

## EFFECT OF INTERNAL AND EXTERNAL TENSIDES ON THE ELECTRICAL PROPERTIES OF POLYMERIC SURFACES

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**Abstract** - The application of a homologous series of bis-quaternary ammonium bromides to human hair increased its electrical conductivity by about four orders of magnitude and reduced the triboelectric charge generated when the hair was combed or brushed dramatically, in most cases to zero. The conductivity increased as the number of poly(ethylene oxide) moieties bridging the quaternary nitrogen atoms increased and the length of the alkyl chains on the nitrogens decreased. Weathering, bleaching and shampooing hair did not significantly alter its conductivity. The triboelectric charge generated on hair by brushing or combing reverses from negative to positive as the ionic state of its surface is altered by immersion in acid or base solutions of varying pH. This observation suggests that either hydroxyl or hydrogen ions are the most mobile ions on the hair surface or that triboelectrification involves an electronic mechanism. By measuring conductivity under high electric fields, the charge transport mechanism of nylon 66, nylon 6 and poly(ethylene terephthalate) fibers was in most cases found to be space charge limited or trapped charge limited. The transport mechanism becomes ohmic, however, when as little as 5% of an internal tenside is added to the fiber.

### INTRODUCTION

Fibers made from pure organic polymers generally have very low electrical conductivities; therefore, fibers formed from these polymers are normally susceptible to the buildup of electrostatic charges and to the well-known problems associated with them. In general, there are two approaches to solving this problem: 1) applying antistatic finishes to the surface of the fibers, and 2) incorporating internal antistatic additives. The vast majority of surface finishes are tensides, most commonly hygroscopic materials such as poly(ethylene oxide) adducts of glycols and amines or ionized materials such as quaternary ammonium compounds or surface-active sulfonates and phosphate esters. Until very recently, the most successful internal additives have also been tensides, most commonly poly(ethylene glycol) derivatives which are incompatible with the fiber polymer and hence form polyblends (Ref. 1-4). Several antistatic fibers (Ref. 5 & 6) have been introduced which depend on carbon, either imbedded in their surfaces, or more recently, dispersed internally, for their antistatic action (Ref. 7). Another type consists of a sheath of nylon containing a small conductive core of carbon dispersed in polyethylene (Ref. 8).

Although it is well established that surface and internal antistatic agents function by increasing fiber conductivity to dissipate the charge buildup (Ref. 9 & 10), the conduction mechanisms are not well understood. Grady and Hersh have examined the conductivity, activation energy for electrical conduction and Seebeck coefficients of a series of nylon fibers with and without internal additives (Ref. 3 & 11). From these measurements they calculated the density and mobility of the charge carriers. Their results suggest that the conduction mechanism of antistatic fibers is different for dry fibers and fibers containing moisture. Some recent studies tend to confirm that corona discharge may play a role in dissipating charges in low diameter fibers (Ref. 6,12,13).

The purpose of this paper is twofold: first, to examine the role played by the presence of external tensides on the electrical conduction and triboelectrification of human hair; and second, to examine the conduction of nylon fibers containing poly(ethylene glycol) under electric fields up to 1.6 MV/m. Such measurement made at high electric fields can give insights into the nature of the conduction mechanisms.

## THE ELECTRICAL PROPERTIES OF HUMAN HAIR

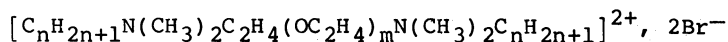
### Experimental methods

Materials and sample preparation. Hair samples for resistance measurements consisted of tresses made from normal brown hair (obtained from DeMeo Bros., New York) cleaned by Soxhlet extraction with a 50/50 chloroform/methanol mixture. The extracted hair was then treated with a series of bis-quaternary ammonium bromides and commercial shampoos. The shampoos were applied twice followed by rinsing with water. The quaternary ammonium compounds were applied by immersion in a 0.5% aqueous solution for about five minutes. The treated tresses were then dried at 45°C in a circulating air oven for one hour. Another set of tresses was prepared from brown hair bleached in a 3% hydrogen peroxide solution at pH 10 and 35°C for one or two hours; hair weathered outdoors for 180 days and subsequently cleaned by Soxhlet extraction with chloroform/methanol; and blond hair immersed in an aqueous solution of copper sulfate containing 32 ppm of Cu for two hours and subsequently rinsed with water. Hair containing an unknown amount of natural sebum was also examined.

