Relationship between triboelectric charging and surface modifications of human hair

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Synopsis
Static charge generation on intact and modified human hair fibers has been studied in the rubbing mode using a variety of metal (stainless steel, aluminum, gold) and polymer (nylon, Teflon, chitosan, polycarbonate, polystyrene) contact probes. Adsorption of long chain alkyl quaternary ammonium salts, cationic polymers, and polymer-detergent complexes was found to decrease the electrochemical potential and increase the conductivity of the fiber surface. On the other hand, modification of the fibers by reduction, bleaching, and oxidative dyeing has only a small effect on triboelectric charging. Measurements of the kinetics of charge decay indicate that none of these treatments leads to increased surface conductivity of the keratin fibers.

It was concluded that the suppression of static charge formation can be achieved by reducing the difference in work functions between the hair and the material it is in contact with. This can be done by the proper choice of comb material or hair surface modification.

INTRODUCTION
Triboelectric charging is a commonly observed phenomenon. When two different materials are brought into contact, charges of opposite sign and equal in magnitude are generated on their surfaces. This is due to the difference in electrochemical surface potentials of the bodies in contact, which causes the injection of electrons from the material of lower electron affinity to the material of higher electron affinity. The process of charge migration continues until a potential barrier is created at the interface by the ionized surface layers, which compensates for the difference in electron affinities. The driving force of the electron transfer process, i.e. the difference in electrochemical potentials between contacting surfaces 1 and 2 (5), can be derived as follows (1,2):

\[ \mu_1 = \mu_1^0 - q V_{s1} \]  
\[ \mu_2 = \mu_2^0 - q V_{s2} \]  
\[ \mu_1^0 = -\phi_1 \]  
\[ \mu_2^0 = -\phi_2 \]  
\[ \Delta \mu = \mu_1 - \mu_2 = \mu_1^0 - \mu_2^0 + q (V_{s2} - V_{s1}) = \phi_2 - \phi_1 + q (V_{s2} - V_{s1}) \]

where \( \mu_1, \mu_2, \mu_1^0, \mu_2^0 \) are the chemical and standard chemical potentials of an electron on each surface, and \( \phi_1 \) and \( \phi_2 \), and \( V_{s1} \) and \( V_{s2} \) are the work functions and surface
potentials, respectively, and q is the electron charge. The standard potential is selected in such a way that an increase of the work function causes a decrease in the value of the electrochemical potential, which reflects a lower escaping tendency of an electron (2). With this formulation (1–5), positive surface potentials $V_{s1}$, $V_{s2} = +V$, which hinder the escape of an electron, would also decrease the value of $\mu$.

For a metal, the work function $\phi$ is defined as the work required to remove electrons from the Fermi level (energy of electrons at 0 K) to the surface. The Fermi level represents both acceptor and donor energies of a metal. For polymers (and organic solids in general), the definition of the work function is not that simple. According to Davis and Lewis (3–5), a polymer can be considered in the first approximation as a molecular crystal, and the polymer work function is defined as lying in the middle between the valence and conduction bands ($E_c + E_v/2$). In this model, the direction of the electron transfer during polymer-metal contact is dependent upon the relative values of polymer and metal work functions. Metal electrons are injected into the polymer if the Fermi level of the metal lies above the electrochemical potential of the polymer ($\phi_m < \phi_p$) and vice versa. The concept of polymer work function was successful in the interpretation of various experimental data (6–8). However, for completely amorphous, disordered polymers, this approach does not seem to be fully warranted. Duke and Fabish's theory (9) assumes that the distribution of energy states in polymer is represented by a Gaussian distribution for each of the molecular ion states (donor and acceptor). The actual distribution of polymer energy levels within ~0.4 eV of the metal Fermi level determines the sign and quantity of the charge transferred. Polymer energy states do not communicate with each other and injection is energy selective. Each metal can inject into certain states of the polymer with which other metals cannot communicate. Duke and Fabish's sampling/non-communicating state model was successfully used to interpret the experimental data on photoemission from polymer surfaces (10) but is also subject to criticism (11). A somewhat simplified approach to the problem of charge transfer during metal-insulator contact was adopted by Gibson (12,13). He identifies polymer acceptor states with lowest unoccupied molecular orbitals (LUMO) and donor states with highest occupied molecular orbitals (HOMO). The direction of the electron transfer is determined by the relative position of the Fermi level of a metal and HOMO or LUMO levels of an organic solid as it is shown in Scheme 1.

![Scheme 1. Electron transfer during organic solid—metal contact.](image-url)
Gibson used this model of electron transfer to demonstrate quantitative correlations of solid state triboelectric charging and molecular structure (12–14). Linear free energy relations (Hammet correlations) were shown to exist for the process of triboelectric charging of a variety of organic solids [substituted salicyl anils (14), polystyrenes (14), polyethylenes (15), poly(arylomethylstyrenes) (13)] by metals. It was thus possible to alter triboelectric charging properties of polymers in a predictable manner by chemical modification. The change in triboelectric charging characteristics could also be achieved by doping with appropriate low molecular weight donors and acceptors. For example, octadecanol was shown to impart electrodonating properties to a polyethylene matrix (16), while increased negative charging (increase in electron-accepting properties) was observed for collagen mixed with p-chloranil (17).

