

## **Effects of some oils, emulsions, and other aqueous systems on the mechanical properties of hair at small deformations**

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*Received August 17, 1992.*

### **Synopsis**

The changes on the forces to 1% deformation,  $F(1)$ , and short-term stress relaxation,  $IR$ , of single hair fibers during and after their immersion in some oils, emulsions, and other aqueous systems are studied. Upon immersion,  $F(1)$  is seen to increase or decrease with time, depending on the available water partitioning characteristics of the immersion system. The recovery behavior of  $F(1)$  after de-immersion is also typical of the immersion system and in most cases takes place in a two-stage time-dependent fashion.

It is also shown that the soft feel, which for several hours characterizes wet hair, results from a water de-immersion recovery pattern with the following features: a first stage where 85% of  $F(1)$  is recovered rapidly in about 5 or 10 minutes, and a second stage of slow recovery where the hair's water-enhanced plasticity decays in about 10 to 12 hours. Furthermore, it is shown that this behavior and the short-term relaxation characteristics of the fibers in general can be modified if some of the solutes remain on the hair shaft. The results suggest that these modifications can be accounted for by three different plasticizing mechanisms: swelling, chaotropicity, and film-water inclusion/exclusion plasticity.

### **INTRODUCTION**

It is customarily accepted by most cosmetic scientists and technicians that a good conditioning of hair is obtained when its optical reflectivity, charge neutralization, and mechanical stiffness are somehow improved (1–3). Mechanical conditioning, the topic of this paper, involves strains within the so called “Hookean region” and at deformations not greater than 1%, where the fiber has been reported to behave viscoelastically (4–7).

Because of the hair's viscoelasticity at small deformations, one would anticipate that its mechanical conditioning as defined by Robbins (8) will depend mainly on the combination of two properties, namely: 1) its response to rapidly varying strains, and 2) its response to semipermanent or very slowly imposed strains.

A thicker fiber will, for instance, oppose a stronger elastic resistance to the rapid strains of combing or natural movement than will a thin one, even when the fibers have the same elastic modulus. However, if the thick fiber relaxes too rapidly to strains of longer duration, such as those imposed during styling, or to the strains of its own weight, it

will give the sensation of limpness after it has been styled. Conversely, if the fiber stress relaxes rather too slowly, its behavior upon styling will be that of a rubber fiber with the sensation of difficulty in manageability.

Measurement of hair stress relaxation should, thus, be helpful in complementing other parameters such as interfiber friction and bending modulus on the evaluation of conditioning agents. The relevance of stress relaxation in conditioning studies becomes evident when it is considered that the compression and extension stresses that compose bending will vary with time unavoidably as the hair's matrix phase relaxes viscoelastically after styling.

Information on hair stress relaxation at small deformations and chemical deposition, solvent swelling, or salt penetration is, however, incomplete or limited to wool shrinkage studies (9–12). For instance, most of the studies on plasticization of keratinous fibers at small deformations have been carried out using water vapor as the only plasticizer (13–18). Also, the abundant data on fiber swelling by water (19–25), solvents (26–28), and other salt solutions does not include stress relaxation information (26). Furthermore, studies of integral and interval water absorption, and free and bound water, have given some attention to the occurrence of stress relaxation but only as a diffusion-assisting mechanism with no external mechanical stresses applied to the fiber (18,29–38).

Before initiating the experiments, it was considered that hair stress relaxation studies can only be valuable for cosmetic purposes if they at least take into account the following phenomena: 1) after washing or conditioning the hair undergoes a short drying period where its diameter, length, stiffness, and stress relaxation are out of equilibrium for several hours; 2) any study of hair mechanical conditioning involving stress relaxation has to take into account long-term equilibrium hysteresis effects; and 3) since the mechanical constraints to which hair is subjected change on a daily basis, the choice of experimental observation time periods for the fiber to relax has to be of practical value.

In this part of the research the effects of simple aqueous systems on the 1% extension forces are analyzed during and after fiber immersion. The after-treatment effects on the short-term relaxation of hair as it dries and goes through an equilibrium moisture hysteresis cycle are also analyzed.

## EXPERIMENTAL CONDITIONS

Single-hair relaxation-recovery experiments were carried out at room temperature using a Dia-Stron® rheometer. The hair length used was 50 mm, and the deformation was set at 1%. The force required to extend the fiber by 1% at a rate of 40 mm/min is called  $F(1)$ . Prior to any experimentation the fibers were washed with a 5% active TEALS water solution and rinsed thoroughly with de-ionized water. Hair tresses were virgin brown De Meo quality; from these a careful selection of fibers having a diameter of  $96 \pm 3 \mu\text{m}$  was made. The fiber diameters were measured only at 60% RH at equilibrium conditions by microscopy (25).

The chamber housing the Dia-Stron was equipped with polyethylene gloves that permitted the immersion of fibers into hermetically closed reservoirs containing the liquids under study. The rapid changes in  $F(1)$  and fiber length upon immersion were moni-

tored by several 1% straining cycles at 40 mm/min and stored in the computer memory as force-deformation data.

Moisture hysteresis cycling measurements of  $F(1)$  and its decay, as well as fiber length variations, were carried out throughout the following equilibrium relative humidities: 10%, 40%, 60%, 79%, and 87% RH.

#### CALCULATION OF THE RELAXATION DATA

The method used to follow the short-term relaxation behavior of hair while at moisture equilibrium or in the process of drying consisted in imposing on it a constant strain of 1% during a period of five minutes. The forces opposed by hair both at the beginning,  $F_0$ , and at the end,  $F_5$ , of the experiment were then registered. Previously, in a separate experiment, the same fiber was immersed in de-ionized water and measurements of the force needed to produce 1% extension,  $F_w$ , were made. The percentage of relaxation undergone by the fiber during the five-minute period, IR, or index of relaxation was then calculated as follows:  $IR = 100 \times (F_0 - F_5) / (F_0 - F_w)$ . The recovery period before starting another experiment with the same fiber was 30 minutes.

It should be pointed out that five minutes of stress relaxation were chosen because the force decay in this period was found to be sensitive to variations in the moisture content of hair produced either by environmental humidity changes in steps of 8% or by the loss of water as the fiber was drying after de-immersion. The effects of each immersion system on  $F(1)$  and IR were carried out in at least five fibers presenting the same diameter. These fibers were mechanically selected from a group of 20 by discarding those whose  $F(1)$  and IR values at 10% and 87% RH equilibrium conditions differed in more than one standard deviation; i.e.,  $21.04 \pm 0.13$  and  $9.20 \pm 0.22$  for  $F(1)$  in gm force, and  $11.03 \pm 0.16$  and  $19.3 \pm 0.34$  in percentages for IR, at 10% and 87% RH, respectively. Measurements on a single fiber were performed five times; their standard deviation was found to be no higher than 0.3% and 2% for those carried out under moisture equilibrium and non-equilibrium conditions, respectively.

## RESULTS AND DISCUSSION

#### IMMERSION OF HAIR IN OILS

Figure 1 shows the variation of  $F(1)$  immediately after the hair was immersed in four different oils, namely, cetyl palmitate, wheat germ oil triglycerides, and, 200 cSt and 350 cSt polydimethylsiloxane oils. In this figure it can be seen that the variation in  $F(1)$  was dependent upon the conditioning history of both hairs and oils. For instance, if the fiber was equilibrated at 87% RH and the oils at 10% RH, the hair showed length contractions and increments in  $F(1)$  that later decayed slowly as time elapsed.

