J. Soc. Cosmet. Chem., 32, 27-36 (January/February 1981)

A hysteresis in heat dried hair

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Received July 22, 1980.

Synopsis

Hair dried with heat and equilibrated at room temperature at a moderate relative humidity will have a lower moisture content than room temperature dried hair. After heat drying, hair absorbs moisture but does not return to the room temperature dried water level until it is rewet or conditioned at a higher relative humidity and dried at room temperature, i.e. a hysteresis exists in heat drying analogous to that from chemical desiccation of hair. Heat drying also makes hair more susceptible to static charge buildup, which is related to the hysteresis, and results in increased flyaway during combing or brushing. Heat drying can also produce a short term decrease in fiber stiffness which is not related to this hysteresis but appears to be due to the direct action of heat on the fibers.

INTRODUCTION

Rebenfeld et al. (1) have described the effects of heating hair in buffer solutions, and Humphries et al. (2) have described a thermochemical method for evaluating human hair. In addition, Menefee et al. (3) have produced phase changes in wool by heating it to high temperatures, and D'Arey and Watt (4) have shown that the equilibrium moisture content of keratin fibers decreases with increasing temperature. Hair dryers and curling irons are capable of producing very high temperatures, therefore it is possible that in use these appliances might damage hair, however such damage has not been reported in the literature. Therefore, we undertook to investigate the effects of heat on moisture in hair and on certain important hair fiber and assembly properties.

EXPERIMENTAL

European dark brown hair fibers (5) were used in this investigation. Wet single fibers were allowed to dry in a constant relative humidity-temperature chamber at 55% R.H. and 22°C, and weighed using a Precision Balance (6). The fibers were then rewet and heat dried. For exaggerated conditions, a variable temperature oven was used and a 16-h drying time. For more practical conditions, hair was dried for 1 h in a simulated hair dryer in which the temperature and air flow could be regulated. The simulated hair dryer was constructed by wrapping a glass tube (4 ft. long by 1 in. diameter) with nickel-chrome wire, and enclosing this in a second glass tube. The temperature was observed with a thermometer and regulated with a powerstat while air flow was regulated with a Matheson 7630 series flow meter. After heat drying, the fibers were equilibrated again to constant conditions and reweighed. Higher humidities were obtained using salt solutions (7).

Wet tensile measurements (8) were made using an Instron Tensile Tester (9). Fibers were first calibrated by measuring the force required to stretch 4-in. fibers to 4.8 in. (20%) at a rate of 0.5 cm/min. After heat treatment, the fibers were retested.

Bleaching and permanent waving of hair was with commercial products, following use directions. Static charge was measured by the method of Mills et al. (10). Fiber stiffness measurements were made by the method of Scott and Robbins (11).

RESULTS AND DISCUSSION

DRYING AND REGAIN RATES

To help select equilibrium conditions for measurement of moisture in hair, rates of drying and reabsorption of moisture were investigated. The procedure used involved shampooing, rinsing, and drying the fibers to constant weight at room temperature (22°C) and 55% R.H. The hair was then rewet, and heat dried, and allowed to equilibrate at constant conditions. The rates of drying and reabsorption were measured by monitoring weight changes. We assume that weight changes represent moisture changes, and if a treatment or manipulation produces structural changes in the hair, then the fibers will not return to their original conditioned weights. Figure 1 depicts the drying rate curve (A) at 22°C and 55% R.H., and the moisture regain rate curve (B) at these same conditions for hair, after heat drying at 110°C for 16 hours. The data points in Figure 1 represent averages for 10 hair fibers. The water content (percent dry weight) is the percentage difference between the weight of the hair immediately after heat drying, which is assumed to be the dry weight, and its weight at various points along curves (A) and (B). Of course the water content of the hair expressed as Percent Dry Weight will depend on the value used for the dry weight which in turn will depend on the conditions used for drying (heat, vacuum, or desiccation) and the time of drying.

Both absorption and desorption rates are rapid, and the fibers generally equilibrate within 3 hours. Moisture regain appears to be slower than the drying process, and the equilibrium moisture content is significantly lower for heat dried hair than for room temperature dried hair. Thus a major part of this investigation became concerned with trying to understand the conditions governing this phenomenon of a lower moisture content for heat dried vs. room temperature dried hair.