While the mechanism of charge transfer during the metal-insulator contact is subject to discussion, the Duke and Fabish model of polymer-polymer contact event seems to account better for some experimental observations (9). It postulates that the charge exchange between two polymers will occur at all energies for which filled donor states of one are aligned with empty acceptor states of the other. That also implies, similar to Gibson’s representation of metal-insulator contact (Scheme 1), that the direction of the polymer-polymer charge exchange would depend on the relative energies of LUMO and HOMO levels of the contacting materials. Very few works have been published on the effect of surface modification on the charge transfer during metal-polymer and polymer-polymer contact (12,18). Changing the surface properties by chemical derivatization was reported to have a profound effect on the triboelectric charging phenomena. Oxidation or ozonolysis of polystyrene and polyethylene, which leads to the formation of ketone, aldehyde, quinone, carboxyl, etc., functionalities was shown to impart electron-accepting properties while surface sulfonation of polystyrene resulted in the increase of electron-donating properties of the polymer.

We have reported earlier (19) on some charging characteristics of hair against various metals and polymers. It was pointed out that the generated charge density and its sign depended upon the material used for rubbing as well as the direction of rubbing. The experimental data could be qualitatively explained in terms of the band model of the electronic structure of polymers and metals, assuming certain characteristic values of work functions for each material under consideration, as suggested by Davis (3–5). In order to explain the directional triboelectric effect, we had to invoke piezoelectricity of cuticle cells as was proposed earlier by Martin (20). The present paper describes the investigation of the effect of various surface modifications of hair on the charge transfer during rubbing. This is important, since the adsorption on hair of long chain alkyl quaternary ammonium salts, cationic polymers, and complexes of cationic polymers with anionic polymers or anionic detergents can produce significant changes in the electrochemical surface potential of the fiber. This results in different charging characteristics in relation to polymers and metals. The effect of treatments such as dyeing, bleaching, and permanent waving was also explored.

Apart from altering the electrochemical potential, surface modification may also affect the conductivity of fibers (21). Therefore, the primary purpose of our studies was to find qualitative correlations between density and sign of generated tribocharge, fiber conductivity, and various modes of surface modification of hair. Our interpretation of the experimental data is based on Davies’ approach (3–5). We assume that both polymers and metals are characterized by work functions which determine the value of the
electrochemical surface potential. Surface treatments and piezoelectric potential can also affect the effective value of the work functions and thus influence the direction of charge transfer during contact.

EXPERIMENTAL

TRIBOELECTRIC CHARGING MEASUREMENTS

The device shown in Figure 1 was employed. A hair tress was mounted in a metal frame (4) in such a way that it formed a smooth layer 0.03 cm thick (approximately four layers of single fibers). The fibers within the tress could be positioned with the cuticle edges pointing either downward or upward. A rubbing element in the form of a half cylinder was attached to an adjustable arm that could be rotated by a variable speed motor. A speed of 70 rotations/minute was used throughout this work. Static charge was produced by contact between the rubbing element and the hair fibers. The magnitude and sign of the generated charge on the fibers mounted in the frame were measured as a function of rubbing time by means of a static detector probe (Keithley 2503) connected to a Keithley 616 electrometer and a chart recorder. The entire setup, except for the electrometer, was housed in a dry box maintained at 25–30% relative humidity under a positive pressure of air passed through several columns filled with Drierite. The surface charge density on the hair tress was calculated from the following relation:

\[
\sigma = \frac{Q}{A} = \frac{C \cdot E}{A}
\]

Figure 1. A device to study triboelectrification of keratin fibers.
where $\sigma$ is the surface charge density (C/cm$^2$), $Q$ is the charge, $A$ is the surface area of the target of the detector probe ($3.142 \times 10^{-2}$ cm$^2$), $E$ is the voltage read by the electrometer, and $C$ is the internal capacitance of the probe, adapter and cable ($2.45 \times 10^{-10}$ F).

The rubbing element was exchangeable so we could evaluate the electrification of hair fibers using a variety of materials such as teflon, aluminum, gold, stainless steel, nylon, etc. We also used solution-cast polymer films as rubbing materials mounted on aluminum, stainless steel, or teflon cylinders. We found that for 20–30 $\mu$m thick films, the cylinder material has no effect on the process of charge transfer between the film and the keratin fibers.

Charge decay measurements were performed with the same experimental setup by following the changes in generated charge density as a function of time.

**FILM PREPARATION**

Films of polystyrene (PS), polycarbonate bisphenol-A (PC), poly(methylmethacrylate) (PMMA), and chitosan acetate (ChA) were cast from 5 wt % solutions in CHCl$_3$, CH$_2$C$_2$C$_2$HCl$_2$ (1:1), CHCl$_3$, and H$_2$O, respectively. The polymer films were dried for 24 hours in the vacuum oven before use.

**SURFACANTS AND POLYMER SAMPLES**

The cationic surfactants used in this study were: decyl (DTAB), dodecyl (DTAC), tetradecyl (TTAB), hexadecyl (HTAB), and octadecyl (OTAB) trimethyl ammonium bromides or chlorides and steralkonium chloride (SC). The anionic surfactants were: sodium dodecyl (SDS), tetradecyl(TTS), hexadecyl (SHS), octadecyl (SOS) sulfonates, and eicosanoic acid (EA). These compounds were practical grade chemicals and were used as received. The quaternary ammonium polymer employed was poly(methacrylamidopropyltrimethyl ammonium chloride) [PMAPTAC, mw $4.3 \times 10^5$ relative to PEO (22)].

