

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

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### **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%  $\text{H}_2\text{O}_2$  solution adjusted to pH 9 was prepared by diluting 30%  $\text{H}_2\text{O}_2$  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

| Cycles | Treatment      | Pretreated |       |         |       | Posttreated |       |         |       |
|--------|----------------|------------|-------|---------|-------|-------------|-------|---------|-------|
|        |                | $\mu$      | s*    | % Stick | s     | $\mu$       | 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

| Cycles | Treatment      | Pretreated |       |         |       | Posttreated |       |         |       |
|--------|----------------|------------|-------|---------|-------|-------------|-------|---------|-------|
|        |                | $\mu$      | s*    | % Stick | s     | $\mu$       | 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

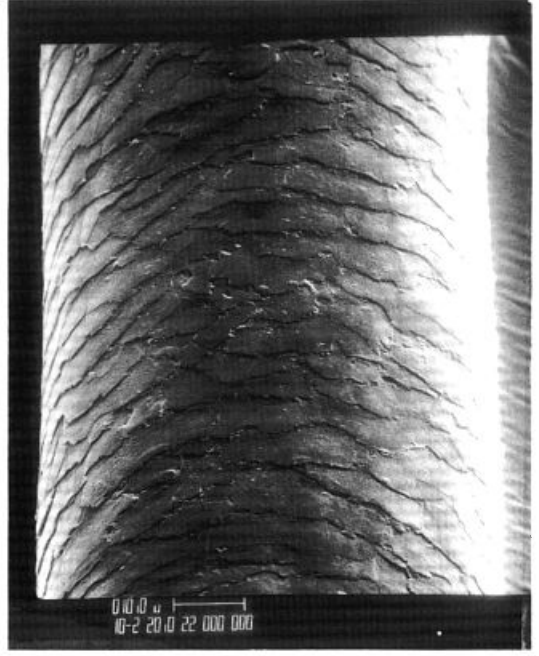


Figure 1b. Blond hair, bleached only.

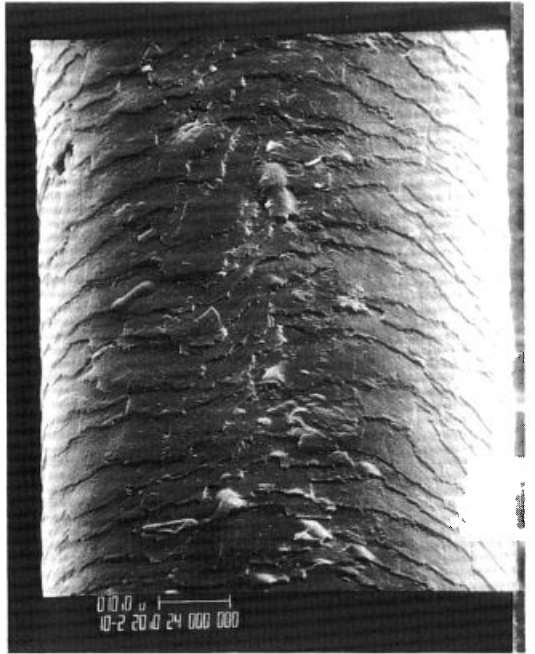
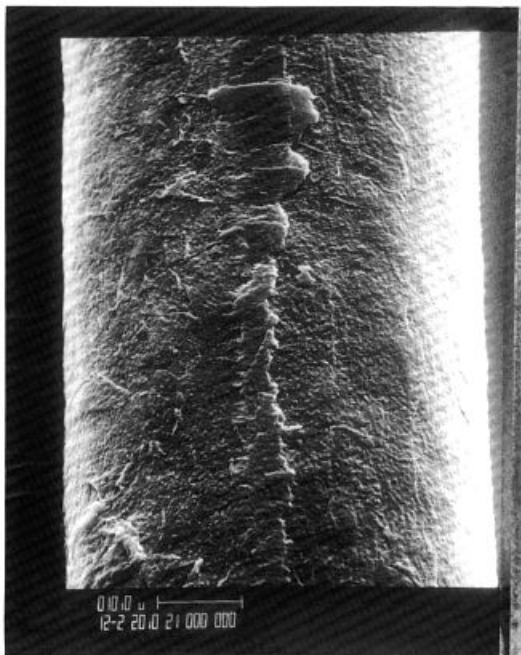
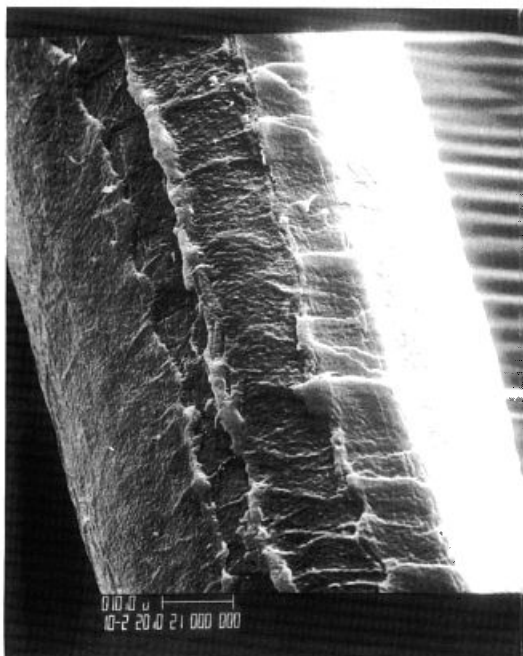


Figure 1d. Brown hair, permed only.