Work with tresses revealed slower and more variable rates compared with single fibers. This may arise from changes in heat transfer caused by neighboring fibers, and their different relative orientations in different tresses (12). Because of these data, most of the subsequent experiments were run on single fibers after conditioning overnight to insure equilibrium, prior to weight measurements.

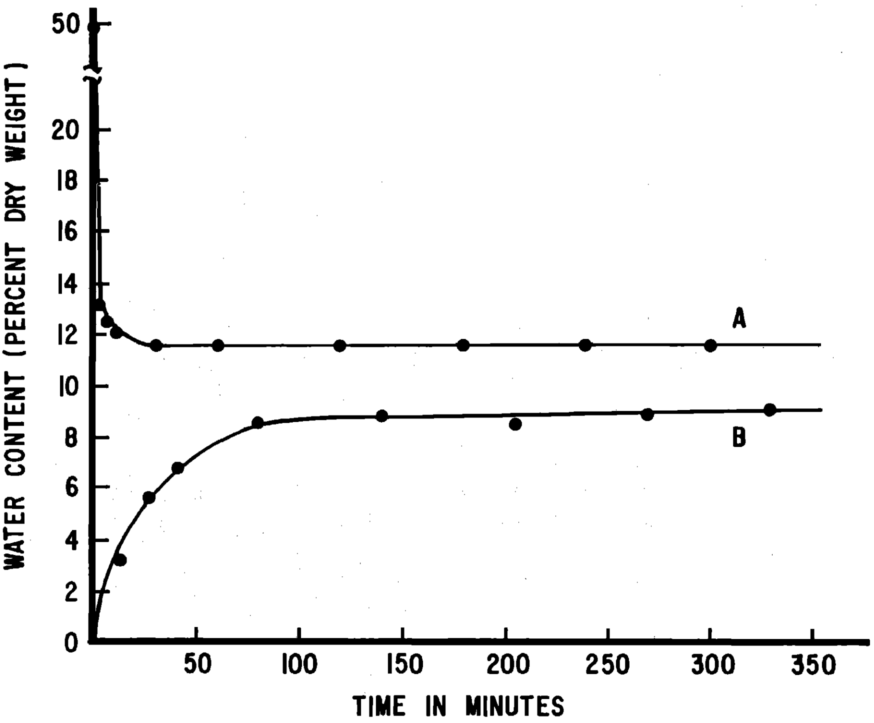

Figure 1. Desorption of water from hair after shampooing (A) and absorption after heat drying (B). Steps A and B were measured at 22°C and 55% R.H. Heat drying was for 16 h at 110°C.

TEMPERATURE AND HEAT DRYING

Commercial hair dryers were found to generate temperatures in excess of 100°C and air flow rates around 40 l/min. Of course, with this type of appliance, the hair encounters such conditions for only brief periods of time, at more reasonable conditions, hair dryers may produce temperatures of up to 50°C for very long periods of time.

To help define experimental conditions for later work and to determine what parameter(s) to explore under more pragmatic experimental conditions, we elected to run the following preliminary experiments. Preconditioned preweighed hair was rewet and heat dried for prolonged periods of time at temperatures ranging from 70°C to 110°C. After heat drying, the fibers were reconditioned and reweighed.

The data are summarized in Table I. As in the rate study, the fibers did not return to their original conditioned weight. This suggests that a structural change, related to the binding of moisture, is produced by heat drying under these conditions. To confirm this conclusion, the material driven off by heat drying was captured in a dry ice-acetone trap. Analysis of the trapped material detected only water.

Our next step was to determine if a similar phenomenon might occur under milder conditions of heat drying. These conditions involved rewetting and then heating preconditioned hair fibers for 1 hour, at several temperatures, in a simulated hair dryer with controlled air flow at a rate of 40 l/min. The results of this experiment are summarized in Table II and show significantly lower moisture contents after heat

Table I

Weight Changes in Hair[1] Heated Under Exaggerated Conditions

Temperature	% Weight Change[2]
70°C	−0.79[3]
90°C	−1.44[3]
110°C	−1.94[3]

[1] Chemically unaltered hair used.

[2] Percent weight change = $(B - A)/A \times 100$ where:
A = equilibrium weight after drying at 22°C
B = equilibrium weight after heat drying

[3] Change significant at $\alpha = 0.05$ level.

