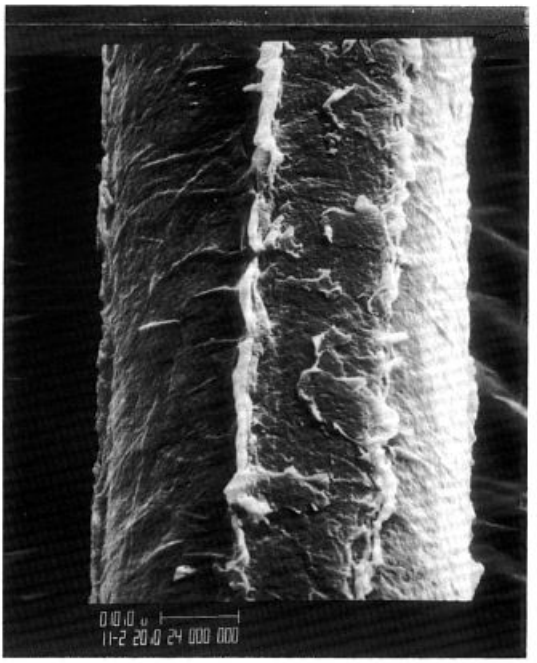

Figure 3c. Brown hair, postpermed after 30 cycles of chlorination.

treatments alone caused little apparent damage to the fiber surfaces, and the fibers were very similar in appearance to the untreated control samples (Figure 1a–d). When cosmetic treatments preceded chlorination, the alteration of fiber surfaces and deformation from rubbing were similar to those seen in the chlorination of control fibers (Figure 2a–d). The wrinkled appearance is one that has generally been associated with the chlorination of keratin fibers and has been attributed to the disruption and loss of protein material through the epicuticle, resulting in collapsed scales (3,4).

When the application of the cosmetic treatment followed chlorination, the surfaces of the fibers were even more drastically affected (Figure 3a–c). Little or no scale structure was apparent, and fiber surfaces were quite smooth. Cuticular material appeared to have been removed with postchlorination bleaching and dyeing. The more drastically altered fiber surfaces resulted, however, in lower values of coefficient of friction. One possible explanation for the lower friction values observed is the sloughing off of the softened cuticle from the underlying structure, leaving a new rubbing surface which is harder. This is expected to be the case, as the new rubbing surface is less penetrated by the chemical treatment and is closer to the cortex, which is more crystalline.

The values of percent weight loss are given in Table III. There was no significant difference between the values of weight loss of the prechlorination cosmetically treated samples and the control samples. Additionally, there was no significant difference between the weight loss of the postchlorination permed samples and the control samples. However, the postchlorination bleached samples exhibited significantly greater weight loss than the other treatments by 10 hours of chlorination. The postdyed samples were

Table III
Effect of Cosmetic Treatment/Sequence and Cycles of Chlorination on the Weight Loss of Blond Hair

Cycles	Treatment	% Wt loss	s*	n**
0	Bleach control	0.8	0.33	6
	Dye control	0.4	0.31	6
	Perm control	0.1	0.15	4
10	Control	0.7	0.45	5
	Prebleach	1.5	0.22	5
	Postbleach	4.4	0.44	5
	Predye	1.4	0.43	6
	Postdye	1.7	0.55	6
	Preperm	0.4	0.48	5
	Postperm	0.2	0.40	5
20	Control	1.6	0.60	5
	Prebleach	1.8	0.38	5
	Postbleach	8.7	0.89	5
	Predye	1.9	0.45	6
	Postdye	5.6	1.80	6
	Preperm	0.4	0.27	5
	Postperm	1.8	0.48	6
30	Control	3.5	1.10	5
	Prebleach	3.3	0.75	5
	Postbleach	12.6	1.61	5
	Predye	3.5	0.84	6
	Postdye	8.7	1.50	6
	Preperm	1.2	0.32	5
	Postperm	4.8	1.14	6

* s = standard deviation.
** n = number of observations.

significantly different from those of the other treatments by 20 hours of chlorination. The rates of weight loss of the postdyed and postbleached samples were also much greater than those of the others. These results correlate well with the loss of surface material noted in SEM analysis. The weight loss of the dyed samples was somewhat less than expected from the SEM results. The deposition of dye molecules into the fiber may compensate for some of the lost cuticular material. These results suggest that as chlorination proceeded, an increasing amount of cuticular material became detached from the substructure and remained held to the fiber by the cell membrane. If the bleach and the dye treatments degraded the cuticle cell membrane, the detached cuticular material could be lost quite readily.

Values of the reduction in the force and the work required to extend wet fibers 20% are given in Table IV. The cosmetic treatments alone caused significant reductions. There was no significant difference between the effects of the bleach and the dye treatments. The perm treatment, however, caused a significantly greater reduction than the other two. Beyak *et al.* (5) found similar results (30% reduction in force for 15% elongation) in a permanent wave treatment of hair involving a ten-minute reducing step and a five-minute neutralizing step. Such a large change in force and work with perming

Table IV
Effect of Cosmetic Treatment/Sequence and Cycles of Chlorination on the Percent Reduction in Force and Work Required for 20% Extension of Blond Hair

