*J. Soc Cosmet. Chem.*, **28**, 273–284 (May 1977)

# Wettability of keratin fiber surfaces

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*Received July 19, 1976. Presented Ninth IFSCC Congress, June 1976, Boston, MA.*

## Synopsis

The WETTING of HAIR FIBERS by WATER has been measured using the Wilhelmy balance technique developed at Textile Research Institute Princeton, N. J. specifically for FIBROUS MATERIALS. The data for selected and treated hair samples suggest cause–effect relationships between WATER WETTABILITY of the FIBER SURFACE and MECHANICAL, WEATHERING, and CHEMICAL FIBER DAMAGE. Critical surface tension of the hair fiber surface has been determined with water-butanol mixtures using the same technique. Furthermore, dispersion and nondispersion contributions to the surface free energy of the fiber have been evaluated by measuring wettabilities against a polar and a nonpolar liquid. The results indicate that the molecular processes occurring at the interface between the keratin fiber surface and a liquid have considerable effect on the surface free energy of the fibers.

## INTRODUCTION

Human hair is an important member of the keratin fiber group. Keratins are structural proteins, which occur widely in the vertebrate epidermis and its appendages. Unlike man-made fibers, human hair is cellular in structure, consisting of a central core called the cortex covered by a sheath of several layers of flattened cuticle cells. The cuticle cell itself consists of various layers, the endocuticle, exocuticle, and the a-layer, proceeding from the inside to the outside in that order. The thin outermost layer that forms a sheath around the cuticle cell is known as the epicuticle and is hydrophobic, whereas, the cortex is hydrophilic. Although, no definitive information is available about the composition of the epicuticle of hair fibers, King and Bradbury [1] have found that the epicuticle obtained from Merino wool consists of 78 per cent protein, 5 per cent lipid, and 4 per cent ash. Values may be of a similar order for hair. The hydrophobicity of the fiber surface may in part be due to the lipid content of the epicuticle.

The characteristic toughness and the insolubility of keratins in water is attributable to the presence of the sulfur-containing amino acid, cystine, which acts as a crosslinking agent. From the work of Wolfram and Lindemann [2] and Swift and Bews [3], it can be seen that the cuticle of hair contains more cystine than the cortex. Histochemical observations of cuticle cross sections by the latter authors show that most of the cystine is concentrated in the exocuticle and especially in the a-layers. This renders these outer layers of the cuticle tough and somewhat brittle. Exposure to ultraviolet rays of the sun can degrade the cuticle material, giving rise to hydrophilic groups in the surface. Severe mechanical damage during washing and combing of hair can destroy the cuticle and expose the hydrophilic cortex. It would appear, therefore, that measurement of the water wettability of the fiber surface could provide useful semiquantitative information about the extent of damage undergone by the fiber.

Apart from the kinds of damage described above, various chemical treatments of hair for aesthetic purposes such as bleaching (oxidation) and waving (reduction) also degrade the cuticle by breaking disulfide bonds and generating hydrophilic groups in the surface. Again, changes in the wettability of the hair surface against water should be a good measure of the extent of oxidation or reduction in the surface regions of the fiber. However, it should be noted that such measurements do not give any information about the changes occurring within the bulk of the fiber.

Knowledge of the surface free energy of the fiber will be useful for the formulator of hair-care products, which are applied in the form of sprays, and are expected to spread spontaneously on the surface. The critical surface tension would be a useful measure of the surface free energy of the hair fiber surface. It should be noted, however, that the conventional method of Zisman [4] for determining the critical surface tension of solids, is of limited applicability in that it represents only the dispersion contribution to the surface free energy.

In the work presented here, an attempt has been made to understand the effect of weathering and mechanical damage on the wettability of the fiber surface against water. The same technique has been used to monitor oxidation and reduction reactions at the fiber surface. The role of dispersion and nondispersion contributions to the surface free energy have been evaluated, and it is hoped that this will lead to a better understanding of the processes occurring at hair-liquid interfaces.

## THEORETICAL

The spreading of liquids on the surface of a solid is governed by the 3 interfacial tensions, $\gamma_{SV}$, $\gamma_{SL}$, and $\gamma_{LV}$, where the symbols S, L, and V stand for solid, liquid, and vapor, respectively. The relationship between these tensions when a liquid surface is in equilibrium contact with a solid surface is given by the Young-Dupré equation:

$$\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL} \tag{1}$$

where $\theta$ is the contact angle. The term $\gamma_{LV} \cos\theta$ is often referred to as the wettability W of the surface.