Specimens for resistance measurements were prepared by arranging 20-30 hair strands from a tress parallel to each other to form a 20 cm long sheet using double-stick tape to hold the ends in place. The sheet was wound on a 0.318 cm thick by 1 cm wide by 6 cm long poly(tetrafluoroethylene) (PTFE) bar as described by Grady and Hersh (Ref. 11 & 14). Electrodes were formed by coating the 1 x 6 cm surfaces of the PTFE bar with a silver conducting paint. The length of hair between the electrodes was thus the thickness of the bar, i.e., 3.18 mm.

The specimens used to determine the influence of the ionic state of the hair on triboelectrification were prepared as described by Bhat, Harper and Kennedy (Ref. 15) by immersing individual tresses of hair for 2-3 hours in solutions of HCl or NaOH at every integral level of pH from 2 to 11. Each tress was immersed ten times followed each time by oven drying at 55°C. The tresses were then immersed overnight in the desired pH solution. The pH of the final solution did not change, thus assuring that equilibrium had been reached.

The quaternary ammonium compounds consisted of five bis-quaternary ammonium bromides containing a poly(ethylene oxide) chain bridging the two quaternary nitrogens and one long hydrocarbon chain attached to each nitrogen having the following general formula (Ref. 16).



These compounds will be denoted by the symbol  $Q_{m,n}$ . Using this notation, the five compounds examined here were  $Q_{1,12}$ ;  $Q_{1,18}$ ;  $Q_{1,22}$ ;  $Q_{7,12}$ ; and  $Q_{7,22}$ . The commercial shampoos and hair conditioners contained a variety of anionic, amphoteric and cationic compounds.

Electrical resistance measurements. Resistance was measured as described by Grady and Hersh (Ref. 11) in which a test voltage  $V_{x+s}$  is applied to the specimen  $R_x$  in series with a standard resistor  $R_s$ . The fiber was located in a controlled atmosphere in an electrically shielded chamber. The voltage  $V_s$  across  $R_s$  was measured with a Keithley 610C electrometer which has an input impedance of  $>10^{14} \Omega$ . If  $R_s \gg R_x$ , the resistance of the sample can be calculated from the relation

$$R_x = V_{x+s} R_s / V_s$$

Since the cross-sectional area and circumference of the hair fibers were not known, the resistivity of the samples could not be calculated. The resistance measurements were normalized, however, by converting into resistance per unit length of hair  $R_\ell$  by the expression

$$R_\ell = R_x n / \ell$$

where  $n$  = the total number of hair fibers between the electrodes and  $\ell$  = the length of the fiber between the electrodes (3.18 mm).  $R_\ell$  will be a valid measure of the relative resistance of the hair samples if it is assumed that the physical dimensions of the individual fibers are not critical variants since, on the average, each specimen contains a large number of randomly chosen hair fibers. Resistance measurements were made at 37.8°C/20% RH, 21.1°C/40% RH and 21.1°C/65% RH on replicate specimens.

**Triboelectrification. a. Apparatus and method.** Charge generated on the samples by rubbing (brushing or combing) was measured by the classical Faraday pail method as described earlier (Ref. 15). In this method the charged body is dropped into a metal container which is enclosed by but electrically insulated from a grounded metal cage. A charge equal in magnitude and polarity to that on the body is induced on the outer surface of the metal container. The magnitude and polarity of this charge was determined directly by connecting the metal container to a Model 610C Keithly Electrometer. To obtain reliable results, it is essential that the outer cage be properly grounded to shield the Faraday pail from stray electric fields.

The standard rubbing procedure consisted of preparing a 20 cm long tress of hair weighing 1.5 g, forming a loop on one end of the tress by folding over the upper 5 cm, and holding the loop in place with plastic ties leaving a 15 cm length of free hair. The tress is hand-held at the tied end and discharged with a Po<sup>210</sup> deionizing bar ("Staticmaster," Nuclear Products Co., El Monte, CA). The hair is then brushed or combed 20 strokes with a similarly discharged brush or comb and dropped into the Faraday pail. Each successive stroke is alternated between the front and back side of the tress as held by the operator. The type and construction of the brush or comb are important variables, but since there is no "standard" brush or comb, all tests were conducted with the same device. The relative velocity of the contacting bodies is an important variable which influences the rate and extent of charge transfer in a triboelectric process; therefore, the velocity with which the brush or comb is traversed through the tress is maintained as constant as possible. Further, since the electrostatic charges may be quickly dissipated, the time lapse between the successive brushing or combing strokes must also be controlled as much as possible. The standard operating procedure consisted of uniformly brushing or combing 20 strokes in a period of ten seconds.