**PREPARATION OF HAIR SAMPLES FOR TRIBOELECTRIC MEASUREMENTS**

Virgin brown hair, purchased from deMeo Brothers, New York, was used throughout this work. It was washed with SDS, rinsed with a large amount of deionized water, and dried at room temperature. In order to modify the surface properties of the keratin fibers, hair swatches were placed into a large excess of polymer or detergent solution of appropriate concentration for 2–6 hours at room temperature, and stirred occasionally. The fibers were then rinsed under running deionized water and exposed to an excess (2–3 liters) of deionized water for 2–4 hours. The purpose of the prolonged pure water exposure was to obtain fiber samples with irreversibly adsorbed polymers or detergents.

To cast a cationic polymer-anionic detergent complex on the fiber surface, the hair was first treated with the cationic polymer, rinsed with H$_2$O, then exposed to the anionic surfactant solution and rinsed again. Detailed procedure descriptions are given in the legends of Figures 9 and 10.
REDUCTION

Hair reduction was performed by the use of: (1) tetraakis(hydroxymethyl)-phosphonium chloride-\(\text{P(CH}_2\text{OH})_4^+\text{Cl}^-\) (THPC) (0.2 M solution in sodium acetate buffer at pH = 5.2, liquor/hair = 50, 15 minute treatment followed by either 1 minute \(\text{H}_2\text{O}\) rinse or 3 minute 2% \(\text{H}_2\text{O}_2\) treatment and \(\text{H}_2\text{O}\) rinse); and (2) thioglycolic acid-\(\text{HSCH}_2\text{COOH}\) (TGA) (0.5% solution of TGA was adjusted to pH = 9.2 using \(\text{NaOH}\), liquor/hair = 50. Hair tresses were treated for 15 minutes at 37øC. Then they were either only rinsed with \(\text{H}_2\text{O}\) for 1 minute or immersed in 2% \(\text{H}_2\text{O}_2\) solution followed by 1 minute rinse with water).

BLEACHING AND DYING

Bleaching was performed with a peroxide-based commercial product (Clairoxide,® Clairol Inc.) for 1 hour at room temperature, following the instructions provided with the product. The tresses were then rinsed and dried.

Commercially available oxidative haircolors in light and dark shades (Nice 'n Easy® #99 and #121, respectively, Clairol Inc.) were used according to the instructions given by the manufacturer. They were applied to hair for 20 min., followed by rinsing with water for 1 minute.

RESULTS AND DISCUSSION

GENERAL COMMENTS

Typical examples of unsmoothed kinetic curves of charge build-up during rubbing of hair fibers in the direction from root to tip or from tip to root are shown in Figure 2. One general feature of the charging process is that the electrical breakdowns of the surrounding atmosphere limit the surface charge densities to less than \(7 \times 10^{-9}\) C/cm². This is illustrated by the charging characteristics shown in Figures 2a and 2c. The recorder trace presented in Figure 2a corresponds to very fast positive charging. Three contacts between the rotating cylinder and the fibers produce the maximum charge density, while the fourth one results in electrical breakdown and reduction of accumulated tribo-charges. Charge buildup represented by the curve shown in Figure 2c is slower but enough to cause the electrical breakdown after the threshold value of charge density is reached. The kinetic curve presented in Figure 2d illustrates the case in which the negative charge density on the fiber surface does not reach a value sufficiently high for electrical discharge. In the case of treated fibers, we have occasionally observed initial slow positive or negative charging followed by charge reversal as is indicated by the data in Figure 2b. The reasons for such behavior are not clear. It should be noted, however, that the sliding contact between the fibers and the probe might involve, apart from electron or ion transfer, additional processes affecting tribocharging, such as:

1. Mass transfer between the contacting surfaces leading to the modification of their electrochemical potentials.
2. Surface abrasion. It is plausible that the surface layers of the polymer film or surface of the hair epicuticle might be characterized by a different work function value as compared to the bulk material (12). This could happen, for example, as a result of chemical reactions of the surface groups with oxygen. Subsequent removal of the
external layer by abrasion would expose unoxidized material and result in altered charging characteristics.

For quantitative treatment of the tribocharging kinetic data, it is usually assumed that the charge build-up follows first-order kinetics (23):

$$\sigma = \sigma_\infty \left(1 - e^{-kt}\right)$$  \hspace{1cm} (7)

where $t$ refers to the total contact time (or number of contacts), $\sigma_\infty$ is the equilibrium charge density, and $k$ is the rate coefficient dependent upon such parameters as frictional coefficient, slip velocity, and the difference in work functions between the contacting materials. The equilibrium charge density, $\sigma_\infty$, can be described in terms of the density of donor or acceptor states, $N$, and the penetration depth, $\psi$, over which the charge is distributed (2):

$$\sigma_\infty = q N \psi = \frac{2 V_c \epsilon}{\psi}$$  \hspace{1cm} (8)

where $V_c$ is the contact potential and $\epsilon$ is the dielectric constant. $V_c$ can be calculated from Eq. 5 by assuming that on contact $\Delta \mu = 0$ and $V_c = (V_{s1} - V_{s2})$:

$$V_c = \frac{\phi_2 - \phi_1}{q}$$  \hspace{1cm} (9)

and consequently

$$\sigma_\infty = \frac{2 \epsilon}{\psi q} (\phi_2 - \phi_1)$$  \hspace{1cm} (10)
Thus, the magnitude and the sign of the transferred charges are determined by the differences in the work functions of the contacting materials.