However, if the fiber was equilibrated at 10% RH and the oil at 87% RH, then upon immersion, the fiber initially presented increments in length and decrements in  $F(1)$ . In both cases if enough time was allowed to elapse with the fiber submerged in the oils, this tendency eventually reversed and the length and  $F(1)$  returned to their initial values before immersion. When hair fibers and oils were equilibrated at the same moisture

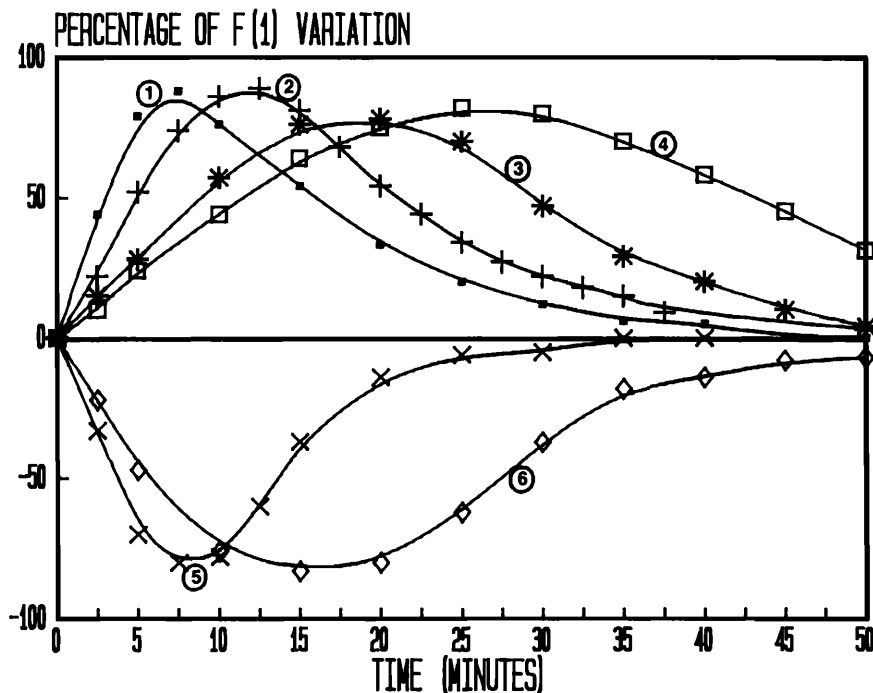


Figure 1. Percentage of F(1) variation as a function of time as follows: of hair conditioned at 87% RH and immersed in cetyl palmitate, (1); wheat germ oil, (2); polydimethylsiloxane 200 cSt, (3); and 350 cSt, (4), all conditioned at 10% RH; of hair conditioned at 10% RH and immersed in wheat germ oil, (5); polydimethylsiloxane 350 cSt, (6), both conditioned at 87% RH.

level, no variations were detected in the force and length values either upon immersion or after de-immersion.

Hysteresis cycle measurements after de-immersion showed that the oils have no significant influences on the equilibrium values of F(1), IR, and length dimensions. An unexpected observation was that fibers being submerged in the oils showed similar hysteresis values upon variation of the environmental moisture surrounding the immersion vessel. These observations indicate that hair fibers sense moisture changes while immersed in the oils. The equilibrium values of F(1)s, relaxation indices, and length dimensions took, however, about 70 hours to be attained.

#### IMMERSION OF HAIR FIBERS IN DIFFERENT AQUEOUS SOLUTIONS

The F(1)s, IRs, and changes in length at equilibrium were measured for hair fibers and immersed and de-immersed in the following aqueous solutions at different concentrations: de-ionized water, LiCl, CaCl<sub>2</sub>, NaCl, MgCl<sub>2</sub>, urea, citric acid, lysine, silk amino acids,<sup>1</sup> and hydrolyzed wheat proteins and wheat oligosaccharides.<sup>2</sup>

<sup>1</sup> Silk amino acids is a Croda product under the trade name of Crosilk liquid.

<sup>2</sup> Hydrolyzed wheat protein and wheat oligosaccharides is a Croda product under the trade name of Cropeptide W.

It was observed, in general, that the  $F(1)$  values of  $96 \pm 3 \mu\text{m}$  diameter hairs reach equilibrium in about 1.5 minutes after immersion in de-ionized water (see section A–B of curve 1 in Figure 2). De-immersion of the fiber from water leads first to a stage of rapid recovery of  $F(1)$  (see section B–C of curve 2 in Figure 2, where it can be seen at the inflection point that the fiber recovers 85% of its initial  $F(1)$  in about five minutes). After this rapid recovery period, the fiber goes through a second long stage where the remaining 15% of  $F(1)$  is recovered rather slowly in about six hours, as portrayed in Figure 3.

The observed transition between the first rapid and second long-term recovery stages described above is certainly associated with the turning point that exists between Fickean and viscoelastic water diffusion as already proposed by Warts (29,30). In Figure 3 are shown also the effects of relative humidity on the rates of recovery that appear to be faster for higher relative humidities.

Presented in Figure 4 are the IRs at different relative humidities measured two hours after de-immersion from de-ionized water. By comparing Figures 3 and 4 it can be seen that for the entire range of humidities,  $F(1)$  reaches its original equilibrium value long before the indices of relaxation do. This time difference for  $F(1)$  and IR to reach equilibrium appears to be of the same nature as that observed by Stam *et al.* (25) and Marsh *et al.* (39). These authors found that fiber weight changes due to moisture absorption reach equilibrium faster than do their length and electrical conductivities.

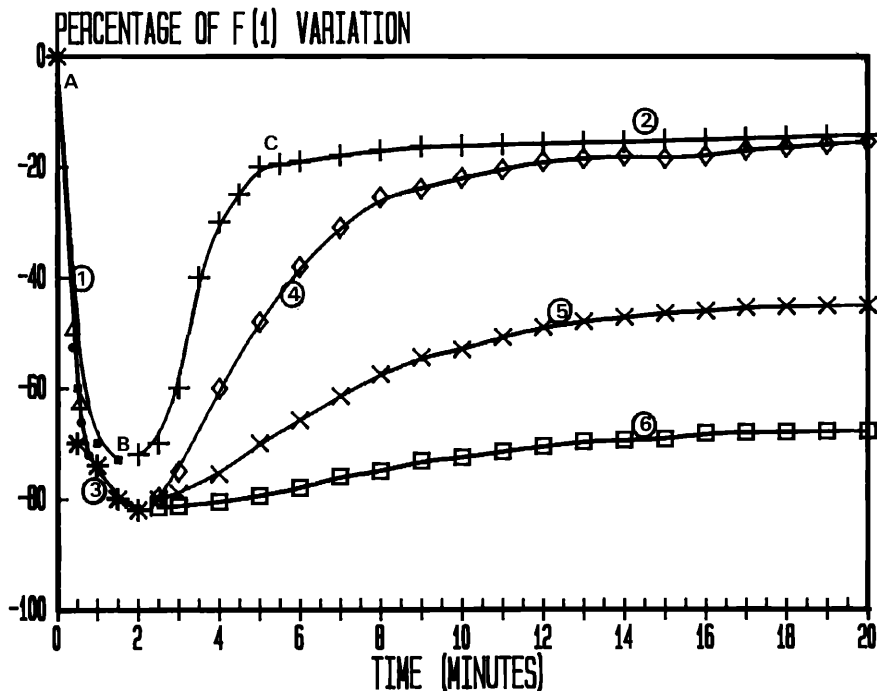


Figure 2. Percentage of  $F(1)$  variation as a function of time measured in hair fibers immediately after immersion, (i), and de-immersion, (d), under the following conditions: in de-ionized water, (i) - (1), (d) - (2); in 5% lysine, (i) - (3  $\Delta$ ), (d) - (4); in 5% silk amino acids, (i) - (3 \*), (d) - (5); in hydrolyzed wheat proteins and wheat oligosaccharides, (i) - (3  $\bullet$ ), (d) - (6).