**b. Ambient test conditions.** It is recognized, of course, that the presence of moisture in the hair greatly reduces charge generation and that the moisture content is very dependent on ambient relative humidity. In order to generate charges large enough to distinguish between various treatments, triboelectrification measurements should be conducted in a low humidity atmosphere. However, it is difficult to maintain low humidities in an open laboratory. As an alternative, the test tress was dried in an oven at a predetermined temperature and tested immediately after removing it from the oven. Following any wet treatment, the test tress was dried in a circulating oven at 55°C for one hour prior to evaluation.

For the experiments made to determine the influence of preconditioning the hair at various pH's prior to triboelectrification, four drying conditions were examined:

- a. immediately following the final treating cycle, dry in N<sub>2</sub> at room temperature (coded "N<sub>2</sub> dry").
- b. "a" followed immediately after testing by oven drying one hour at 55°C (coded "oven dry").
- c. "b" followed by 24 hours conditioning at 22°C and 65% RH, (coded "conditioned"), and
- d. two days after "c" dry in oven one hour at 55°C (coded "redried").

### Results and Discussion

External tensides. The resistance and contact charging of the hair were found to decrease, as expected, with increasing RH. To reduce the volume of data presented, only the resistance per unit length of hair ( $R_\ell$ ) measured at 20% RH and the charge generated on the dried fiber are listed in Table 1. From the results obtained, the following inferences may be drawn.

TABLE 1. Electrical properties of hair treated with tensides

Treatment	Charge generated on tress rubbed with nylon brush (nC)	$R_\ell$ at 20% RH (log $\Omega$ /cm)
Extracted (control)	739	18.2
Q1,22*	117	16.5
Q1,18*	-	16.0
Q1,12*	0	13.4
Q7,12*	0	12.7
Q7,22*	0	14.0
Shampoo A	50	18.2
B	69	18.1
C**	40	17.2
D	76	17.4
E	151	-
Extracted (control)	-	18.2
1 hour bleach	-	17.8
2 hour bleach	-	18.2
Weathered 180 days	-	17.8
Natural sebum	-	17.6
Extracted	-	18.3
Extracted (control)	-	18.1
32 ppm copper	-	18.1

\*bis-Quaternary ammonium bromide. See text for structure

\*\*Conditioning shampoo containing polymer JR-400 supplied by the Union Carbide Corporation.

a. As the RH increased from 20 to 65%, the resistance per unit length was observed to decrease by about four orders of magnitude. The presence of quaternary compounds reduced the sensitivity of  $R_\ell$  to moisture by a small amount.

b. Treatment of hair with shampoos (followed by rinsing) does not significantly reduce its electrical resistance although the charge generated triboelectrically is reduced. The one shampoo examined which contained a conditioner appeared to have a slight beneficial effect, which was noticeable only at the low humidity level.

c. The bis-quaternary ammonium compounds, which were not rinsed out of the hair after application, significantly decrease the electrical resistance. As shown in Fig. 1 and 2, the chemical structure of the Q compounds appears to influence the magnitude of the decrease. The compounds with the shortest alkyl groups (Q1,12; Q7,12) and longest ethoxy chains (Q7,12; Q7,22) produced the greatest decrease (Fig. 1). It is tempting to speculate that conductivity might be a function of the oxygen content of the Q-compounds (which would account for both the number of ethoxy groups which are known to enhance conductivity as well as for the content of alkyl non-polar groups which retard conductivity). A plot of resistivity vs. oxygen content (Figure 2) shows such a dependence except for the Q1,12 which is anomalously low. Thus it appears that the length of the alkyl chain plays a more important role in retarding surface conductivity than ethoxy groups in increasing the conductivity. However, the add-ons of the various compounds are not known exactly and therefore such an inference cannot be conclusively verified at this time.

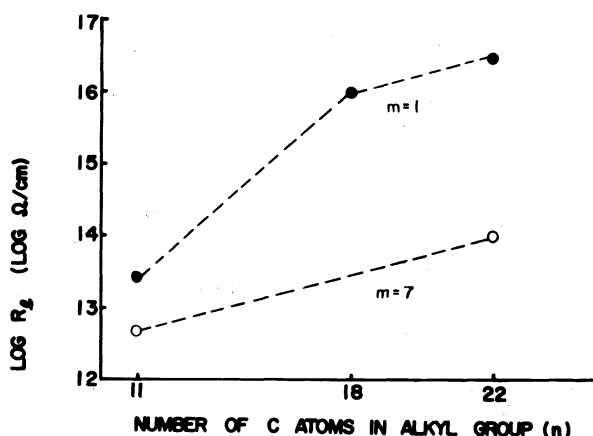


Fig. 1. Resistance per unit length of hair fibers coated with bis-quaternary ammonium bromides as a function of number of carbon atoms in alkyl group attached to each nitrogen (n) and number of ethylene oxide groups (m) bridging the nitrogen atoms.