Determination of the wettability of a fiber by the Wilhelmy balance principle involves the measurement of the force acting (upward or downward), depending on the contact angle) on a counterbalanced single fiber when contact with the liquid surface is established. Equations relevant to this situation have been developed by Miller and Young [5]. The vertical force acting on the fiber is given by

$$F_w = w - F_b \tag{2}$$

where w is the wetting force, $F_w$ is the electrobalance force reading corrected for force reading in air, and $F_b$ is the buoyancy force on the fiber. The buoyancy force on the fiber is given by

$$F_b = lad \tag{3}$$

where l equals immersed length of the fiber, a equals area of the fiber cross section, and d equals density of the liquid. Substituting for $F_b$ in equation (2) leads to equation (4):

$$F_w = w - lad \tag{4}$$

Therefore, a plot of $F_w$ as a function of immersion depth l should give a straight line with slope (−ad) and intercept w. Wettability W, defined as the wetting force per unit length of the wetted perimeter, is given by w/P, where P is the perimeter of the fiber, i.e.,

$$W = \frac{w}{P} = \gamma_{LV} \cos\theta \tag{5}$$

The interfacial tension between a solid and a liquid phase in equilibrium is given by

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - A \tag{6}$$

where A is the work of adhesion. Substituting eq. (1) in (6) gives

$$A = \gamma_{LV}(1 + \cos\theta) = \gamma_{LV} + W \tag{7}$$

It should be noted that the work of adhesion is physically more meaningful than either W or the contact angle, since it quantifies solid-liquid interactions in such a way that the attraction between a series of liquids and one or more solids can be compared directly. Therefore, some results have been expressed in terms of the work of adhesion instead of wettability or contact angle.

Equation (7) can be written in logarithmic form

$$\log(1 + \cos\theta) = \log A - \log \gamma_{LV} \tag{8}$$

According to Fowkes [6], if only dispersion interactions are involved, a plot of log (1 + cos $\theta$) for a series of liquids on a given solid versus log $\gamma_{LV}$ should be linear with a slope of −1, and the intercept on the $\gamma_{LV}$ axis at log 2 (cos $\theta$ = 1) should give the so-called critical surface tension, a measure of the surface free energy of the solid. Conventional Zisman plots have been found to be nonlinear for the solid-liquid systems used in this work, suggesting that there are contributions from interactions other than dispersion forces.

Therefore, dispersion and polar contributions to surface free energy have been evaluated by the method of Wu [7]. This method uses the "reciprocal means" approach for the dispersion and polar contributions to the work of adhesion A in eq. (7), so that we obtain

$$\gamma_{LV}\cos\theta = -\gamma_{LV} + \frac{4\gamma_S{}^d\gamma_L{}^d}{\gamma_S{}^d + \gamma_L{}^d} + \frac{4\gamma_S{}^p\gamma_L{}^p}{\gamma_S{}^p + \gamma_L{}^p} \tag{9}$$

By measuring cos $\theta$ (or, in our case, $\gamma_{LV}$ cos $\theta$) for a solid in 2 different liquids, 1 polar and the other nonpolar, 2 simultaneous equations are obtained, which can be solved for $\gamma_S^d$ and $\gamma_S^p$. Values of $\gamma_L^d$ and $\gamma_L^p$ for the 2 liquids must be known (for details see the original reference). Symbols "d" and "p" stand for dispersion and polar contributions, respectively.

## EXPERIMENTAL

### MATERIALS

European dark brown hair* has been used throughout this work. The hair was cleaned by extraction with methylene chloride followed by exhaustive rinsing with distilled water. All specimens were conditioned at 65 per cent RH and 70°F.

Water used in this work was distilled twice in an all-glass apparatus. For preparing water-butanol solutions analytical reagent grade n-butanol was used. These solutions were prepared according to the method of Shuyten *et al.* [8], and their surface tensions were measured by the standard capillary rise method. Fischer purified reagent grade methylene iodide was redistilled under vacuum (38°C, ~2 mm Hg). Hydrogen peroxide† for oxidation was electronic grade. Dithiothreitol used in reduction was obtained from Calbiochem.‡

### WETTING FORCE MEASUREMENTS

The apparatus for the wetting force measurements has been described elsewhere [5]. It consists of an electrobalance and a microscope stage for raising and lowering the liquid level. The fiber is glued to a small wire hook mounted on the beam of the balance and counterbalanced in air. The liquid level is raised to immerse the fiber 1 mm at a time up to an immersed length of 5 mm. The fiber is then allowed to remain immersed in the liquid for ~15 min during which time the force on the electrobalance reaches a constant level. Advancing wetting forces at immersion depths of 1–5 mm and the force after it has reached a constant level are read from the chart. All measurements were made in an environment of 65 per cent RH and 70°F.