Cycles	Treatment	Force	s*	n**	Work	s	n
0	Bleach control	7.48	1.14	9	13.02	2.93	8
	Dye control	6.41	1.51	7	9.89	3.12	7
	Perm control	43.82	3.40	6	51.54	5.79	6
10	Control	4.03	1.34	11	8.00	3.03	8
	Prebleach	14.15	3.42	14	17.50	5.43	14
	Postbleach	11.91	2.07	8	17.02	4.60	10
	Predye	19.79	4.51	10	24.57	6.02	10
	Postdye	12.51	1.94	8	11.96	2.87	7
	Preperm	50.93	6.77	10	60.12	6.17	12
	Postperm	49.58	4.99	10	54.51	4.46	10
20	Control	7.76	1.61	11	13.35	3.78	8
	Prebleach	20.77	2.96	14	24.56	3.93	14
	Postbleach	20.77	2.96	9	24.55	4.14	10
	Predye	25.17	3.51	10	26.93	5.20	10
	Postdye	22.96	4.27	9	21.64	5.44	9
	Preperm	58.29	5.58	10	64.56	4.60	12
	Postperm	59.86	3.47	8	61.62	5.28	9
30	Control	19.19	1.75	11	21.62	3.58	8
	Prebleach	27.67	2.86	14	32.24	4.28	14
	Postbleach	30.26	4.34	7	36.05	4.30	7
	Predye	33.83	3.07	10	36.89	3.64	10
	Postdye	31.89	3.99	8	35.48	7.27	10
	Preperm	62.50	5.15	10	69.26	4.92	12
	Postperm	65.72	4.32	8	68.14	4.20	8

* s = standard deviation.
** n = number of observations.

could be due to the incomplete reformation of disulfide crosslinks. The effect of combining the cosmetic treatments with chlorination appeared to be additive. The effect of treatment sequence for each cosmetic treatment, however, was not significant, suggesting that both treatment sequences affected the cortex of the fiber to a similar extent. Therefore, the cuticle did not contribute significantly to the tensile properties of wet hair fibers at low extensions (20%).

Values of the ratio of knot breaking-to-fiber tenacity are given in Table V. Only perming caused a significant increase in K/T in the control samples. Analysis of variance indicated no significant effect of treatment sequence on the values of this parameter. All treatments produced a similar significant increase in K/T when cycles of chlorination increased from 0 to 15, with no further significant change occurring beyond 15 cycles. These results are similar to those seen in the study of the effect of pH (1). Once again, the results indicated that the treated fibers were more flexible.

CONCLUSIONS

Two distinct trends were seen when chlorination was combined with cosmetic treatments, depending upon whether the treatment was applied to the hair before or after

Table V
Effect of Cosmetic Treatment/Sequence and Cycles of Chlorination on the Ratio of Knot Breaking-to-Fiber Tenacity (K/T) of Blond Hair

Cycles	Treatment	K/T	s*
0	Control	0.600	0.134
	Bleach control	0.661	0.055
	Dye control	0.630	0.071
	Perm control	0.774	0.077
15	Control	0.924	0.077
	Prebleach	0.920	0.118
	Postbleach	0.886	0.095
	Predye	0.933	0.095
	Postdye	0.816	0.045
	Preperm	0.829	0.114
	Postperm	0.901	0.089
30	Control	0.955	0.148
	Prebleach	0.915	0.096
	Postbleach	0.808	0.063
	Predye	0.881	0.145
	Postdye	0.871	0.055
	Preperm	0.955	0.071
	Postperm	0.844	0.118

* s = standard deviation for eight observations.

chlorination. The chlorination procedure was carried out in solutions with 10 ppm chlorine concentration, which is somewhat stronger than typically found in swimming pools. Consequently, the effect of cycles of chlorination seen on the properties examined may be accelerated.

The main effect of applying the cosmetic treatment to hair before chlorination was on the wet tensile properties of the fibers. There was a significant decrease in the force required to extend fibers 20% over the decrease given by chlorination alone. The pre-chlorination treatments showed limited effects on interfiber friction, surface morphology, weight loss, and knot strength.

Postchlorination treatments more greatly affected interfiber friction, cuticular morphology, and the weight of the fibers. Both blond and brown hair were affected in a similar manner. The bleaching, dyeing, and perming treatments were strong enough to degrade and remove cuticular material that had been weakened by prior chlorination. This accounted for the smooth appearance of the surfaces, significant weight loss, and, also, the observed decrease in the coefficient of friction of samples chlorinated between 15 and 30 hours. The changes in tensile properties and knot strength were similar to those found with the pretreatments, in spite of greater cuticular damage by posttreatment with cosmetic chemicals.

REFERENCES

(1) N. B. Fair and B. S. Gupta, The chlorine-hair interaction. II. Effect of chlorination at varied pH levels on hair properties, *J. Soc. Cosmet. Chem.*, **38**, 371–384 (1987).

(2) J. Lindberg and N. Gralen, Measurement of friction between single fibers. II. Frictional properties of wool fibers measured by the fiber-twist method, *Text. Res. J.*, **18,** 287–301 (1948).
(3) G. J. Schuringa, T. Konings, and A. J. Ultee, Jr., Osmotic active substances of the Allwörden reaction, *Text. Res. J.*, **23,** 645–646 (1953).
(4) J. H. Bradbury and J. D. Leeder, Keratin fibers. IV. Mechanism of the Allwörden reaction, *Aust. J. Biol. Sci.*, **25,** 133–138 (1972).
(5) R. Beyak, C. F. Meyer, and G. S. Kass, Elasticity and tensile properties of human hair. I. Single fiber test method, *J. Soc. Cosmet. Chem.*, **20,** 615–626 (1969).