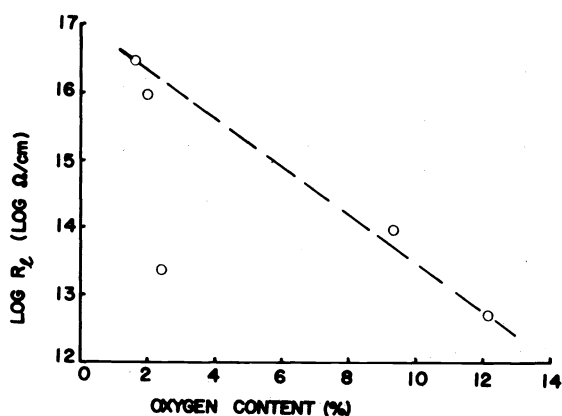


Fig. 2. Resistance per unit length of hair fibers coated with bis-quaternary ammonium bromides as a function of oxygen content.

d. The  $R_L$  value of  $10^{13}$ - $10^{14}$   $\Omega/\text{cm}$  for the clean (control or shampooed) hair at 65% RH converts to a volume resistivity of  $10^9$ - $10^{9.6}$   $\Omega \cdot \text{cm}^2/\text{cm}$  assuming a fiber density of  $1.32 \text{ g/cm}^3$  and a linear density of about 50 denier (or an equivalent diameter of  $74 \times 10^{-4} \text{ cm}$ ). This value is the same as that reported in the literature (Ref. 9 & 17).

e. It is generally believed (Ref. 10) that for a fiber to be antistatic, it should have a surface resistivity of  $<10^{12}$   $\Omega/\text{sq}$ . Using the assumptions listed in (d) concerning the physical properties of the hair and that its cross-section is circular, this value corresponds to a  $R_L$  of  $10^{13.5}$ . Based on this resistance criterion, only the treatments with Q7,22; Q7,12 and Q1,12 - particularly the latter two - can be considered to impart antistatic character to hair at low humidities. As shown in Table 1, the triboelectric charging measurements confirm the validity of the criterion.

f. Peroxide bleaching and weathering have little or no effect on the electrical resistance of hair.

g. The presence of minute amounts of copper in the hair does not change the resistance. It may therefore be concluded that the copper ions remain immobile and provide no continuous conducting medium at such low levels.

h. The presence of natural sebum, the amount of which is unknown, seems to cause a slight reduction in resistance at low humidities. The magnitude of this reduction is too small to be of any practical significance.

Effect of acid-base absorption on triboelectric properties. The magnitude of triboelectric charges generated by brushing (with a nylon brush) or combing (with an aluminum or nylon comb) the acid or base treated tresses were measured after drying under the four conditions listed in the section on ambient test conditions. Although these measurements have been reported elsewhere (Ref. 15), some of them are reproduced here in order to illustrate the dramatic influence of the ionic state of human hair on its triboelectric characteristics. The results, for the first two charging implements, are plotted against treatment pH in Fig. 3 and 4. When combing with the nylon

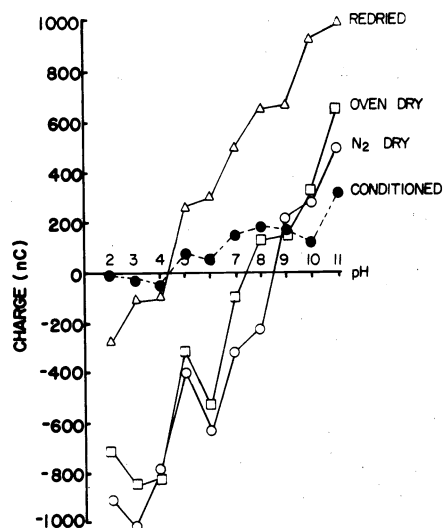


Fig. 3. Charge generated on hair after immersion in acid-base solution at indicated pH and brushing with nylon brush. Drying conditions are defined in section "Ambient test conditions." (From Ref. 15).

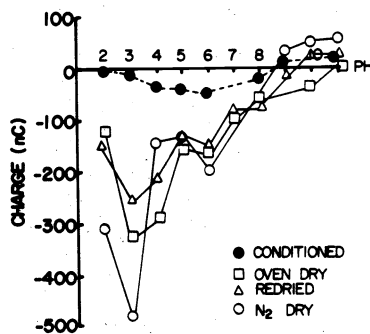


Fig. 4. Charge generated on hair after immersion in acid-base solution at indicated pH and combing with aluminum comb. Drying conditions are defined in section "Ambient test conditions." (From Ref. 15).

comb, the countercharge on the comb was also measured. Its charge was equal in magnitude to the charge on the hair within experimental error and of opposite polarity. Several trends have been noted in these results (Ref. 15).

a. The polarity and magnitude of triboelectric charge generated on acid-base treated-hair show a definite dependence on the pH of the treatment. Hair treated at low pH acquired an excess negative charge in every instance. The charge gradually changes from a large negative value to a large positive value as the pH increases. The polarity switches from negative to positive in the vicinity of pH eight for the samples dried in N<sub>2</sub> or air. The pH at which charge reversal takes place is listed in Table 2.