Perimeters of the fibers were determined microscopically. Values of the perimeters calculated from the major and minor axes of the elliptical cross section have been found to agree with the actual measured values within ~3 per cent.

Electron micrographs were made with a scanning electron microscope.** Fiber specimens were coated with gold prior to microscopic examination.

## RESULTS AND DISCUSSION

### WETTING BEHAVIOR OF HAIR-WATER SYSTEM

The recorder trace obtained in a typical measurement of wetting force is shown in Fig. 1. At the first contact with the water surface, an upward (negative) force is experienced

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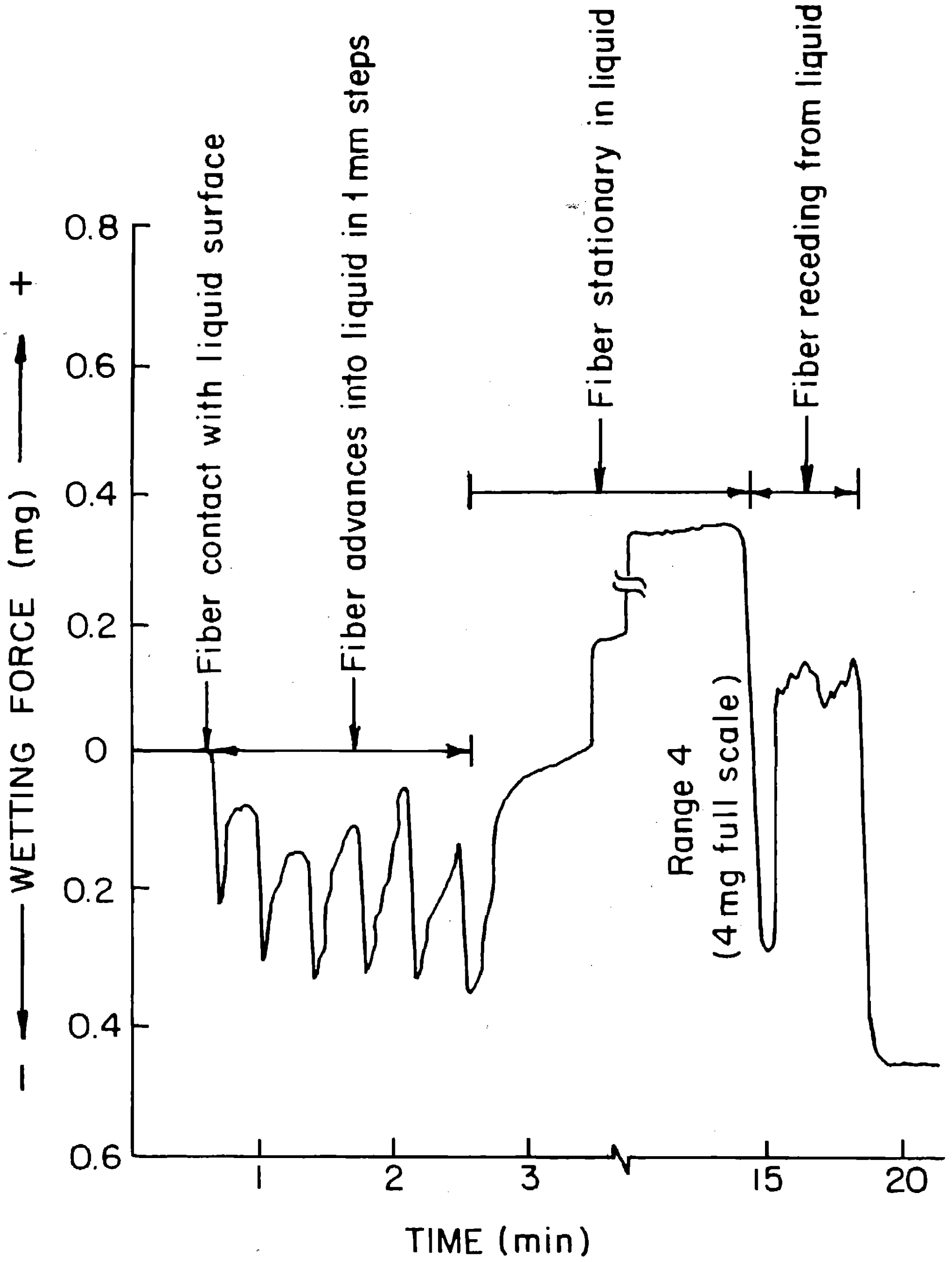