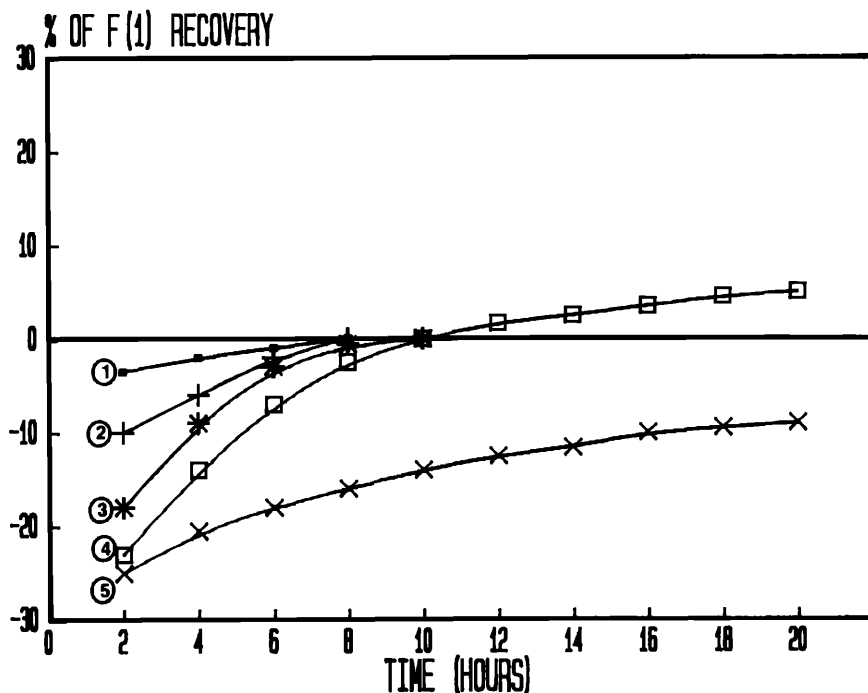


Figure 3. Percentage of F(1) variation as a function of time after two hours of de-immersion from de-ionized water at 60% RH, (1); 40% RH, (2); and 10% RH, (3); and from solutions of 5% hydrolyzed wheat proteins and wheat oligosaccharides, (4); and 5% silk amino acids, (5), both at 60% RH.

The phenomena described above implies that the soft feel sensation and relative ease in manageability of wet hair after one or two hours of drying is due to its 85% recovery of F(1) combined with its long-term great deformability. Hysteresis cycle measurements of F(1), IR, and length dimensions at different equilibrium relative humidities (see Figures 5, 6, and 7) showed, on the other hand, that there was no difference in the equilibrium mechanical properties of the fiber before and after immersion in de-ionized water as expected.

The immersion of hair fibers in aqueous solutions of LiCl, NaCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub> resulted in time variations of length and F(1)s whose direction of variation was very much dependent on the salts concentrations and the moisture levels at which the hair fibers were conditioned. For instance, hair fibers conditioned from 0% to 5% RH and immersed in saturated solutions of LiCl presented length increments and decrements in their F(1)s (see Figure 8). Alternatively, if the same fibers were conditioned above 10% RH and immersed in saturated LiCl solutions, they showed instead contractions in length and increments in their F(1)s, which then leveled off with the immersion time (see Figure 8).

For hair fibers conditioned at a particular moisture level, the observed increments in their F(1)s and length dimensions upon immersion decreased in the following order: LiCl, CaCl<sub>2</sub>, NaCl, and MgCl<sub>2</sub>, i.e., the lesser the moisture content in hair, the stronger, in the order described above, that the salt had to be in order to produce contractions in length and increments in F(1). These effects are well illustrated in Figure

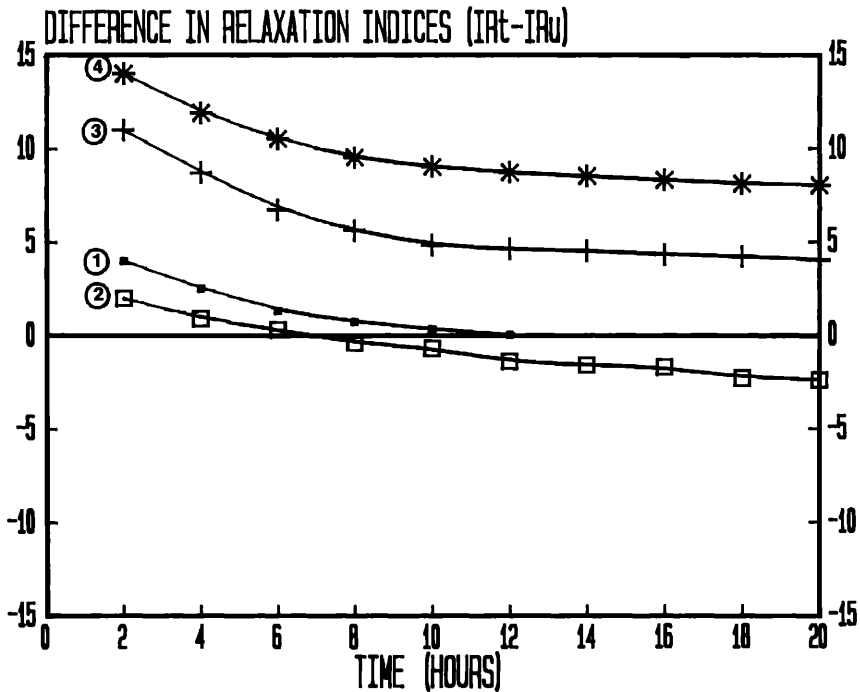


Figure 4. Difference in relaxation indices ( $IR_t - IR_u$ ) as a function of time after de-immersion as follows: from de-ionized water at 40% RH, (1); from solutions of 5% hydrolyzed wheat proteins and wheat oligosaccharides, (2); from 5% lysine, (3); and 5% silk amino acids, (4); at 40% RH.  $IR_t$  and  $IR_u$  are the relaxation indices of treated and untreated fibers, respectively.

9, where it can be seen that for fibers conditioned at 87% RH, the  $F(1)$  increments were positive for  $LiCl$  and  $CaCl_2$  and negative for  $NaCl$  and  $MgCl_2$  at saturation levels.

A time recovery pattern similar to that presented by fibers de-immersed from de-ionized water was seen to characterize the withdrawal of hair from the salt solutions. The more striking effects of these ionic solutions were, however, those displayed by the fiber at equilibrium after de-immersion without rinsing the fibers. Figures 5, 6, and 7 depict the hysteresis cycles of  $F(1)$ s, IRs, and lengths, respectively, for the untreated and treated fibers. It can be noted that while there are no significant differences on the hysteresis characteristics of  $F(1)$ s before and after treatment, the hysteresis values of the IRs and length increments have been shifted to higher levels. The magnitude of these shifts seemed to decrease with this type of salts in the same order as described earlier (see Figure 6). These results can be interpreted in the following way: the presence of these ions, in particular those of  $LiCl$ , on the treated hair leaves intact its  $F(1)$ , or capacity to respond to very rapid deformations. However, because of the large increments in short-term relaxation and fiber dimensions induced by these ions, the hair is more plastic and softer to permanent strains than the untreated hair. It is noteworthy to mention here that the effects mentioned above partially faded when the fiber was thoroughly rinsed.