TABLE 2. pH at which hair is treated to give zero net charge transfer when brushed or combed

Rubbing object	pH to give zero net charge for drying conditions stated				Polarity change with increasing pH
	N <sub>2</sub>	Oven	Condi- tioned	Redried	
Nylon brush	8.5	7.4	4.3	4.3	- to + on hair
Aluminum comb	8.6	10.7	8.6	9.4	- to + on hair
Nylon comb	8.6	8.7	5.4	6.1	- to + on hair
Nylon comb	8.5	8.7	6.0	6.0	+ to - on comb

b. There is no noticeable difference in the charge-pH relationship for hair dried under nitrogen flow at room temperature or in an oven at 55°C following the final acid-base treatment. Thus, such level of heat introduces no complication in triboelectric charge measurement.

c. As expected, preconditioning the tresses at 65% RH reduces the magnitude of the charge. The gradual shift of polarity from negative to positive with increasing pH persists, and for the polymeric rubbing objects the charge vs. pH curve shifts by three or four pH units towards the acid side. Upon subsequent drying, this shift of the curve is maintained, and the magnitude of the charge is increased as expected.

d. The unusually low charge observed for hair treated at pH two is inconsistent with the well-defined trend for charge to increase with the pH of the treatment. This anomalous behavior is perhaps attributable to structural changes associated with absorption of a large quantity of the acid at low pH.

The dependence of the magnitude and polarity of triboelectric charge transferred when hair (or other keratin materials) conditioned in solutions of varying pH is rubbed has not been observed earlier. Lunn and Evans (Ref. 18) assert that the charge generated on hair by combing with a variety of commercially available combs is of positive polarity and identify their observation to be consistent with published triboelectric series and some theories of asymmetric rubbing. They do not report the acid-base state of the hair. Medley (Ref. 19) has reported that acidified horn keratin becomes positively charged when separated from filter paper (cellulose), but after exposure to dilute alkali, becomes negatively charged. This effect is opposite to that observed here. In contrast, Medley also observed effects in the same direction as illustrated in Fig. 3 and 4 in that acidic ion-exchange resins develop negative charges when shaken from filter paper and basic resins are charged positively. WIRA (Ref. 20) also reported effects consistent with those observed here in that when two pieces of keratin buffered to different pH values are rubbed, the most acidic becomes negative.

Medley explains his observations in terms of the relative mobilities of the excess ions on the keratin surface. The dependence of the algebraic charge on the pH at which the hair was exposed before rubbing as illustrated in Fig. 3 and 4 suggests that if an ionic mechanism is responsible for the charge transfer, it is the H<sup>+</sup> and OH<sup>-</sup> ions which are migrating. In contrast, Medley suggests that it is the acid cation and base anion which migrate to explain his observations (Ref. 21). An electronic mechanism is not ruled out by these observations, however. For example, it may be argued that increasing the number of positively charged amine groups by treating the protein with acid will increase the electron affinity of the keratin to the point where its contact potential becomes negative with respect to nylon. Electrons will then flow to the acidified keratin and charge it negatively.

## THE MECHANISM OF CONDUCTION IN FIBERS CONTAINING INTERNAL TENSIDES

Conductivity in high electric fields

A number of charge transport mechanisms in polymers can be characterized by measuring the electrical conductivity as a function of electric field strength. This information can be obtained by examining the dependence of current (I) on voltage (V) applied across a sample of known length. Basically three modes of behavior are observed. First, conduction can be ohmic, i.e.,

$$J = \sigma E = qn\mu E \quad (1)$$

where J is the current density,  $\sigma$  is the conductivity, E is the electric field strength, n is the density of the charge carriers, q their charge and  $\mu$  their drift mobility. Since  $J = IA$  and  $E = V/d$  where I is the current through the sample and A is its cross-sectional area, and V is the electrical potential across the fiber of length d,

$$I \propto V \quad (2)$$

Thus for ohmic conduction in which charge carriers move freely through the fiber, current is directly proportional to voltage. If carriers in excess of those intrinsically present in the fiber are injected into the fiber and charge mobility in the fiber is low, a space charge will build up in the fiber. If there are no potential barriers at the surface (traps), the current density will be (Ref. 22)

$$J = 9\epsilon\mu V^2/8d^3, \quad (3)$$

a relation known as Child's Law for the trap-free insulator. From Eq. 3 it is evident that

$$I \propto V^2, \quad (4)$$

and that a plot of  $\log I$  vs.  $\log V$  would have a slope of 2 as indicated in Fig. 5. At low field strengths at which the fiber can transport all the