According to our previous interpretation of the tribo-charging characteristics of hair, the keratin work function is modified by the piezoelectric potential $V_{pp}$ appearing during tangential friction of the cuticles:

$$\phi_{\text{eff}}^{\text{keratin}} = \phi_{\text{keratin}} + q V_{pp} \text{ for rubbing in the direction from root to tip}$$  

$$\phi_{\text{eff}}^{\text{keratin}} = \phi_{\text{keratin}} - q V_{pp} \text{ for rubbing in the direction from tip to root}$$  

It should be remembered that the piezoelectric potential is only present when the cuticles are being subjected to frictional stress. It is thus undetectable in non-rubbing contact electrification experiments and will not be present on a relaxed fiber surface. In contrast to this, surface potentials $V_{s1}$ and $V_{s2}$ appearing in Eqs. (1) and (2) are permanent and gradually build up during electron transfer. In order to differentiate between $V_{pp}$ and $V_{s1,2}$, we have defined effective work function of keratin $\phi_{\text{eff}}^{\text{keratin}}$ according to Eqs. (11) and (12) which include the piezoelectric factor.

It follows from this that if the work function of the contact probe is close to the work function of keratin ($\phi_{\text{keratin}}$), this additional surface potential caused by the piezoelectric effect determines which of the contacting surfaces is donor or acceptor.

Figure 3 shows the kinetic curves (based on the points from continuous recordings at

![Figure 3](image-url)
10-sec intervals) of charge build-up on untreated keratin fibers for both modes of rubbing by various probes. All the materials except PMMA produced positive charges on the fiber surface when rubbing was in the direction from root to tip. When the direction of rubbing was changed to from tip to root, PC and ChA reversed the sign of tribocharges accumulated on the fibers. These data suggest that PC and ChA are characterized by work functions very close to that of hair, that PMMA has a lower value of the work function, and that other materials tested lie above hair in the triboelectric series. In Table I, literature values of the work functions of the insulators and metals employed in this study are collected.

Unfortunately, there is a considerable discrepancy between various sources, mainly due to the use of different experimental procedures and materials with varying degree of purity. However, the general trend is evident, $\phi_{\text{teflon}} > \phi_{\text{polyethylene}}, \phi_{\text{polypropylene}}, \phi_{\text{polystyrene}}, \phi_{\text{gold}} > \phi_{\text{polycarbonate}} > \phi_{\text{PMMA}} > \phi_{\text{polyamide}}, \phi_{\text{aluminum}}$ and is consistent with the data shown in Figure 3, with the exception of polyamide and aluminum which seem to possess a higher work function in relation to PMMA and PC than the one shown in Table I. It should also be noted that the values of work functions for polymers measured in air are usually higher than those found in vacuum experiments (Table I) though that does not affect the relative position of a material in a triboelectric series. Since our measurements were carried out in an air atmosphere, the interpretation of the results should be based on the work function values given in the third column of Table I.

Quantitative analysis of the kinetic triboelectrification data, as exemplified by the curves shown in Figures 2 and 3, by the use of Eq. 7 was attempted but did not yield consistent results. In many cases, charging curves were non-exponential, and so it was impossible to calculate the values of the parameters $\sigma_\infty$ and $k$. Repeatability was also not very good (in terms of numerical values of $k$ and $\sigma_\infty$), probably because of mass transfer, surface contamination, and surface abrasion during sliding contact between the probe and fiber surface. This required frequent changes of probes and hair fibers in order to obtain reproducible measurements. Similar problems were encountered and reported by other authors working in this field (see for example (8)).

Additional information concerning the mechanism of fiber conductivity was derived from charge decay measurements. Figure 4 shows examples of discharge kinetic curves obtained for various initial charge densities in the range $1.16 \times 10^{-9}$ to $5.41 \times 10^{-9}$ C/cm$^2$ for untreated fibers. It can be seen that the charge migration was insignificant for low initial charge densities and increased dramatically with the increase of initial surface potential. According to Watson (29), the time dependence of the parameter

$$\frac{1}{V_1^2} \frac{dV}{dt} \sim \frac{1}{\sigma_1^2} \frac{d\sigma}{dt}$$

where $V$, $\sigma$ are surface potential and surface charge density and the subscript 1 denotes the values of these quantities at time 0, provides a test for the type of discharge mechanism:

1. In the case of an ideal trap-free system (ideal dielectric), $1/\sigma_1^2 \frac{d\sigma}{dt}$ should be constant with time for $0 < t < t_{1/2}$, where $t_{1/2}$ is the half-time of the decay.
2. In the case of insulators containing a large number of carrier traps, $1/\sigma_1^2 \frac{d\sigma}{dt}$ should decrease with time.
3. In the case of dielectrics in which the conduction is due to ionic species, charge
Table I
Work Functions of Various Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Measured in Vacuum</th>
<th>Measured in Air</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polymers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Teflon®</td>
<td>6.71 ± 0.28 (8)</td>
<td>1.03 (8)</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>5.75 (2)</td>
<td></td>
</tr>
<tr>
<td>Polypropylene</td>
<td>4.26 (4)</td>
<td></td>
</tr>
<tr>
<td>Polystyrene</td>
<td>5.24 ± 0.24 (8)i</td>
<td>4.8 (8)i</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>6.04 ± 0.47 (8)</td>
<td>7.2 (8)</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>4.90 (2)</td>
<td></td>
</tr>
<tr>
<td><strong>Metals</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gold</td>
<td>4.8 (24)3</td>
<td>3.0 (26)</td>
</tr>
<tr>
<td>Aluminum</td>
<td>5.85 ± 0.82 (8)</td>
<td>4.40 (8)</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>4.80 (2)</td>
<td></td>
</tr>
<tr>
<td>Polyamide (nylon®6,6)</td>
<td>4.26 (4)</td>
<td></td>
</tr>
<tr>
<td><strong>Metals</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gold</td>
<td>5.2 (8)</td>
<td>4.46 (28)</td>
</tr>
<tr>
<td>Aluminum</td>
<td>5.45 (27)</td>
<td></td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>5.30 ± 0.53 (8)</td>
<td></td>
</tr>
<tr>
<td>Polyamide (nylon®6,6)</td>
<td>4.0 ± 0.9 (8)</td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>4.1 (24)3</td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>4.08 (4)</td>
<td></td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>4.3 ± 0.5 (4)</td>
<td></td>
</tr>
<tr>
<td>Polyamide (nylon®6,6)</td>
<td>4.3 ± 0.5 (2)</td>
<td></td>
</tr>
</tbody>
</table>

1 Low density; 2high density; 3calculated as the centroid energy $E = (E_{donor} + E_{acceptor})/2$, $E_{donor} = 6.1$ eV for PMMA and 7.1 eV for PS and $E_{acceptor} = 2.0$ eV for PMMA and 2.5 eV for PS found in metal/polymer contact-charge-exchange measurements; 4termed "acrylic" in (8); 5range for the literature data quoted by (26).

The data presented in Figure 4 clearly indicate that the charge density decays for untreated fibers are non-exponential ($t_{1/2}$ decreases with the increase in $\sigma_1$) and $1/\sigma_1^2$ d$\sigma$/dt is not constant for $0 < t < t_{1/2}$. Moreover, a high residual charge remains on
the fibers. This suggests that the charge carriers have become trapped on the hair surface, that thermal release rates are slow, and that the charges can remain trapped indefinitely. According to the literature data (21), the conductivity of hair fibers increases at higher humidities due to water absorption and higher ionic mobility. A similar phenomenon can be observed at low relative humidities when ion-containing and hygroscopic species are adsorbed on the surface of keratin fibers. In this case the carrier transport becomes ionic and charge decays are exponential. This is illustrated by the data shown in Figure 5 obtained for dyed hair treated with PMAPTAC-SDS.
complex. In this case, charge decays are very fast, of the order of $10^1$ sec, and $t_{1/2}$ is constant with $\sigma_1$. However, generation of higher surface charge densities results in electrical breakdowns which seem to affect the kinetics of discharge. That is probably why an increase in $t_{1/2}$ was observed after the first electrical breakdown occurred (between the 7th and 8th contact, Figure 5).

It is noteworthy that very fast surface charge decays are again non-exponential. This was observed in the case of the fibers modified with cationic polymers and surfactants, when a high density of ionic species was introduced on the fiber surface (Figure 8, Table II).

### Table II

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>$T_{1/2}$ (min)</th>
<th>$K$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decyltrimethyl ammonium bromide</td>
<td>11.7</td>
<td>0.059</td>
</tr>
<tr>
<td>Dodecyltrimethyl ammonium chloride</td>
<td>8.9</td>
<td>0.078</td>
</tr>
<tr>
<td>Tetradecyltrimethyl ammonium bromide</td>
<td>4.4</td>
<td>0.157</td>
</tr>
<tr>
<td>Hexadecyltrimethyl ammonium bromide</td>
<td>1.4</td>
<td>0.495</td>
</tr>
<tr>
<td>Octadecyltrimethyl ammonium iodide</td>
<td>1.2</td>
<td>Nonexponential</td>
</tr>
</tbody>
</table>

### EFFECT OF ADSORBED LONG CHAIN ALKYL QUATERNARY AMMONIUM SALTS

Long chain alkyl quaternary ammonium salts (quats) are readily adsorbed and retained on the surface of keratin fibers due to coulombic and hydrophobic interactions (30,31). Adsorption studies of cationic detergents on keratin as well as on other anionic or amphoteric surfaces indicate that surfactants may form well-defined monolayers (vertically or horizontally oriented in relation to the surface, depending on the concentration of the treatment solutions) or bilayers on the surface. Some experimental data obtained for human hair suggest that the cationic surfactant can penetrate into the cortex of the fiber. As a result of surfactant adsorption, reductions of wet and dry combing forces are usually observed. Long chain alkyl quaternary ammonium salts are also known to impart antistatic properties to hair (21,32), wool, and many other natural or synthetic textiles. The mechanism of static charge elimination is not obvious. It might be connected with either increased surface conductivity (21) or with a reduction of the work function gap between the hydrocarbon-modified surface and hydrocarbon comb materials (hard rubbers, polyethylene, polypropylene, etc.).