Table II

Weight Changes in Hair[1] Heated in a Simulated Hair Dryer

Temperature	% Weight Change[2]
40°C	−0.63[3]
50°C	−0.66[3]
70°C	−0.48[3]
90°C	−1.00[3]
110°C	−1.85[3]

[1] Chemically unaltered hair used.

[2] Percent weight change = $(B - A)/A \times 100$ where:
A = equilibrium weight after drying at 22°C
B = equilibrium weight after heat drying

[3] Change significant at $\alpha = 0.05$ level.

Table III

Weight Changes After Resoaking Heat Dried Hair

	% Weight Change	
Temperature	After Heat Drying	After Resoaking and R. T. Drying
40°C	−0.62[1]	+0.13
50°C	−0.66[1]	−0.20
70°C	−0.48[1]	−0.11
90°C	−1.00[1]	−0.19
110°C	−1.85[1]	−0.28[1]

[1] Change significant at $\alpha = 0.05$ level.

drying at all temperatures compared to room temperature drying. Therefore, one may conclude that structural alterations are produced in hair by "normal" heat drying.

We then decided to re-examine these same hair fibers by resoaking in dilute surfactant solution for 1 h and allowing the fibers to come to constant weight to determine if these structure changes were permanent. The data from this experiment are summarized in Table III and show that heat drying produces only temporary changes in the bonding of moisture in hair in all cases except at 110°C, i.e. changes are reversed by shampooing. Apparently heating to 110°C or above produces irreversible changes in hair. If heating to lower temperatures produces irreversible changes, they are too small to be detected in our experimental system.

This difference in the moisture content of room temperature and heat dried hair is reminiscent of the hysteresis in the moisture binding by human hair and wool fiber demonstrated by Speakman nearly 50 years ago (13). In this classical study, Speakman demonstrated that the moisture content of human hair, by dehydration from the wet state, is higher than by regain after drying over a chemical desiccant such as P_2O_5 in vacuum. Similar hysteresis phenomena have been demonstrated for high polymers (14) and by other proteins such as wool fibers (15) and casein (16).

Several explanations have been offered to explain this hysteresis phenomenon (14, 17-20). One of these, by Urquhart, suggests that the primary water binding sites are the polar groups of the fiber, which can also bond to each other via intrachain hydrogen bond crosslinks, so when a fiber is completely dry, intrachain crosslinks are at a maximum, and only a few free polar sites remain. On the other hand, when a fiber is completely hydrated, intrachain hydrogen bond crosslinks are at a minimum. Therefore, on absorption of moisture, the free polar sites hydrate first followed by rupture of the hydrogen-bonded crosslinks to free polar groups which are hydrated. Thus, on absorption, the number of active or free groups available for moisture binding is lower at all stages than it is during desorption, which accounts for the lower amount of moisture on absorption. These data, and Tables I and II, clearly show that a hysteresis occurs by heat drying hair, and that the size of this moisture binding gap depends on the temperature, i.e. on the extent of drying. Speakman (13) reported a hysteresis of about 2 percent at 55% R.H. via desiccation and our results under our most severe conditions of drying are in line with this value.

Watt (21) has shown that the hysteresis will disappear for single wool fibers under certain conditions of desorption. In view of this, we decided to determine what factors might affect the size, or existence of, this heat drying hysteresis, and what physical properties it might influence. We elected to first examine the effects of changing humidities, primarily to higher humidities, since resoaking in water eliminates the hysteresis.

EFFECTS OF HIGHER AND VARYING HUMIDITIES

Hair fibers were shampooed, rinsed, conditioned at 55% R.H. (22°C), and weighed. These same fibers were then rewet and heat dried at 90°C for one hour. Ninety degrees Celsius was selected because it gave the largest hysteresis which was reversible. Several of these fibers were then conditioned for 16 hours at 55% R.H., several at 65% R.H., some at 75%, and the remaining at 85% R.H. The final part of this experiment involved re-equilibrating the fibers at the starting 55% R.H. and reweighing them.

The results summarized in Table IV show that the hysteresis is still present in the fibers conditioned at 55% R.H., but the fibers conditioned at higher humidities do not show a weight loss hysteresis. In fact these fibers show a weight gain which is not significant after conditioning at 65% R.H. but is significant after conditioning at 75% and 85% R.H. The reason for this weight increase is not clear at this time. Since the weight pick up is so small (.26% to .33%) we elected not to investigate this apparent anomaly; although we conclude that higher humidities have the same effect as soaking hair in water by eliminating the heat drying hysteresis. This also suggests that hair problems

Table IV
Effect of Increased Humidity

% R.H.	% Weight Change
55	−1.26[1]
65	+0.26
75	+0.29[1]
85	+0.33[1]

[1] Change significant at $\alpha = 0.05$ level.

associated with this heat drying hysteresis will be eliminated when the hair encounters higher humidity for several hours. The effects of shorter exposures to higher humidity were not measured.