Figure 1. Wetting force curve (advancing and receding) for human hair fiber in water

by the fiber which quickly reduces with time. On further immersion of the fiber, the upward force on the fiber is reinstated (in fact it is slightly higher due to the additional buoyant force on the fiber). This pattern is observed during the immersion of each millimeter of the fiber up to a depth of 5 mm. When the fiber is left in the water, the upward force slowly decreases, and in most cases, the direction of the force changes to the downward (positive) direction and reaches an approximately constant value. This value is referred to as the "equilibrium" wetting force $w_e$. All the results pertaining to the so-called "equilibrium" condition are designated by the subscript 'e'. The advancing wetting force is calculated from the 5 force readings obtained during the immersion of millimeter lengths of the fiber by linear regression analysis using eq. (4). The intercept is the advancing wetting force $w_a$. Results pertaining to this condition are designated by the subscript 'a'.

The time-dependent change in the wetting force toward more positive values cannot be attributed to absorption of water into the fiber, because the amount absorbed is much too small to account for the difference between $w_a$ and $w_e$. To understand the time dependence of the wetting behavior of hair fibers illustrated in Fig. 1, glass, nylon, and polypropylene fibers were examined [9], and qualitatively all of them exhibited a similar behavior, i.e., $w_e > w_a$. In the case of glass and nylon fibers, both $w_e$ and $w_a$ were positive, whereas, in the case of polypropylene both were negative. In the case of untreated hair, $w_e$ was positive in most cases and $w_a$ was negative. Even a platinum wire exhibited the same behavior. However, the difference between the two wetting forces ($w_e - w_a$) was much larger for hair and nylon fibers than for glass and polypropylene fibers and the platinum wire. This would suggest that the time-dependent increase in the wetting force occurring when the fiber is left in the water at a depth of 5 mm may at least partly be due to interaction of the liquid with the surface molecules of the solid; in the case of hair and nylon, hydrogen bond breaking can occur. It is possible that the lower wetting force $w_a$ observed when a new interface is established between the solid and the liquid, is partly due to the high advancing velocity (~15 mm/min) and partly due to the lowering of the surface energy of the solid as a result of adsorption of molecules of water vapor during conditioning at 65 per cent RH. When such a conditioned solid is brought into contact with the liquid surface, adsorbed liquid molecules reorient at the solid-liquid interface reducing $\gamma_{SL}$, thus increasing the wettability of the solid surface. This phenomena has been observed by Shafrin and Zisman [10] in the case of glass at various relative humidities. In the case of polymers that interact with the liquid, however, a further increase in wettability would be caused by relaxation of polymer molecules in the surface regions and orientation of polar groups toward the liquid and nonpolar groups away from the liquid. This situation is strongly indicated in the wetting behavior of hair fiber against water.

## EFFECT OF WEATHERING AND MECHANICAL DAMAGE

In the case of long hair fibers, the extent of weathering and mechanical damage is likely to be greater near the tip than near the root. Therefore, a 10-in. long hair fiber was cut into 6 sections and the wettability of each section was determined by immersing the end closest to the tip. The advancing and "equilibrium" contact angles calculated from measured wetting forces are reported in Table I. In this Table, A is the tip section (may not be the natural tip) and F is the root section. As can be seen, the tip end is more hy-

Table I

Contact Angles (Calculated) of Water Against Hair Measured Along the Length of the Fiber

| Fiber section | $\theta_a$(degrees) | $\theta_r$(degrees) |
|---|---|---|
| A | 72 | 64 |
| B | 73 | 68 |
| C | 67 | 68 |
| D | 99 | 81 |
| E | 101 | 76 |
| F | 103 | 89 |