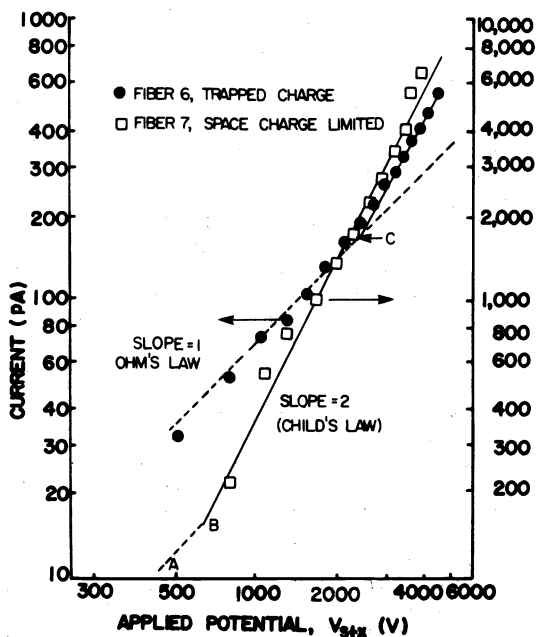


Fig. 5. Log current vs. log voltage plot for nylon 66 containing no additives and for semidull nylon 66 fiber (nos. 6 and 7, respectively, in Table 3). Theoretical lines for ohmic, space-charge limited and trapped-charge limited conduction are indicated.



injected charge, Eq. 1 applies and the slope of the initial part of the curve from point A to B will be 1 (i.e., it will exhibit ohmic behavior over this short "induction" period before the space charge is formed.

If injected charges are trapped at the surface, the buildup of space charge will be delayed. The delay can be expressed by including in Eq. 4 a trap-limiting parameter  $\theta$  giving the ratio of trapped to free charge:

$$J = q\epsilon\mu V^2\theta/8d^3 \quad (5)$$

Trapping has the effect of extending the ohmic induction region of Child's Law to a higher voltage as shown in Fig. 5 at point C. As the potential and field strength are increased, a point may be reached where the current increases sharply to the value corresponding to the trap-free model.

This technique for examining conduction in polymers was first suggested by Lambert (Ref. 23), but has not heretofore been utilized on fibers. The advantage of the technique arises from the clear distinctions shown between the different mechanisms of charge transport and the relative ease with which they can be interpreted both theoretically and experimentally.

#### Results of high field measurements

High field conductivity measurements were made on fibers conditioned at 21.1°C and 65% RH. Prior to evaluation, the fibers were purified by washing in a non-ionic detergent in water followed by extracting in  $\text{CCl}_4$  as described earlier (Ref. 11). Current-voltage relationships were recorded automatically on an X-Y recorder (Ref. 11). The applied voltage was increased in increments of 50 V up to a maximum of 5 kV. For the 3.18 mm lengths of fiber held on the PTFE holders, the highest field strength was 1.67 MV/m. After any change in potential, the new voltage was held constant until all transients and polarization currents disappeared and the current reached a steady-state value as indicated on the X-Y recorder. A typical recorder curve is shown in Fig. 6 for a nylon 66 fiber containing 6% of polyethoxylated stearyl alcohol (PSA) (fiber No. 13 in Table 3). The  $\log I$  vs.  $\log V$  plot for this fiber is shown in Fig. 7. Also shown in Fig. 7 is the plot for the same base polymer containing 15% polyethylene glycol of molecular weight 20,000 (PEG-20M). Both fibers exhibit ohmic behavior.

The  $\log I$  vs.  $\log V$  plots were examined visually, and when they were reasonably linear, the slope of the curve was determined by a least-square regression analysis. The identification of the fibers examined and a summary of results obtained are presented in Table 3. Plots typical of fibers exhibiting space-charge limited conduction and trapped-charge limited conduction are shown in Fig. 5.