Upon immersion in citric acid solutions, hair acted very much in the same manner as that described for the above-mentioned salts. The main difference was that citric acid did not seem to cause any aftereffect on the hair's  $F(1)$ , IR, and length hysteresis values.

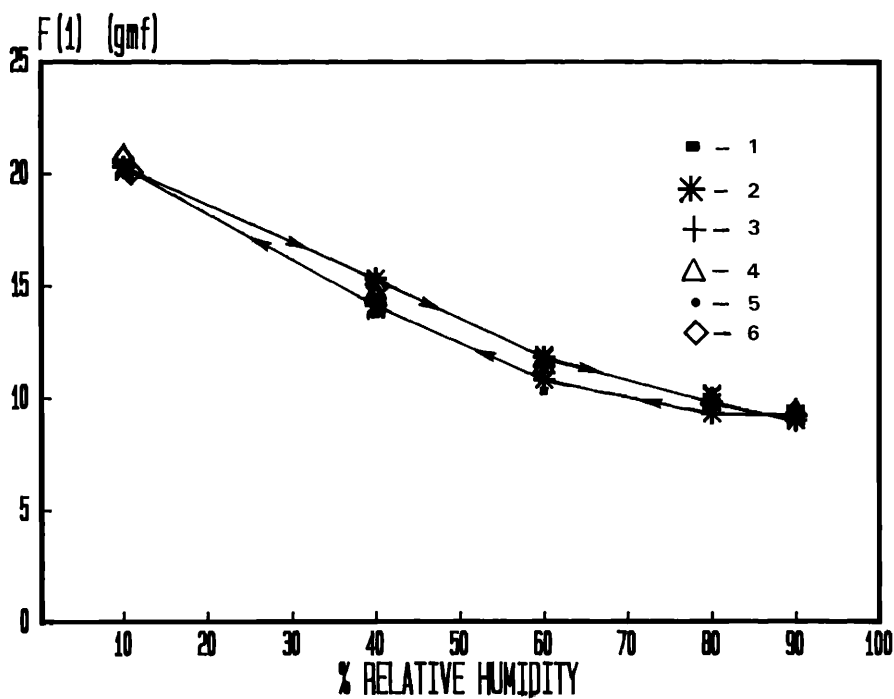


Figure 5. Hysteresis curves of F(1) after 10 minutes of fiber treatment in de-ionized water, (1); 5% LiCl, (2); 5% CaCl<sub>2</sub>, (3); 5% MgCl<sub>2</sub>, (4); 5% NaCl, (5); and 5% urea, (6).

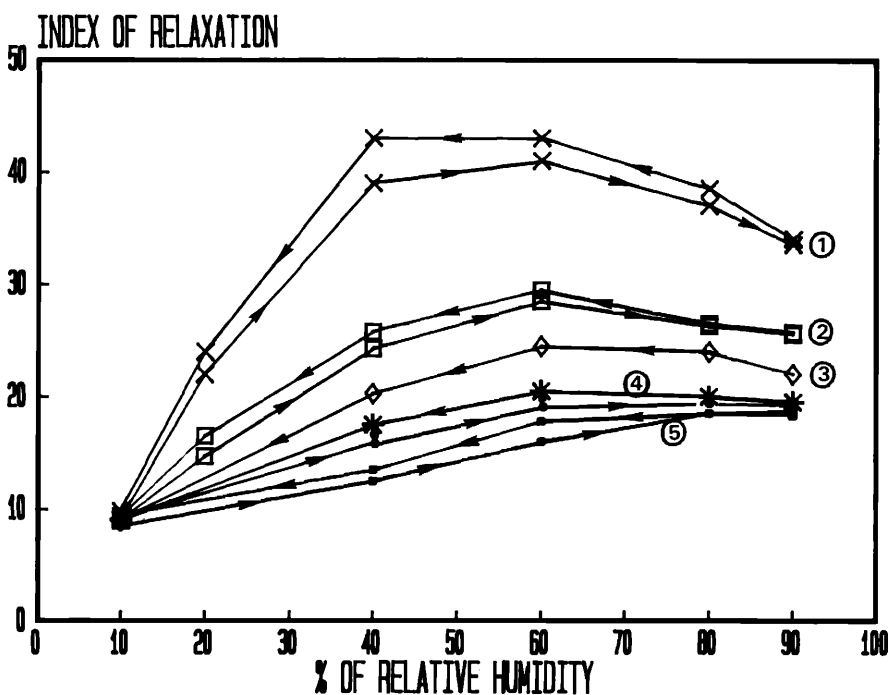


Figure 6. Hysteresis curves of relaxation indices after 10 minutes of fiber treatment in de-ionized water, (5); 5% MgCl<sub>2</sub>, (4 ●); 5% NaCl, (4 \*); 5% CaCl<sub>2</sub>, (3); 5% urea, (2); and 5% LiCl, (1).



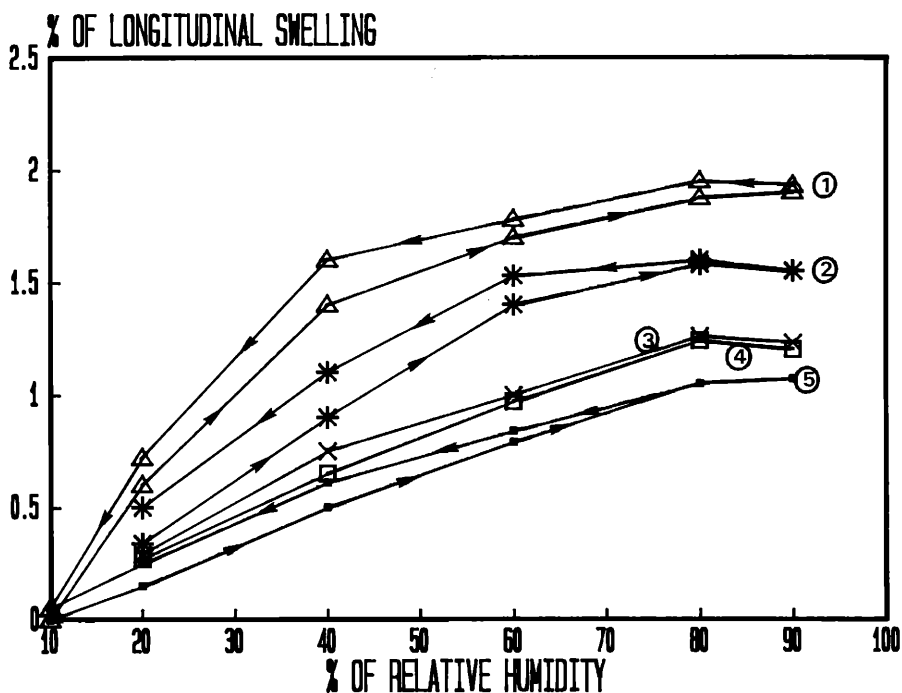


Figure 7. Longitudinal swelling as a function of moisture after 10 minutes of fiber treatment in de-ionized water, (5); 5% MgCl<sub>2</sub>, (4); 5% NaCl, (3); 5% CaCl<sub>2</sub>, (2); and 5% LiCl, (1).