We have found that adsorbed long chain alkyl quaternary ammonium salts cause a considerable decrease of the electrochemical potential of the fiber surface (by increasing the value of the effective work function). The diagram in Scheme 2 illustrates qualitatively the relative changes in electrochemical potentials of contacting surfaces for hexadecyltrimethyl ammonium chloride treated fibers as compared to untreated hair. This diagram was constructed based on the following observations. Both modes of rubbing (root-to-tip and tip-to-root) of quat-treated fibers by the probes characterized by the work function lower (PMMA) and close to keratin (PC) result in a high density of negative charges on hair. In the case of PC, the directional triboelectric effect observed for untreated fibers disappears (Figure 6a). Rubbing against teflon,® which is characterized by a very high work function value (Table I), in the direction from
Scheme 2. Relative changes in electrochemical potential of hexadecyltrimethyl ammonium chloride treated fibers as compared to untreated hair.

root to tip produces a high density of positive charges (Figure 6b). Apparently, the reduction of the electrochemical potential of the fiber surface is not sufficient to match the one of the teflon\textsuperscript{®} surface. For rubbing in the direction from tip to root, the electrochemical potential gap between contacting surfaces is smaller and some reduction of transferred charge was observed for hexadecyl and decyl derivatives (Figure 6b). This could be the result of mass transfer caused by increased roughness of the keratin fiber surface (rubbing against the cuticles). The ability of various long chain alkyl quaternary ammonium salts to modify the electrochemical potential of the fiber surface is best demonstrated by rubbing against stainless steel (Figure 6c). Although the value of the work function for stainless steel is not known, it can be inferred from the charging data (Figure 3) that it lies somewhere between the values characteristic for teflon\textsuperscript{®} and polycarbonate. The data shown in Figure 6c indicate that the keratin fibers modified with short chain alkyl quats (decyl, dodecyl) exhibit weaker electron acceptor properties than the ones with adsorbed long chain alkyl analogues (octadecyl, stearalkonium).

There may be two explanations of this result:

1. Van der Waals interactions between the adsorbate and the surface increase with the number of methylene units in the hydrocarbon chain. Hence, surface density of longer chain alkyl quats might be higher, producing a larger number of the surface acceptor states; and

2. If a complete monolayer or bilayer of surfactant is formed on the fiber surface, it should be thicker for longer chain alkyl quats and consequently provide a more efficient barrier against the electron transfer from keratin to the stainless steel probe. A similar effect of quat chain length was found for a homologous series of alkylidimethylpropylmethacrylamide ammonium halides which is discussed in a separate paper (33).

The deposition of cationic surfactants considerably increases the fiber conductivity. Table II shows the half times and first-order rate constants for the charge decays from
fibers treated with various long chain alkyl quaternary ammonium salts. Longer chain alkyl quats exhibit much higher ability to increase conductivity than their short chain alkyl analogues. This dependence is similar to the one observed in charging experiments in which long chain alkyl cationic surfactants were found to be more effective in
modifying electrochemical surface potential. It should also be noted that very fast decays recorded for octadecyltrimethyl ammonium iodide are non-exponential.

Lunn and Evans (21) in their study on the mechanism of static charging of hair also measured half times of charge decay and stated that the increase in fiber conductivity produced by treating hair with a creme rinse containing a quat and then rinsing was not sufficient to account for their antistatic action. This may be true, as it is possible that half times of charge decay, even of the order of 1 minute (Table II), could still not be sufficiently small to prevent electrostatic charging under practical combing conditions. Lunn and Evans also evaluated the reduction in combing forces produced by the same treatment and observed that such a decrease is accompanied by reduced electrostatic charging during the passage of a comb through a hair tress. As a result of these observations, they concluded that the mechanism of action of these agents is primarily based on their lubricating effect on hair. In our opinion, however, this explanation ignores the electronic nature of charge transfer phenomena and cannot fully account for the observed features of this process. While reduced combing forces should decrease the rate of charge generation (rate coefficient $K$ in Eq. 7 was found to be dependent upon frictional coefficient and slip velocity), it should not affect the value of the equilibrium charge density $\sigma_\infty$. This parameter, according to Eq. 10 and as demonstrated by our data, is determined by the difference in work function of the contacting surfaces. A diminished driving force for electron transfer, i.e. a decrease in $\phi_2 - \phi_1$, and in some cases increased conductivity should thus be responsible for the suppression of static charges in fibers treated with quaternary ammonium salts.

**EFFECT OF ADSORBED CATIONIC POLYMER**

Figure 7 shows the kinetic curves of charge generation of hair fibers, treated with PMAPTAC at various concentrations, obtained by rubbing against PC film. In this

![Figure 7. Kinetic curves of charge generation by rubbing PMAPTAC-treated fibers against polycarbonate.](image-url)
case, a PC probe was chosen as the rubbing material since it is characterized by a value of work function very close to keratin. Therefore, it should be sensitive to very small changes of the electrochemical potential of the fiber surface produced by adsorption of cationic polymer. Experimental data obtained by rubbing hair fibers in the direction from root to tip indicate that the formation of a complete mono- or multilayer of adsorbed cationic polymer, which corresponds to the highest concentration of treatment solution 1 g/dl (34), reverses the sign of the generated charge (untreated fiber charges positively against PC when rubbed in the direction from root to tip, Figure 3). Lower concentration treatments decrease only the rate of positive charge accumulation (Figure 7). When PMAPTAC-modified fibers are rubbed in the direction from tip to root, negative charges are transferred to the fiber surface (Figure 7). Low concentration treatments, which correspond to incomplete surface coverage, produce high negative charge densities of $6-7 \cdot 10^{-9}$ C/cm², while high concentration treatments result in low charge density of about $1.5 \cdot 10^{-9}$ C/cm². Since the results of rubbing in the direction from root to tip suggest that the adsorbed cationic polymer layer has acceptor properties, the low charge densities observed at high concentration treatments suggest that increased conductivity of the fiber and/or lower rate of charge generation have to be the explanation of this result, since the charge generation and dissipation are competitive processes.