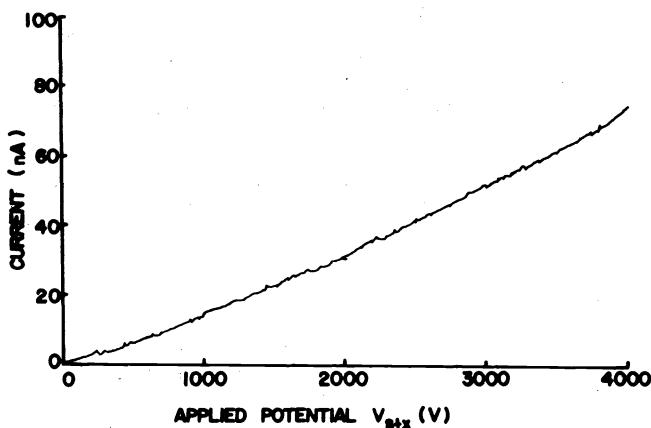


Fig. 6. Current as a function of voltage applied to experimental antistatic nylon 66 fiber containing 6% polyethoxylated stearyl alcohol (no. 13, Table 3) as recorded on X-Y recorder.

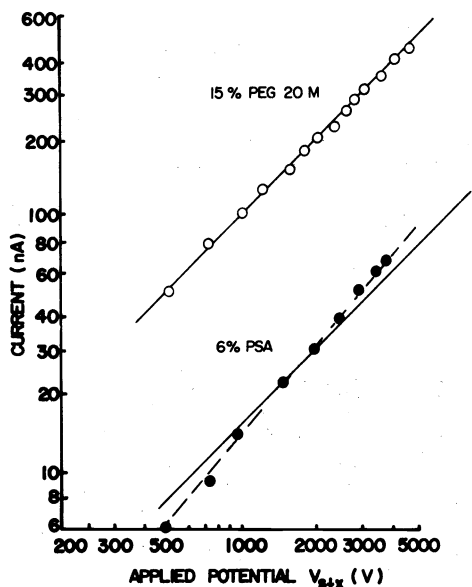


Fig. 7. Log current vs. log voltage plot for experimental antistatic nylon 66 fibers containing 6% polyethoxylated stearyl alcohol and 15% PEG-20M (nos. 13 and 16, respectively, in Table 3). The solid lines have a slope of 1 and the dashed line has a slope of 0.9.

Commercially available fibers generally contain small quantities of heat and light stabilizers and a larger quantity of  $TiO_2$  which is added to deluster the fiber. The fibers examined consisted of several commercial nylon 66, nylon 6 and poly(ethylene terephthalate) (PET) fibers, several commercial fibers containing antistatic agents, and a group of especially prepared experimental samples identified as fibers 6 and 13-17 in Table 3. This last group consists of "pure" nylon 66 (containing no additives) and this polymer containing 6% of added PSA and varying quantities of PEG-20M.

Of the nine nylon 66 commercial fibers examined, seven exhibited trapped-charge or space-charge limited conduction. The other two were ohmic. The fiber without additives also seemed to exhibit trapped-charge conduction (Fig. 5). Three of the four commercial antistatic fibers and all five experimental fibers with added tensides exhibited ohmic conduction.

Conduction in nylon 6 was more confusing. The semidull sample was ohmic, while the dull fiber (containing a larger quantity of  $TiO_2$ ) and special high modulus fiber (highly oriented) were intermediate in behavior between ohmic and space-charge limited. The slopes of the  $\log I$  vs.  $\log V$  curves were 1.3 and 1.5 respectively for these two fibers. When an internal antistatic agent was added to the dull fiber (fiber 23), there was no change in slope. Fiber 24, a commercial nylon 6 antistatic fiber made by a different producer, was ohmic, however.

All three PET fibers had a second power or higher dependence of current on voltage. Two of these were reasonably close to the value expected for space-charge limited conduction (2.0 and 2.2). The third (fiber 25) exhibited a 2.5 power dependence, a value which may be too high for this mechanism.

#### SUMMARY AND CONCLUSIONS

The application of tensides to human hair in the form of commercial shampoos followed by rinsing does not change the electrical resistance or triboelectrification properties of the hair. On the other hand, when an homologous series of five bis-quaternary ammonium bromides were applied to the hair and allowed to remain, the electrical conduction increased by about four orders of magnitude and the charge generated by brushing with a nylon brush dropped dramatically, in four cases to zero. The conductivity increased as the number of poly(ethylene oxide) moieties bridging the quaternary nitrogen atoms increased and as the length of the alkyl chains on the quaternary nitrogens decreased. Weathering and bleaching of the hair had little effect on its conductivity and triboelectrification properties. When