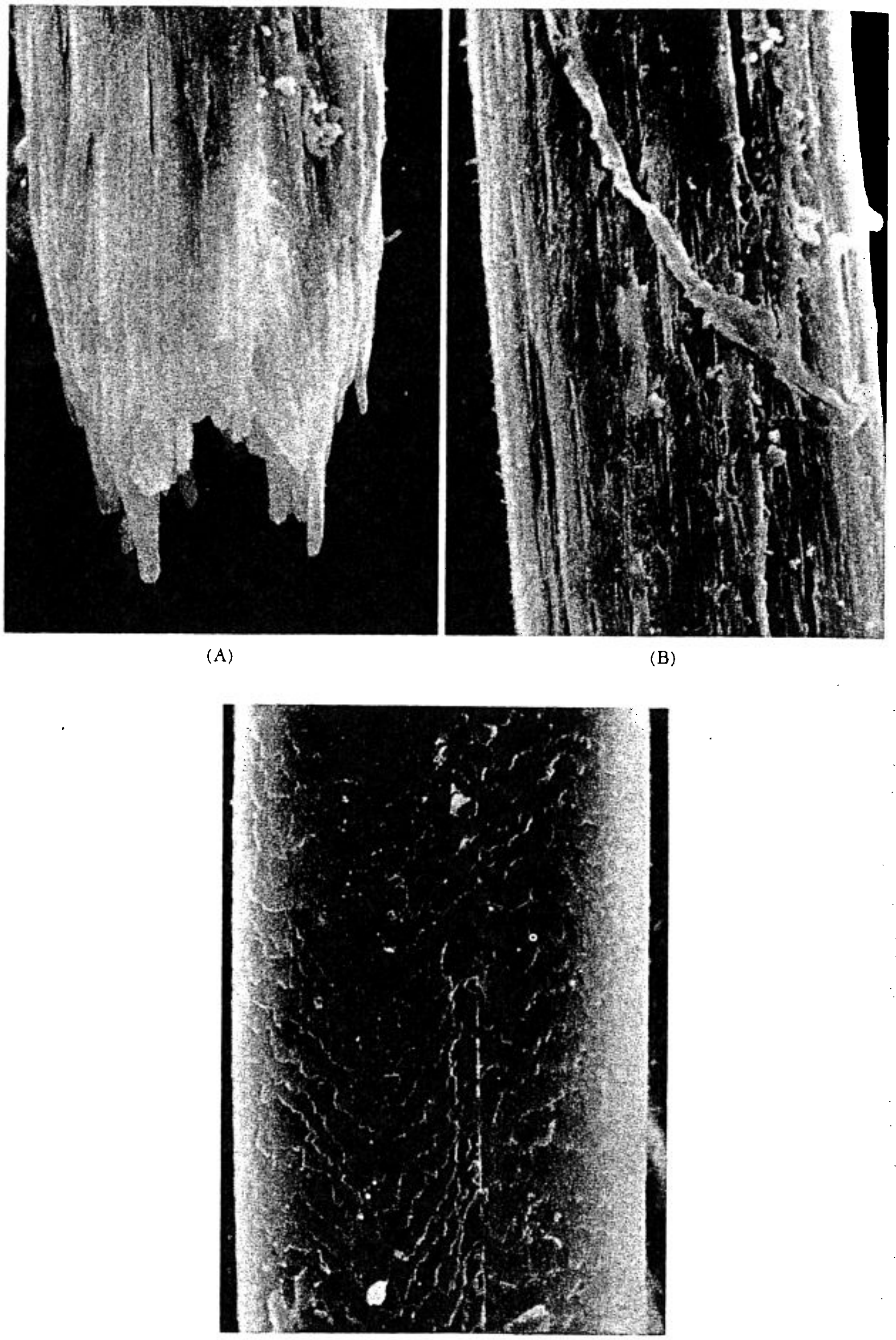
drophilic than the root end. This may be due to degradation of the protein by the ultraviolet rays of the sun or by environmental factors that generate hydrophilic groups at the surface, or it may be due to loss of cuticle by mechanical damage.

To establish the difference in the wetting behavior of the cortex and the cuticle, wettability of the tip (natural tips were chosen by viewing in the microscope) and the root ends of hair fibers were measured. Damaged tips with the cortex exposed yielded positive wetting forces, while the root ends, with cuticle intact, gave negative wetting forces. Scanning electron micrographs of one of these fibers are shown in Fig. 2 along with the measured advancing wetting forces.

### EFFECT OF CHEMICAL OXIDATION AND REDUCTION

Oxidation of hair samples was carried out with a 3 per cent solution of hydrogen peroxide adjusted to a pH of ~10 with 0.1 *N* ammonium hydroxide. Single fibers mounted on hooks were immersed in this solution for 2 min at a time followed by exhaustive rinsing with distilled water. Fibers were conditioned at 65 per cent RH and 70°F prior to measurement. Successive treatments of 2-min duration were carried out on the same fibers. Reduction was carried out in the same way using a $2.5 \times 10^{-2}\,M$ solution of dithiothreitol, but the fibers were rinsed with deoxygenated distilled water.