Other salts that fell in this same category and led to decay and recovery patterns of F(1) similar to those produced by de-ionized water were NaNO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>.

Changes in the F(1)s or hair upon immersion in urea solutions were observed to depend also on the conditioning history of hair and on the urea concentration. The dependence of F(1) on concentration presented, however, peculiar characteristics; at concentrations lower than 10%, F(1) decreased monotonically with time and then leveled off at equilibrium values lower than that observed in the case of pure de-ionized water (see Figure 10). In contrast, at urea concentrations higher than 10%, up to saturation, F(1) showed increases, always accompanied by fiber length contractions that lasted only for a short period of time, after which F(1) started to decrease to a level lower than that observed for de-ionized water. Also, the fiber swelled 2% more in length than when immersed in pure water.

An inspection of the hysteresis cycle of IR values in Figure 6 indicates that hair treated with a 5% urea solution is slightly more plasticized than before treatment. No changes in the behavior of F(1) were, however, detected after treatment (see Figure 5). The effects of urea were seen to be totally reversible, in that upon thoroughly rinsing the fiber with de-ionized water, the hair recovered its typical normal untreated behavior.

Immersion of hair in aqueous solutions of lysine resulted in variations of F(1)s that were dependent on the lysine concentration and hair conditioning history. Upon de-immersion from a 5% lysine solution, it was seen that the time for F(1) and IR to attain equilibrium at any moisture level was slightly longer than that presented by the agents described so far (see Figures 2 and 3). Equilibration of the fiber through the hysteresis

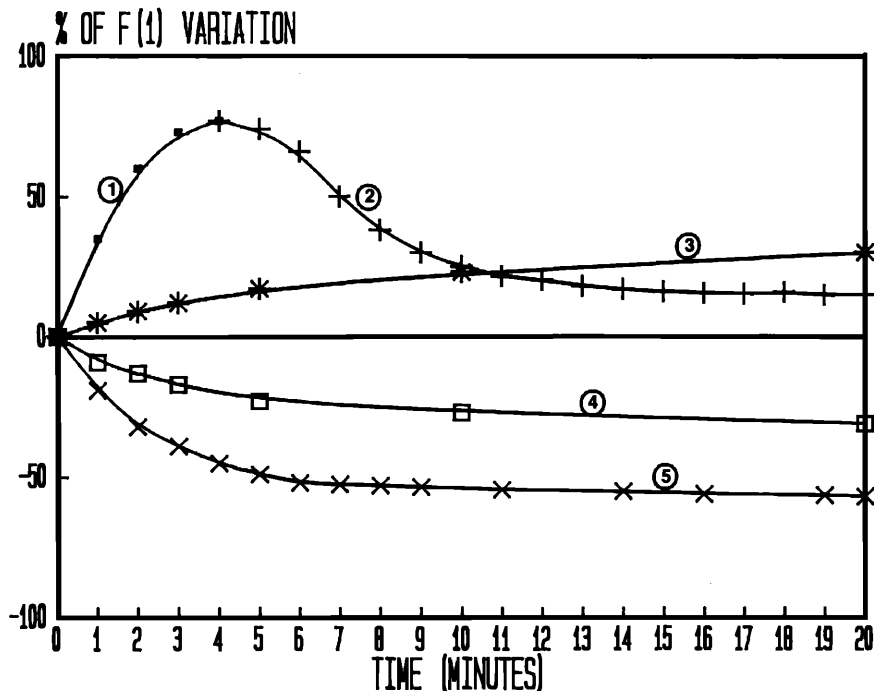


Figure 8. Percentages of F(1) variation as a function of time of hair fibers conditioned at 87% RH after immersion, (i), and de-immersion, (d), in LiCl solutions as follows: at saturation, (i) - (1), (d) - (2); 35%, (i) - (3); of hair fibers conditioned at 5% RH at saturation, (i) - (4); and 35%, (i) - (5).

cycle showed that the presence of lysine on the fiber causes decreases and increases in the equilibrium values of F(1) and IRs, respectively (see Figure 11). Hence, it seems that this amino acid confers an overall plasticization to the fiber.

The behavior of hair fibers immersed in silk amino acids, and in hydrolyzed wheat proteins and wheat oligosaccharides, presented substantial differences when compared to any of the immersion systems already described above. For instance, the behavior of F(1)s and length upon immersion in these systems was always unidirectional and independent of the amino acid and oligosaccharide concentrations. Equilibration of the F(1)s and IRs after de-immersion from these solutions also took more time than with any of the other immersion systems (see Figure 2).

The above results can be explained by considering that when these proteins are absorbed onto the hair, they retard the desorption of water, thereby causing a delay in the turning point that exists between viscoelastic and Fickian diffusion (29,32). It is important to note here that similar modifications in the water absorption isotherm of wool have been induced by the physical and chemical treatment of these fibers (42).

The hysteresis behavior of F(1)s and IRs of fibers treated with a 5% silk amino acids solution shows that they have been greatly plasticized (see Figure 12). The effects of a 5% solution of hydrolyzed wheat proteins and wheat oligosaccharides seems, in contrast, to render the fiber stiffer, although its rate of relaxation as measured by the IR seems to increase at low humidities and to decrease at high levels of moisture (see Figure 12).

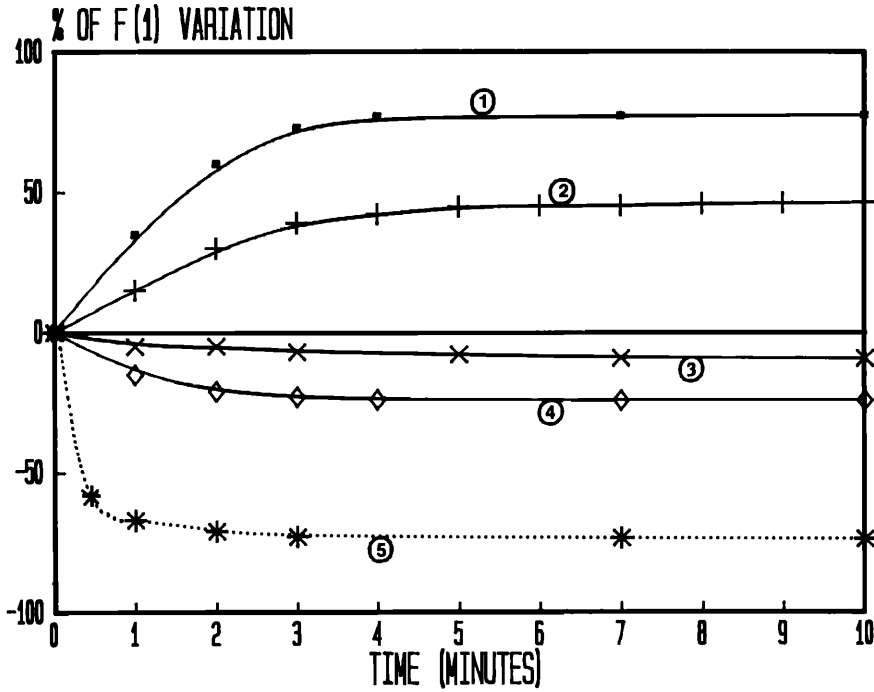


Figure 9. Percentages of F(1) variation as a function of time of fibers immersed in saturated solutions of the following salts: LiCl, (1); CaCl<sub>2</sub>, (2); MgCl<sub>2</sub>, (3); NaCl, (4); and de-ionized water, (5).