PERCENT MOISTURE

The values expressed in Tables I and II show small weight changes in hair from loss of moisture. These values are based on changes in the total weight of hair. Perhaps a more realistic way to express these changes is as changes in the weight of moisture of the hair relative to equilibrium moisture content at 55% R.H. Our data from Figure 1 shows the moisture content of hair to be 11.5% of its dry weight. Using this figure, we calculated the equilibrium moisture content of hair at 55% R.H. and room temperature to be 10.3% of its total weight. The values in Table V show the percentage change in the actual amount of moisture in the hair calculated from the weight changes in Table II relative to this equilibrium moisture content:

$$\%\text{ Change in Total Moisture of hair} = \frac{\%\text{ Weight Change Due To Heat}}{10.3\%} \times 100.$$

Subsequent results on physical properties of hair confirm that this is a more realistic estimate of the magnitude of the moisture changes in hair due to heat drying.

Table V
Percent Moisture Loss from Heat Drying

Drying Temperature	Percent Change[1] In Total Weight Of Hair[2]	Percent Change[1] In Total Moisture of Hair[2]
40°C	−0.63	−6.1
50°C	−0.66	−6.4
70°C	−0.48	−4.6
90°C	−1.00	−9.7
110°C	−1.85	−17.9

[1] Values represent the difference between the percent weight loss due to heat drying (Table 2 Values) and the percent moisture content (10.3%) calculated from Figure 1.
[2] Change significant at $\alpha = 0.05$ level.

Table VI
Weight Changes in Damaged Hair After Heat Drying and Rewetting

Hair Type	% Weight Change After Heat[1] Drying	 After Resoak And R.T. Drying
Untreated	−1.85[3]	−0.28[3]
Permanent Waved[2]	−1.90[3]	−0.66[3]
Bleached[2]	−2.10[3]	−0.58[3]

[1] These fibers were all heat dried to 110°C for one hour in a simulated hair dryer.
[2] See experimental section for procedure.
[3] Change significant at $\alpha = 0.05$ level.

PERMANENT WAVING AND BLEACHING

The data in Table VI show that a similar heat drying hysteresis exists for both permanent waved and bleached hair. There was no significant difference in the size of the hysteresis gap among the three hair types. All hair types, on resoaking, fail to return to the original room temperature dried weights suggesting that permanent structural changes have been produced in the fibers, and this is greater but not significantly different for the damaged hair compared to the chemically altered hair.

FLYAWAY

The effects of relative humidity on static-induced flyaway were demonstrated by Mills et al. (10) who showed that flyaway decreases with increasing relative humidity. This effect is due to increased moisture binding by the hair at higher relative humidities. This in turn decreases the electrical resistance of the fibers and thus lowers their capacity to acquire a static charge. Therefore, the decrease in moisture content of hair produced by heat drying should have an adverse effect on flyaway.

Table VII summarizes the data from an experiment which shows that heat drying hair significantly increases its ability to acquire a static charge. The increase immediately after heat drying was expected, however, the large difference 24 h after heat drying

Table VII
Heat Drying and Flyaway

Treatment Or Conditioning of Tresses	Relative Static Charge[1]
Day 1—Shampoo and Dry at 55% R.H. and 22°C.	—
Day 2—24 Hours After Shampooing	7.6
Day 3—Immediately After Heat Drying 1 Hour at 50°C in Simulated Dryer	37.9[2]
Day 4—24 Hours After Heat Drying	22.0[2]

[1] Data are static charge peak heights from oscillograph readings of charge on comb using the method of Mills et al. (7) Control tresses were run days 2, 3, and 4, and their readings did not change significantly. All readings were done at 55% R.H.
[2] Static Charge value different from Day 2 value at $\alpha = 0.05$ level.

suggests that the heat drying induced hysteresis, even hours after drying, may play a significant role in the chargeability of the hair, and thus produce a greater tendency for flyaway hair after heat drying vs. room temperature drying. However, since the hysteresis is eliminated by high humidity, the flyaway difference should also be eliminated by high humidity.