The increase in wetting expressed as work of adhesion (see equation (7)) caused by both oxidation and reduction are shown in Fig. 3 as a function of treatment time. As expected, both oxidation and reduction increase the wettability of the surface. These increases are attributed to the generation of sulfonic acid groups in the case of oxidation and of thiol groups in the case of reduction, both of which are hydrophilic. The data presented here are inadequate for a comparison of the hydrophilic nature of the scission products and for the determination of the extent of disulfide cleavage in these 2 reactions. Wettability or work of adhesion are only indirect means of assessing the quantitative effects of these reactions. Oxidation of cystine by hydrogen peroxide is complicated by the reversible nature of several intermediate steps eventually leading to the formation of cysteic acid [11]. It is possible that under these conditions of oxidation cleavage of peptide linkages may also occur to some extent, which may account for the discontinuous nature of the "oxidation" curve in Fig. 3 after a 6-min oxidation time. Reaction of hydrogen peroxide with peptide bonds is known to occur in wool and silk at 60°C [12], and, though the reaction may not be extensive at room temperature, it may not be ruled out. It should be noted that wettability or work of adhesion is a measure of reactions occurring at the fiber surface only.



(A)

(B)

(C)

**Figure 2.** SEMs of tip and root ends of an untreated human hair fiber: (A) tip end, 640 X, $F_W$ = 0.041 mg; (B) ~0.5 mm from tip, 640 X; (C) toward the root end, 640 X, $F_W$ = 0.330 mg

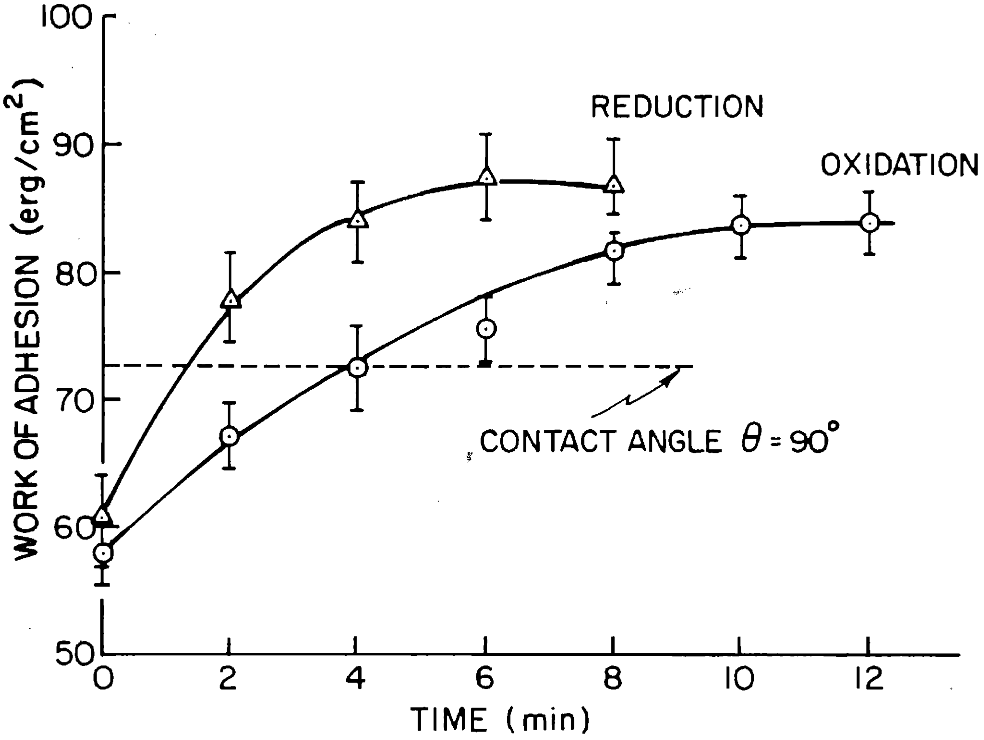


Figure 3. Effect of oxidation and reduction treatments on human hair fiber wettability

## CRITICAL SURFACE TENSION OF HAIR

The determination of the critical surface tension of keratins in various forms using alcohol-water solutions has been achieved by several authors. A summary of these investigations has been given by El-Shimi and Goddard [13].

The method employed in this investigation of using n-butanol-water solutions is based on the work of Feldtman and McPhee [14] on wool. n-Butanol-water solutions covering a surface tension range from 37 to 72.5 dyn/cm were used. In earlier measurements, the direction of immersion into the liquid with respect to hair scales was ignored. Later, wettability was found to depend on the scale direction of immersion [9], and therefore, measurements were carried out in both scale directions. Both advancing and equilibrium wetting forces were utilized to evaluate the corresponding values of cos $\theta$. A plot of cos $\theta_a$ versus $\gamma_{LV}$ according to the Zisman approach [4], was found to be nonlinear, suggesting contributions from nondispersion interactions. A logarithmic plot of $(1 + \cos\theta)$ versus $\gamma_{LV}$ according to equation (8) is shown in Fig. 4 for a single hair fiber. As expected, the plots for the advancing and the equilibrium measurements are both linear. The slope of the line and the value of $\gamma_c$ (critical surface tension) at $(1 + \cos\theta)$ equals 2, i.e., at a contact angle of 0°, were calculated for each of 5 fibers by linear regression analysis, and the average values are reported in Table II. The $\gamma_{ca}$ values are close to the $\gamma_c$ of pure bulk water with respect to nonpolar liquids, which has been found to be ~22 dyn/cm [6]. This supports the idea that conditioning the hair fibers at 65 per cent RH might have led to the adsorption of a multimolecular