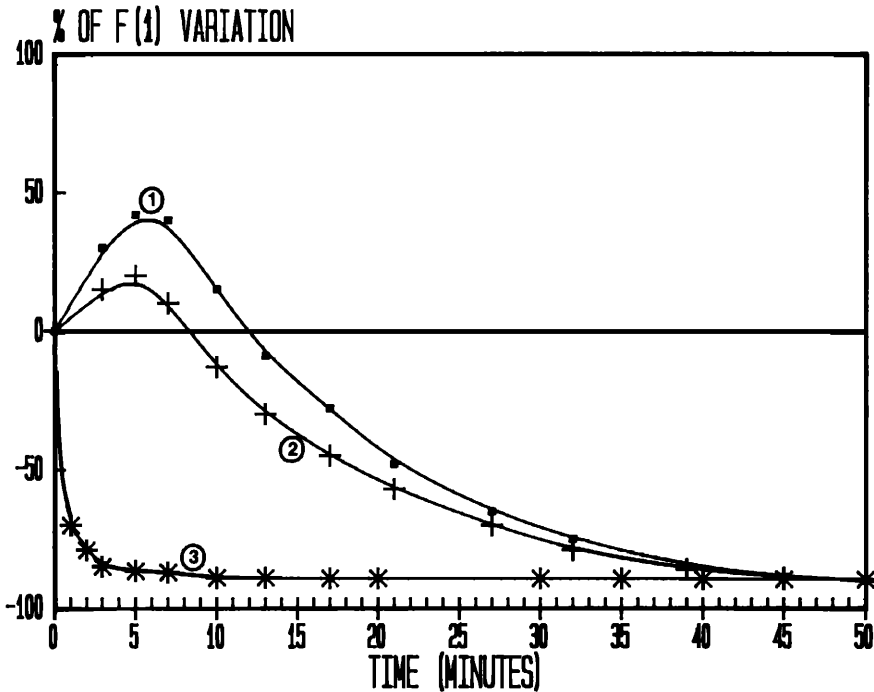


Figure 10. Percentages of F(1) variation as a function of time of fibers immersed in urea solutions as follows: 35% (1); 15% (2); and 5% (3).  
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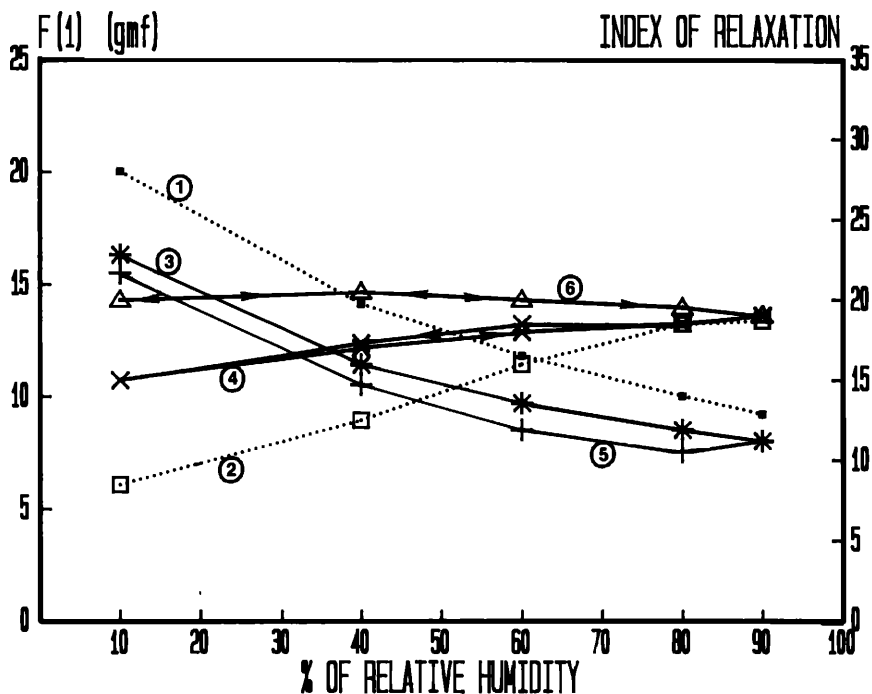


Figure 11. Hysteresis curves of different fibers as follows: F(1) - (1), and IR - (2), of an untreated fiber; F(1) - (3), and IR - (4), of a 10-minute-treated fiber in 5% lysine; and F(1) - (5), and IR - (6), of a 10-minute-treated fiber in 5% silk amino acids.

#### IMMERSION OF HAIR IN DIFFERENT SOLVENTS AND IN W/O AND O/W EMULSIONS

Hair products are often presented in emulsion form and sometimes contain solvents such as glycerine or propylene glycol. It was, therefore, considered appropriate to study the separate effects of glycerine, propylene glycol, propanol, ethanol, and methanol, and also of some w/o and o/w emulsions, on the F(1)s and IRs of hair. Immersion of hair fibers in these liquids resulted again in F(1) and length variations that were strongly dependent on the moisture content of both the fibers and liquids (see Figure 13).

The solvents produced increments or decrements in F(1), depending on whether they were conditioned at lower or higher humidities than the hair fibers. In Figure 13 are shown F(1) variations in time of hairs conditioned at 87% RH and immersed in solvents conditioned at 10% RH. It should be pointed out that this type of solvent conditioning effect was only characteristic of glycerine and propylene glycol. The addition of small amounts of water to the solvents eliminated the need for their conditioning, as would be expected.

The immersion in w/o and o/w emulsions was found, on the other hand, to induce length extensions and F(1) decrements for all fibers conditioned at relative humidities lower than 87% RH. In Figure 13 it can be appreciated, for instance, that the emulsions decrease the values of F(1) of fibers conditioned at 87% RH, although not as low as in the case of pure de-ionized water. No aftereffect could be detected in the hysteresis cycles of F(1)s, IRs, and length dimensions of fibers de-immersed from all these solvents and

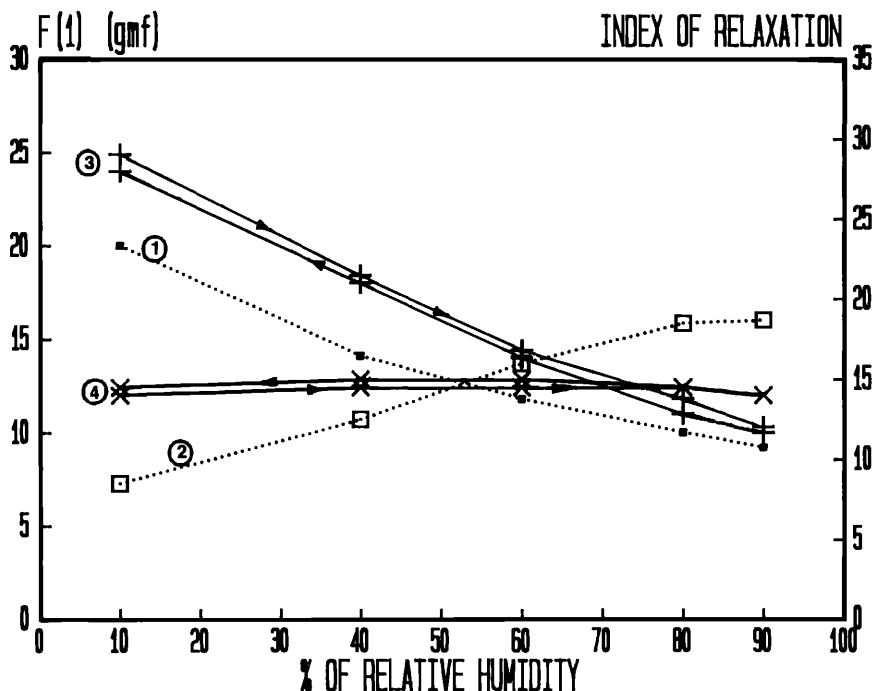


Figure 12. Hysteresis curves of fibers treated 10 minutes in a 5% solution of hydrolyzed wheat proteins and wheat oligosaccharides as follows: F(1) - (1), and IR - (2) of untreated fibers; and F(1) - (3), and IR - (4) of treated fibers.