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



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

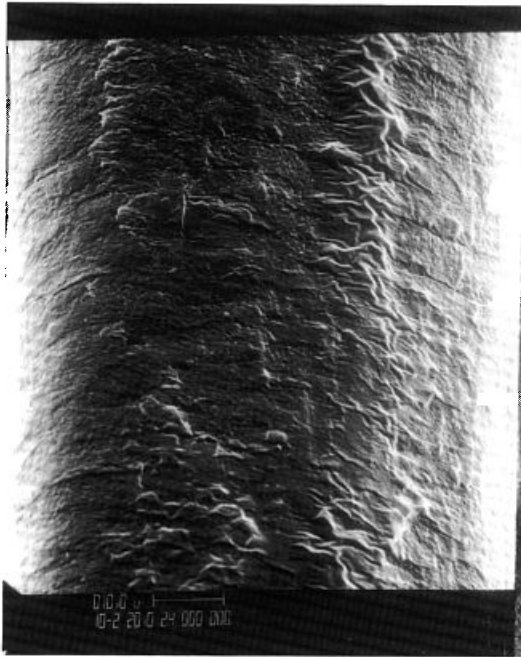


Figure 2c. Blond hair, predyed, then 30 cycles of chlorination.

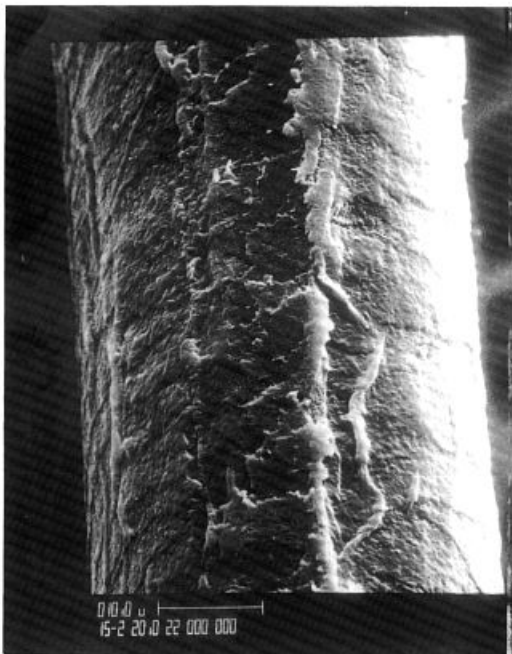
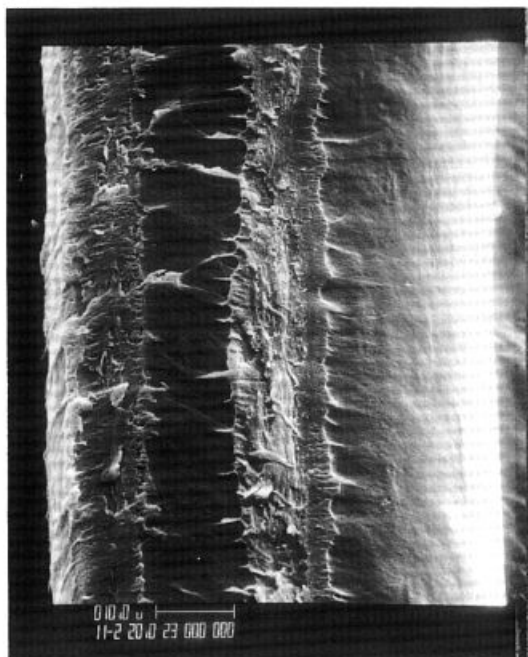
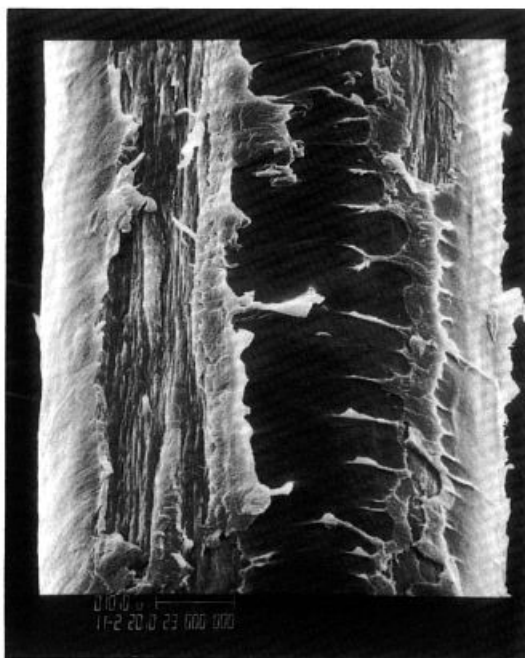


Figure 2d. Brown hair, prepermed, then 30 cycles of chlorination.

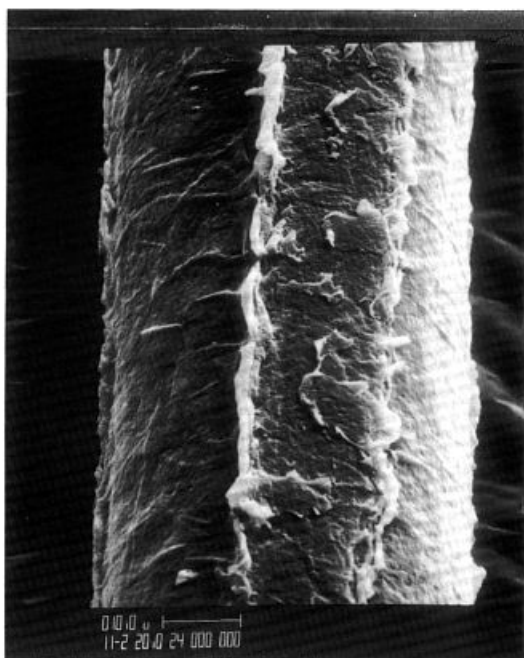


**Figure 3a.** Blond hair, postbleached after 30 cycles of chlorination.



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





**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.

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