The data of charge decay measurements are given in Figure 8. As the concentration of ionic species on the surface is increased, the charge decays become faster. The curves obtained at intermediate concentration treatments were exponential, which enabled the calculation of the first-order decay rate constants. Very low (0.001% treatment) and very high (1.0% treatment) surface coverage by the cationic polymer results in either slow or fast non-exponential discharge.

![Figure 8](image-url)

**Figure 8.** Charge decay kinetic curves for hair treated at various concentrations of PMAPTAC solution.
EFFECT OF THE COMPLEX ADSORBED CATIONIC POLYMER-ANIONIC DETERGENT

Formation of a saturated monolayer of cationic polyelectrolyte on the keratin fiber reverses the character of the surface from anionic to cationic (34). Subsequent exposure of the fibers modified in this way to oppositely charged polymers or detergents results in the formation of a polymer-polymer or polymer-detergent complex on the surface. Figure 9 shows the kinetic curves of charge build-up for rubbing against PC and stainless steel of keratin fibers modified with the complex PMAPTAC-SDS. PC is

![Graph showing kinetic curves of tribocharge generation](image)

Figure 9. Kinetic curves of tribocharge generation of keratin fibers modified with the complex PMAPTAC-SDS. Fibers were treated for 2 hours in 1g/dl PMAPTAC solution, rinsed with H₂O and kept in deionized water for 1 hour, then exposed for 4 hours to SDS solutions of various concentrations followed by rinsing with H₂O.
Insensitive to the changes of the concentration of SDS treatment solution and charges modified fibers negatively (Figure 9a). Only at higher concentrations of SDS (0.5–1.0%) is the conductivity of the fiber increased as reflected by the decrease of transferred charge for rubbing in the direction from tip to root. The difference in electrochemical potentials between stainless steel and the polymer-detergent complex modified surface is diminished. Various degrees of surface modification resulting from increasing concentration of detergent treatment can be distinguished for rubbing in the direction from root to tip (Figure 9b). On the other hand, for rubbing in the opposite direction, stainless steel is insensitive to increasing concentration of detergent on the surface. This might be rationalized by assuming unequal modification of keratin surface electrochemical potentials for both modes of rubbing as a result of complex deposition. Relative changes of energy levels accounting for the above-discussed experimental data are presented in Scheme 3.

Scheme 3. Relative changes in electrochemical potential of PMAPTAC-SDS treated fibers as compared to untreated hair.

We have also compared the electrification characteristics of fibers modified with complexes containing anionic detergents with different chain lengths (Figure 10). There seems to be little difference between dodecyl, tetradecyl, and hexadecyl sulfates. Eicosanoic acid was applied as a suspension and from a completely homogenous alkaline solution. In both cases it formed thick deposits on the fiber surface which considerably increased the surface conductivity. Consequently, if charge generation was not too fast, considerable reduction in charge density was observed (PC both directions of rubbing, stainless steel rubbing from tip to root). Similarly, as in the case of long chain alkyl quaternary salts, PC and teflon® probes were not sensitive to the surface modification, producing a high density of negative and positive charges, respectively, for both directions of sliding (sodium tetradecyl sulfate complex modified fibers behaved erratically and unexpectedly, showing a high density of positive charges for tip-to-root rubbing against PC). For stainless steel, the charge densities were reduced (Figure 10b), though the effect of the hydrophobic chain length is not clearly seen. Differences in experimental data obtained for PMAPTAC-SDS complex treated hair and stainless steel as
Figure 10. Kinetic curves of tribocharge generation on keratin fibers modified with the complex PMAPTAC-anionic detergents of various chain lengths. Fibers were treated for 2 hours at 1g/dl PMAPTAC solution, rinsed with H₂O and kept in deionized water for 1 hour, then exposed to anionic surfactant for 100 min followed by soaking in H₂O for 12 hours.

rubbing material, presented in Figures 9 and 10, are the consequence of different treatment procedures given in detail in figure descriptions.

The rates of charge decay of complex-treated fibers were usually exponential and fast as is exemplified by the data shown in Figure 5. This is justified by the presence of the saturated monolayer of cationic polymer which was shown (Figure 8) to increase considerably the ionic surface conductivity of the fibers.

EFFECT OF FIBER REDUCTION ON TRIBOELECTRIC CHARGING

Reduction of keratin fibers with both THPC and TGA results in a change in the electrochemical potential of the fiber surface. In the case of a nylon® probe, the direction
of the charge transfer was reversed in comparison with untreated fibers for rubbing from root to tip (for both THPC- and TGA-modified keratin, Figure 11a,b). The sign of the charge generated by chitosan acetate was negative only for TGA-treated keratin (Figure 11b). The signs and magnitudes of charges generated by rubbing from tip to root are in accord with all our previous observations and with the data obtained for rubbing in the direction from root to tip.

Figure 11. Tribocharge generation on keratin fibers reduced with (a) THPC (15 minutes at 23°C) and (b) TGA (10.6% solution, pH = 9.2, 15 min at 37°C).