emulsions, except for the glycerine and propylene glycol systems that gave rise to fibers with a strong hysteresis effect. In Figure 14 it is shown, for instance, that as moisture increases, hairs de-immersed from glycerine and propylene glycol follow the normal behavior shown by untreated fibers. However, once the fibers have been brought to a high humidity level, their F(1) and IR Values do not change appreciably as moisture is decreased, i.e., the F(1) and IR equilibrium values of the two half portions of the hysteresis cycle differ significantly. Further moisture cycles did not seem to cause any change (see Figure 14).

The dependency of F(1) and length variations presented by most fibers immediately after immersion in the liquid systems suggests that moisture transport between hair and solution equilibrates through a water partition mechanism that is strongly dependent upon the water structure and water concentration in the liquid system. For instance, when hair is conditioned at 87% RH and immersed in the oils, glycerine, and propylene glycol, all conditioned at 10% RH (see Figures 1 and 13), and in the saturated solutions of LiCl, CaCl<sub>2</sub>, and urea (see Figures 8 and 9), length contractions and F(1) increments take place because water is transferred from hair to the immersion system.

Conversely, when hair conditioned at 5% RH is immersed in saturated solutions of LiCl and CaCl<sub>2</sub>, the oils (see Figure 1), glycerine, and propylene glycol (the latter three conditioned at 87% RH; see Figure 13), or if hair conditioned at 87% RH is immersed in the emulsions and the saturated solutions of NaCl, MgCl<sub>2</sub>, or citric acid (see Figures 8, 9, and 13), then the hair swells and F(1) decreases because moisture is transferred

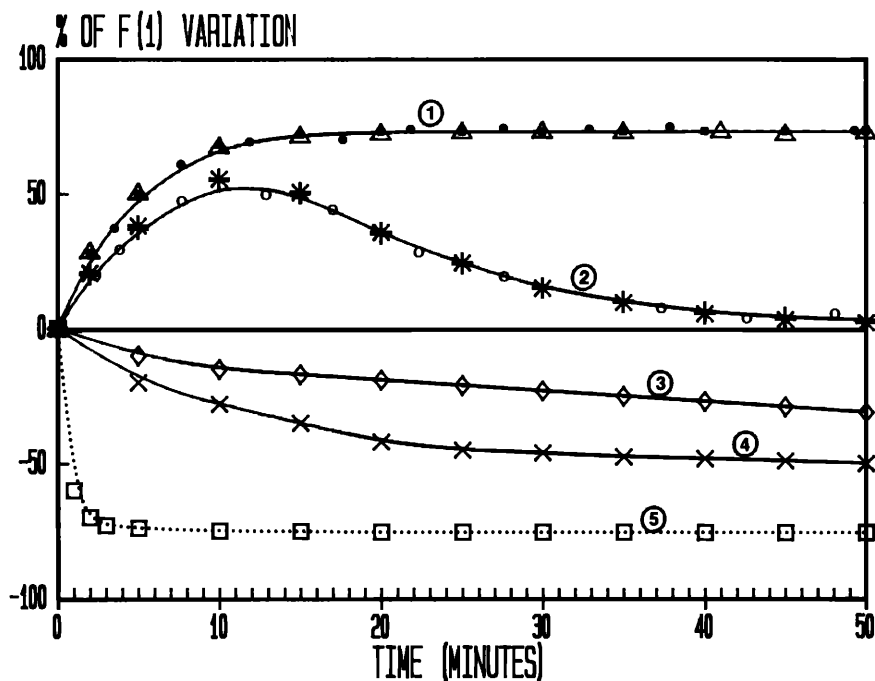


Figure 13. Percentages of F(1) variation as a function of time of fibers immersed in the following systems: methanol, (1 ■); ethanol, (1 △); propanol, (1 ●); glycerine, (2 \*); propylene glycol, (2 ○); w/o, 50/50 water/lanolin emulsion 3600 cSt, (3); o/w, 50/50% PEG lanolin emulsion 4200 cSt (4); and de-ionized water (5).

from the immersion system into the hair fibers, although the degree of swelling and F(1) decay is not as high as in the case of de-ionized water.

The effects of liquid systems that produce only unidirectional changes in F(1) and fiber length regardless of the moisture content in hair and solute concentration can, thus, be explained by their less organized water structure. According to these arguments, the availability of water for hair, upon immersion, will be higher in the aqueous solutions of proteins,  $\text{Na}_2\text{CO}_3$ , and  $\text{NaNO}_3$ , while in the emulsions and saturated solutions of  $\text{LiCl}$ ,  $\text{CaCl}_2$ ,  $\text{NaCl}$ , and  $\text{MgCl}_2$ , hair will compete for water in a more structured environment. As has already been shown by some researchers, water forms part of a highly ordered structure in solutions of these salts and in some emulsions (43,44,48).

The particular behavior of urea solutions in hair seems to indicate that immediately after immersion, moisture exclusion from hair takes place by a water-partitioning mechanism and, as a consequence, the fiber contracts. As time elapses, however, with the simultaneous diffusion of urea into the amorphous matrix of hair, swelling by hydrogen bond breakage becomes the dominant process. The case of saturated solutions of  $\text{LiCl}$  might follow similar lines of reasoning, although, instead of swelling, one would expect super-contraction to occur (40,41). It seems thus, in general, that before oils, ions, or solvents diffuse into the hair shaft, the fiber undergoes a moisture equilibration process.

In order to elucidate the role of moisture on the F(1)s, IRs, and length dimensions of fibers at different equilibrium conditions, several fibers were subjected to hysteresis



Figure 14. Hysteresis curves of fibers treated as follows: F(1) - (1 +), and IR - (2 □), after 10-minute treatment in 100% glycerine; and F(1) - (1 ○), and IR (2 ●), after 10-minute treatment in 100% propylene glycol.

cycling experiments while immersed in polydimethylsiloxane oil 350 cSt. These fibers were those treated in aqueous solutions of 5% LiCl, 5% urea, and 100% glycerine. Parallel to these experiments, water absorption determinations of two groups of 17-gm tresses treated in the same manner (plus a control) were carried out (see Figures 15 and 16); the first group was immersed in polydimethylsiloxane oil while the second was not immersed.

The control and 5% LiCl-treated tresses immersed in the oil absorbed only 0.1% of their total weight during a period of 70 hours after the chamber relative humidity was changed from 12% to 87% RH; in fact, water diffusion into hair throughout the oil was so slow that both tresses absorbed only 4% after 30 days (see Figure 16). In contrast, those not immersed in oil and treated with 5% LiCl, glycerine, propylene glycol, and hydrolyzed wheat proteins and wheat oligosaccharides absorbed rather rapidly percentages of water that ranged from 5% to 20% in about 70 hours (see Figure 15).