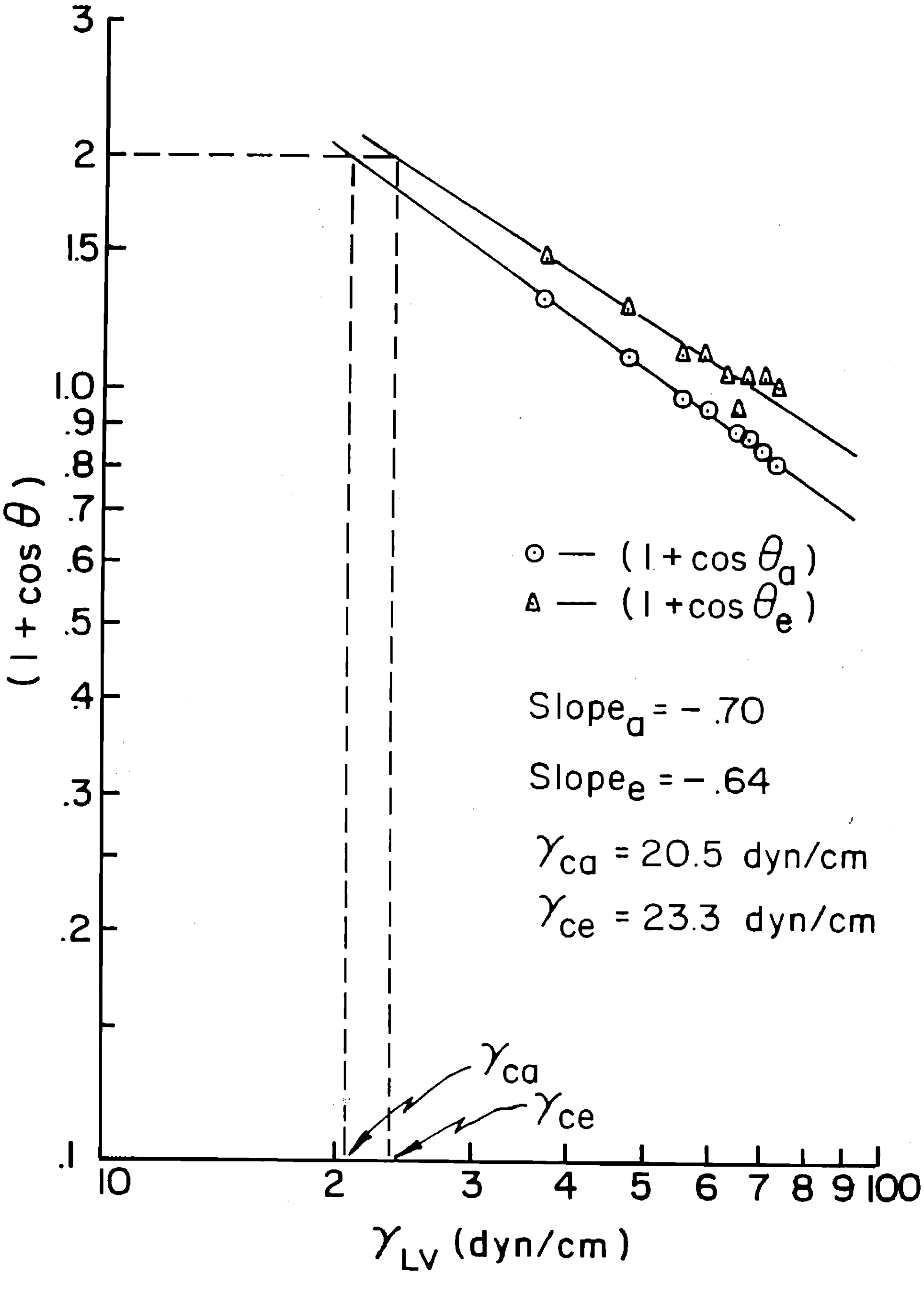


Figure 4. Variation of (1 + cos $\theta$) with $\gamma_{LV}$ for 1 human hair fiber measured in against-scale direction