PMMA film, which is characterized by a work function lower than keratin and which charges untreated fibers negatively in both modes of rubbing, showed an unexpected characteristic. It initially produced a low density of negative charges on the fibers, but then the direction of charge transfer was reversed with the polymer film acting as an acceptor (Figure 11a,b). If the electrochemical potential of the fiber surface is increased, as is suggested by the direction of charge transfer for rubbing with chitosan acetate and nylon® probes, then PMMA film should exhibit an even stronger tendency to charge keratin negatively. We cannot offer, at the present time, any reasonable explanation for this unexpected behavior of PMMA film. Oxidation of reduced keratin with H2O2 did not have any additional influence on tribocharging, and the obtained kinetic curves resemble those obtained for reduced hair.

The rates of charge decay for reduced hair were of the same order of magnitude as for untreated fibers (t_{1/6} = 11.4 min for σ_1 = 3.20 \cdot 10^{-9} \text{C/cm}^2 \text{ at 28\% RH for hair reduced with TGA and oxidized with H}_2\text{O}_2).}

EFFECT OF FIBER BLEACHING ON TRIBOELECTRIC CHARGING

Hair bleaching resulted in a very small change of charging characteristics for both modes of rubbing as compared to untreated fibers (Figure 12). The PC probe generated

* The time after which surface density decayed to one-sixteenth of its initial value.
TRIBOELECTRIC CHARGING OF HAIR

very low positive charge density (in contrast to high positive charge density observed for untreated fibers, Figure 3) for sliding in the direction from root to tip, and nylon® charged hair negatively for the reversed direction of sliding. These data suggest some decrease of the keratin work function. Bleaching has no significant effect on the fiber conductivity ($t_{1/2} = 15.6 \text{ min for } \sigma_1 = 4.98 \cdot 10^{-9} \text{ C/cm}^2 \text{ at } 29\% \text{ RH}$).

EFFECT OF OXIDATIVE DYEING

Deposition of oxidative hair dyes in hair reduced the electrochemical potential of the fiber surface. This is supported by the data presented in Figure 13a,b. Both chitosan acetate and nylon® probes produced higher density of negative charges for rubbing in the direction from root to tip. As in the case of reduced hair, the PMMA probe showed initial negative charging followed by the charge reversal. In addition to this, oxidative dyeing does not seem to increase the conductivity of the fibers ($t_{1/2} = 13.2 \text{ min for } \sigma_1 = 4.35 \cdot 10^{-9} \text{ C/cm}^2 \text{ at } 30\% \text{ RH for hair dyed with a light shade oxidative haircolor}$).

Figure 12. Tribocharge generation on bleached keratin fibers.
Figure 13. Tribocharge generation on hair fibers dyed with (a) Dark shade haircolor (Nice 'n Easy #121) and (b) Light shade haircolor (Nice 'n Easy #99).

CONCLUSIONS

The triboelectric charging of human hair was found to be affected by two factors: (1) the relative positions of keratin and material used for rubbing in the triboelectric series; and (2) the ability of the fiber surface to dissipate accumulated static charges. The effective work function for untreated hair was determined to be dependent upon the direction of rubbing and close to the values characteristic for PC (3.85–4.8 eV, Table I) and chitosan acetate. At low relative humidities, the fibers behave like typical insulators. Charge density decays are nonexponential and high residual charge remains trapped indefinitely on the fibers.

Adsorption of long chain alkyl cationic surfactants was shown to increase the effective work function of hair fibers. Consequently, the driving force for the electron transfer between modified keratin and such materials as stainless steel, polyethylene, polypropylene, or hard rubber is diminished. Also, charge decays are greatly accelerated and exponential. The relative importance of these two factors under practical cosmetic situations is not clear. The degree of fiber surface modification was strongly dependent upon the length of the surfactant alkyl chain. Longer chain alkyl quats (hexadecyl, octadecyl) were found to be much more effective in modifying the surface properties than their short chain alkyl analogues.

Adsorption of cationic polymers and the formation of polymer-detergent complexes were shown to have an effect on the effective work function and conductivity of keratin similar to that of the cationic surfactants. In the case of these treatments, however, the increase of the work function was not so pronounced and controllable. Also, in practice, the use of cationic polymer-detergent complex does not lead to a control of static charge generation.

Modification of hair surface by reduction, bleaching, and oxidative dyeing results in very small changes of charging characteristics as compared to untreated fibers. They also have an insignificant effect on the fiber conductivities at low humidity.
Probably the most important general conclusion which can be drawn from the presented data is that the combination of two factors, an increase in surface conductivity and a decrease in the electrochemical surface potential gap between the rubbing material and keratin, can provide an antistatic effect. Since the electrochemical surface potential of the fiber strongly depends on the type of modification it was subjected to, there is no single comb material which would at the same time match the electrochemical surface potential of untreated hair and that of hair modified with cationic surfactants, cationic polymers, fluorosurfactants, and silicon polymers or surfactants.

It should also be stressed that the process of triboelectric charging of hair tresses during combing is much more complex as compared to the simple rubbing described in this paper. In the present experiments, the fibers were subjected to similar elongation and stress in all charge generation experiments, since the distance between the rubbing probe and the plane formed by the fibers arranged in a tress was constant.

During combing, such parameters as fiber elongation, stress, and magnitude of frictional forces between the comb and fiber undergo variations during the movement of a comb from the upper point of a tress towards the fiber tips. Consequently, non-uniform distribution of triboelectric charge density along the length of the fiber tress is usually observed (21). This might also affect the correlation between surface modification and triboelectric charging and lead to quantitatively different results than those presented in this paper.

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