This observation is somewhat surprising since the detected changes in the hysteresis values of F(1) and IR of both fibers, i.e., those immersed and not immersed in polydimethylsiloxane oil, were found not to be significantly different within the 70-hour period in spite of their great differences in absorbed moisture content.

This apparent contradiction might be explained if it is taken into account that the first layer absorbed onto the polar protein groups, called also the n-BET monolayer, has been reported to be of the order of 0.38 moles of water per 100 g of protein for wool (23,45). Although this monolayer might be of different dimensions in hair, it is quite possible

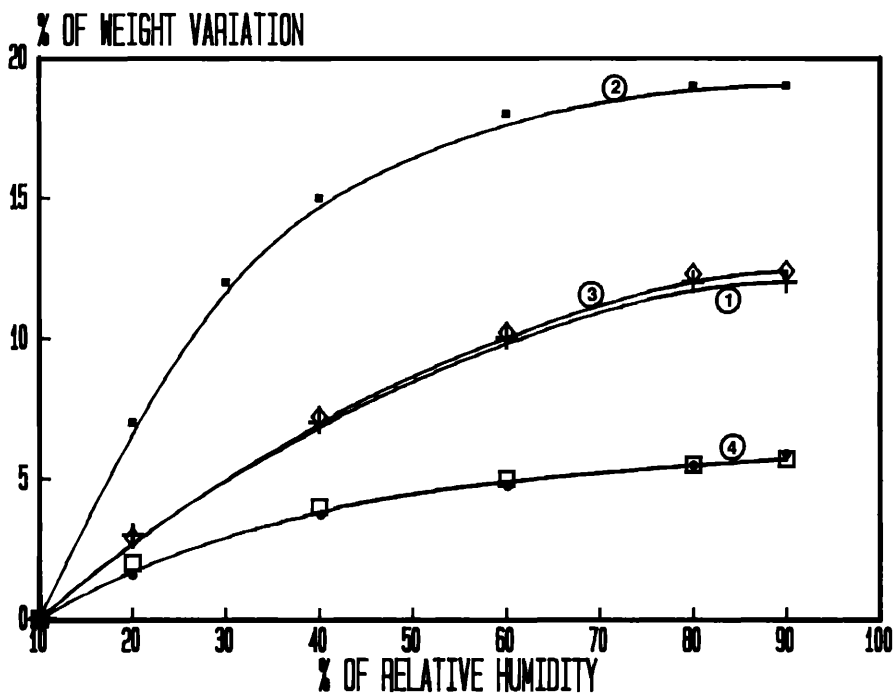


Figure 15. Weight variation percentages as a function of moisture of 17-g tresses after treatment under the following conditions: untreated fiber, (1); 10 minutes in 5% LiCl, (2); 10 minutes in 5% hydrolyzed wheat proteins and wheat oligosaccharides, (3); 10 minutes in 100% glycerine, (4 □); and 100% propylene glycol, (4 ●).

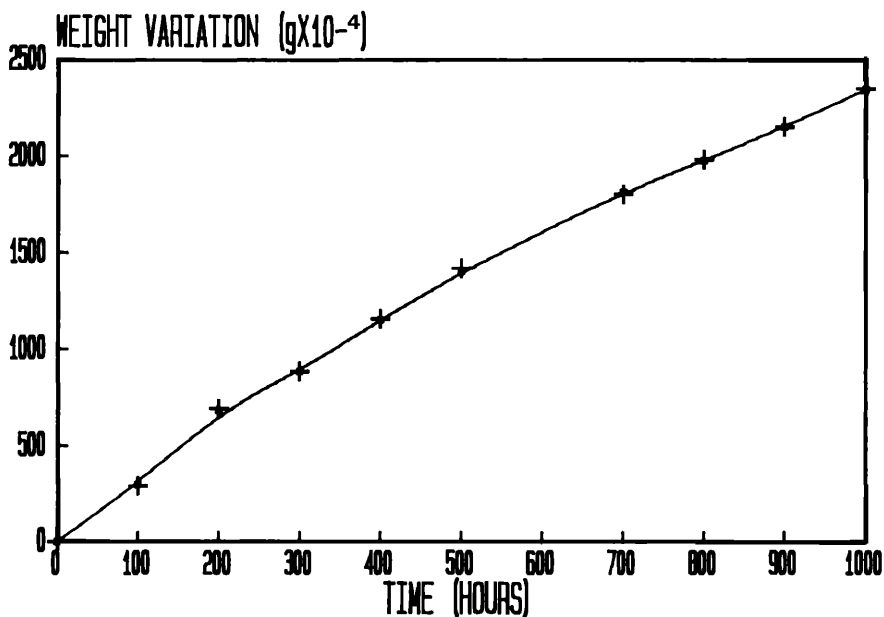


Figure 16. Percentages of weight variation as a function of time of hair tresses immersed in 350 cSt polydimethylsiloxane oil after a change from 10% to 87% RH as follows: untreated control, (■); and a tress treated in 5% LiCl during 10 minutes, (+).

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that the changes observed in  $F(1)$  and IR values for both fibers, immersed and non-immersed in oil, depend only on the small water contents of their respective monolayers.

The changes in equilibrium values of  $F(1)$ s, IRs, and length values after treatment in the aqueous solutions of salts and urea can, thus, be explained if it is assumed that these chemicals modify the hydrogen-bonding relaxation processes associated with water in this monolayer (4,15,16,19,37). For instance, the large fiber IR increments accompanied by small IR hysteresis effects induced by LiCl and urea solutions in particular (see Figure 6) might be due to their ability to disrupt slightly the hair protein water structure, i.e., their chaotropic action (43,44).

The strong hysteresis effects observed in fibers treated with glycerine and propylene glycol might be, on the other hand, due to the solvation of hair proteins once the solvents penetrate, swelling the fiber. Finally, the induced effects of proteins and amino acids on the  $F(1)$ s and IRs of hair might result from interaction of the following phenomena: 1) upon diffusion into hair the amino acids increase the number of hydrophilic groups capable of interacting with the hair water-adsorbing sites; and 2) in the case of wheat proteins and wheat oligosaccharides, the later substance might form simultaneously a film that reduces the amount of absorbed water by volume exclusion of water molecules. It is noteworthy that similar mechanisms have been invoked to explain water absorption modifications in wool treated with polymer molecules and other compounds containing amino and carboxylic groups (42,46,47).

## CONCLUSIONS

Changes in the forces to extension and length contractions of hair fibers have been shown to take place in a manner that depends on the nature of the immersion systems. Most of these effects are due to the partitioning of components across the fiber-liquid interface. This partitioning might involve several transport mechanisms such as osmosis, diffusion, and migration. Further investigation is being carried out to assess the role of each mechanism and that of the pH solution. It has also been shown that the short decay in force to deform a hair fiber by 1%,  $F(1)$ , is modified if some liquid system components remain on the fibers.

## ACKNOWLEDGMENTS

The author is grateful to Kevin F. Gallagher for his valuable criticisms and enthusiastic support throughout the completion of this work. Also the helpful discussions with Herb Eldestein and Roger T. Jones of Croda, England; Mario Garcia of Clairol; and Philip Miner of Cheseborough Ponds, are gratefully appreciated.

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