Table II
Critical Surface Tension of Hair Fibers

| Scale direction | Advancing |  | "Equilibrium" |  |
|---|---|---|---|---|
|  | Slope | $\gamma_{ca}^{(dyn/cm)}$ | Slope | $\gamma_{ce}^{(dyn/cm)}$ |
| Ignored | −0.72 ± 0.03 | 19.4 ± 1.0 | −0.67 ± 0.16 | 24.8 ± 3.9 |
| Against scale | −0.75 ± 0.09 | 20.9 ± 2.4 | −0.68 ± 0.11 | 26.0 ± 6.9 |
| With scale | −0.78 ± 0.10 | 20.0 ± 2.0 | −0.70 ± 0.11 | 24.9 ± 3.0 |

Note: Each entry is an interfiber average for 5 fibers reported at 95 per cent confidence level.

layer of water molecules, thus reducing the surface free energy of the keratin surface. The values of $\gamma_{ce}$ obtained in this work are close to those reported by Alter and Cook [15], i.e., ~26 dyn/cm, although the variability is high. The measurement of $\gamma_c$ using alcohol-water solutions is known to give a value of ~26 dyn/cm irrespective of the solid surface. This is attributed to the adsorption of alcohol molecules on the solid with the hydrocarbon chain oriented towards the liquid, so that all surfaces behave like hydrocarbon surfaces. Thus, the difference between $\gamma_{ca}$ and $\gamma_{ce}$ in our work may be due to the replacement of adsorbed water molecules by butanol molecules at the interface.

The observation that the slopes in Fig. 4 are greater than −1 (see also average values in Table II) suggests contributions from nondispersion interactions. According to Dann [16], polar interactions make a significant contribution to $\gamma_c$. Therefore, the $\gamma_c$ values in Table II cannot represent the total surface free energy of the hair keratin. Alternative methods capable of evaluating both dispersion and nondispersion contributions to the surface free energy have to be used.

## DISPERSION AND NONDISPERSION CONTRIBUTIONS TO $\gamma_c$ OF HAIR

As has been mentioned earlier, such a method is based on the evaluation of cos $\theta$ in 2 different liquids, one polar, i.e., water ($\gamma_L^d$ = 22.0 dyn/cm, $\gamma_L^p$ = 50.5 dyn/cm), and the other nonpolar, i.e., methylene iodide ($\gamma_L^d$ = 44.1 dyn/cm, $\gamma_L^p$ = 6.7 dyn/cm). The values of cos $\theta$, $\gamma_{LV}$, $\gamma_L^d$, and $\gamma_L^p$ for each liquid is substituted in equation (9), resulting in 2 simultaneous equations with the unknowns, $\gamma_S^d$ and $\gamma_S^p$ (for details see El-Shimi and Goddard [13]). The equations can be solved graphically to obtain the values of the unknowns.

Such equations were obtained for advancing and "equilibrium" conditions by using the corresponding values of cos $\theta$. The values of $\gamma_S^d$ and $\gamma_S^p$ obtained for both the above

Table III
Dispersion and Nondispersion Contributions to $\gamma_c$ of Hair Fibers (dyn/cm)

| Scale Direction | Advancing |  |  | "Equilibrium" |  |  |
|---|---|---|---|---|---|---|
|  | $\gamma_S^d$ | $\gamma_S^p$ | $\gamma_S^d + \gamma_S^p$ | $\gamma_S^d$ | $\gamma_S^p$ | $\gamma_S^s + \gamma_S^p$ |
| Against scale | 24.8 ± 2.2 | 2.6 ± 1.3 | 26.8 ± 1.4 | 19.5 ± 1.9 | 11.5 ± 1.7 | 31.0 ± 1.6 |
| With scale | 23.9 ± 2.2 | 2.5 ± 1.5 | 26.5 ± 1.0 | 19.5 ± 2.4 | 10.0 ± 2.0 | 29.6 ± 2.2 |

Note: Each entry is an interfiber average for 10 fibers reported at 95 per cent confidence limit.

conditions are given in Table III. The nondispersion or polar contribution $\gamma_s^p$ in the advancing mode is small compared to the dispersion contribution $\gamma_s^d$. In the "equilibrium" condition, when the fiber is left in the liquid for ~15 min, it is seen that $\gamma_s^p$ increases considerably and $\gamma_s^d$ decreases slightly, thus leading to a net increase in the total surface free energy. The increase seems to be due to the interaction of hair and water leading to hydrogen bond breaking and consequent orientation of the macromolecules in the surface regions, as was suggested earlier.

## ACKNOWLEDGMENT

The work reported here was conducted as part of a project on "Studies of the Modification of Human Hair Properties by Surface Treatments" sponsored by a group of corporate Textile Research Institute participants.

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