TENSILE PROPERTIES

The tensile properties of heat dried hair were examined from two points of view. First, we wanted to determine if the hysteresis in moisture binding affects the tensile properties of human hair, and second, we wanted to determine if cumulative heat drying might adversely damage the hair, which might show up as a decrease in the tensile properties.

To determine if the hysteresis affects the tensile properties, we decided to first examine the dry tensile properties of hair fibers immediately after heat drying at 50°C for 1 h in a simulated dryer. The results of this experiment do not show a significant effect for a single low temperature heat drying temperature, suggesting that the hysteresis in moisture binding does not affect the dry tensile properties of hair.

To determine if tensile damage might be produced by cumulative heat drying, we treated precalibrated hair fibers of cosmetically altered and unaltered hair 25 times, shampooing and heat drying in a simulated hair dryer, at both 50°C and 100°C, and evaluated these fibers for changes in the wet load-elongation properties. The results of this study are summarized in Table VIII. These data show no significant effects at 50°C, however, at 100°C significant but small decreases in the wet tensile properties were observed. Thus, we conclude that normal heat drying of human hair does not produce meaningful tensile damage, although excessive heating can damage the hair.

FIBER STIFFNESS

The wool fiber literature (22) shows that all parameters of load elongation, with the exception of extensibility, decrease with increasing temperature. Since the Hookean

Table VIII
Wet Tensile Damage from Heat Drying

Hair Type	Drying Temperature	% Change In Force to 20% Extension
Unaltered	22°C	0
	50°C	−0.2
	100°C	−4.3[1]
Bleached	22°C	+0.3
	50°C	−0.5
	100°C	−2.1[1]
Permanent waved	22°C	+0.9
	50°C	+0.5
	100°C	−6.7[1]

[1] Change significant at $\alpha = 0.05$ level.

Table IX

Hair Drying and Fiber Stiffness

	Treatment Or Conditioning of Fibers	Stiffness Index[1] (mm)
Step 1	Shampoo and Dry at 55% R.H. and 22°C	—
Step 2	24 Hours After Shampooing	6.78
Step 3	Immediately After Heat Drying, 1 Hour at 50°C in Simulated Dryer.	4.85[2]
Step 4	24 Hours After Heat Drying	6.33

[1] Hanging fiber method of Scott and Robbins (8) used to evaluate stiffness index. Readings taken at 55% R.H.

[2] Stiffness value different from Step 2 value at $\alpha = 0.05$ level

slope and limit decrease with increasing temperature, fiber stiffness should also decrease. However, since heat drying decreases the moisture content of hair and hair fiber stiffness increases with decreasing moisture content (11) the effects of heat drying on hair fiber stiffness are not predictable. Therefore we decided to examine the effects of heat drying on hair fiber stiffness, a fundamental fiber property.

The data are summarized in Table IX. Step 3 represents the stiffness index immediately after removing the fibers from the simulated hair dryer. This point shows a significant and substantial decrease in fiber stiffness indicating that increased temperature is dominant in governing the stiffness properties. After re-equilibration at 55% R.H. and room temperature (24 h), the fibers return to their "normal" stiffness level in spite of the moisture binding hysteresis. This effect suggests that when heat appliances such as hot combs and styling irons are used on hair, the fibers are more pliable because of the heat. Therefore they conform more readily in styling operations. However, after removing the heat source and equilibration to room temperature hair fiber stiffness returns to normal, unaffected by the hysteresis in moisture binding and in this respect is a contrast to the flyaway effects.

CONCLUSIONS

Hair that has been heat dried and then equilibrated at room temperature and moderate humidity will contain less moisture than it would if it were dried at room temperature, i.e. a hysteresis exists in heat drying similar to that found in chemical desiccation. However, heat dried hair will return to its room temperature dried moisture level if it is resoaked in water or conditioned at higher humidities.

Heat drying will increase the tendency of hair to acquire a static charge during combing and this charge buildup seems to be related to the heat drying hysteresis. Heat drying can also produce a short term decrease in fiber stiffness. This decrease in fiber stiffness is related to the action of heat on the fibers, but is not related to the hysteresis. Heat drying at moderate temperature has no effect on the tensile properties, although small changes in the tensile properties were detected in hair dried at very high temperature.

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