TABLE 3. Slope of log I vs. log V curves and indicated conduction mechanisms

Fiber no.	Pro-ducer	Size <sup>a</sup>	Additive <sup>b</sup>	Log volume conductivity	Character of log I vs. log V curve	
				$\sigma_v$ (S/cm)	Slope <sup>c</sup>	Indicated mechanism
<u>NYLON 66</u>						
1	A	7/1	TiO <sub>2</sub> (SD)	-10.9	1.2	Trapped charge
2	A	15/1	TiO <sub>2</sub> (SD)	-11.3	1.0	Trapped charge(?)
3	A	15/3	TiO <sub>2</sub> (SD)	-11.2	1.9	Space charge
4	A	20/1	TiO <sub>2</sub> (SD)	-11.3	1.0	Ohmic
5	A	70/34	TiO <sub>2</sub> (SD)	-10.8	1.5+3.6	Trapped charge(?)
6	B	127/13	None	-12.1	1.0+2.0	Trapped charge
7	B	70/34	TiO <sub>2</sub> (SD)	-10.9	2.1	Space charge
8	B	15/1	TiO <sub>2</sub> (SD)	-11.3	1.0	Ohmic
9	B	39/9	Antistat	-8.0	1.5+2.3	Trapped charge(?)
10	B	50/17	Antistat	-7.8	0.8	Ohmic
11	B	70/26	Antistat	-8.0	1.1	Ohmic
12	B	200/68	Antistat	-8.3	0.9	Ohmic
13	B	47/13	6% PSA	-8.5	0.9	Ohmic
14	B	115/13	5% PEG	-8.0	0.8	Ohmic
15	B	127/13	10% PEG	-8.0	0.9	Ohmic
16	B	124/13	15% PEG	-7.0	1.0	Ohmic
17	B	119/13	20% PEG	-7.4	1.0	Ohmic
18	C	15/1	TiO <sub>2</sub> (SD)	-10.2	1.0+4.5	Trapped charge
19	C	70/26	TiO <sub>2</sub> (SD)	-10.2	2.2	Space charge
<u>NYLON 6</u>						
20	D	20/1	TiO <sub>2</sub> (SD)	-11.0	1.0	Ohmic
21	D	15/3	TiO <sub>2</sub> (SD) (HM)	-10.8	1.5	Intermediate
22	E	40/13	TiO <sub>2</sub> (D)	-10.3	1.3	Intermediate
23	E	40/13	Antistat	-7.6	1.3	Intermediate
24	F	40/10	Antistat	-6.8	1.0	Ohmic
<u>POLY(ETHYLENE TEREPHTHALATE)</u>						
25	A	70/14	TiO <sub>2</sub> (SD)	-9.1	2.5	Intermediate
26	A	70/34	TiO <sub>2</sub> (SD)	-10.9	2.2	Space charge
27	C	70/15	TiO <sub>2</sub> (SD)	-11.9	2.0	Space charge

<sup>a</sup>Denier/no. of filaments<sup>b</sup>SD = semidull commercial fiber containing TiO<sub>2</sub>

Antistat = commercial fiber containing internal antistat of undisclosed nature

PSA = polyethoxylated stearyl alcohol [C<sub>18</sub>H<sub>37</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>H], n ≈ 12PEG = polyethylene glycol, MW 20,000 [HOCH<sub>2</sub>(CH<sub>2</sub>OCH<sub>2</sub>)<sub>n</sub>CH<sub>2</sub>OH], n ≈ 500. (Union Carbide Corp. Carbowax - 20M)

HM = high modulus fiber

D = dull commercial fiber containing TiO<sub>2</sub><sup>c</sup>Horizontal arrow indicates abrupt change in slope

the resistance of the hair is reduced to about  $10^{14} - 10^{15} \Omega/\text{cm}$ , triboelectrification is no longer a problem, a value in agreement with theoretical charge dissipation mechanisms.

The triboelectric charging of hair by brushing or combing with nylon or aluminum implements varies with the ionic state of its surface as altered by immersion in acid or base solutions. The charge generated increases essentially monotonically from negative to positive as the pH of the immersion solution increases from 2 to 11. The point at which no net charge is transferred (and the polarity of the charge reverses) ranges from pH 4.5 to 8.5 depending on ambient conditions and rubbing materials. These observations suggest that if the triboelectrification mechanism is ionic, hydroxyl and hydrogen ions are the most mobile ions on the hair surface. An alternative electronic mechanism in which electrons are transferred during contact is also possible.

The mechanisms of charge transport in nylon 66, nylon 6 and poly(ethylene terephthalate) fibers were examined by making conductivity measurements at high electric field strengths (up to 1.6 MV/m). The technique described by Lambert in which the slope of the log current vs. log voltage curve is examined was then utilized to interpret the results. The charge transport mechanism in nylon fibers was found to change from essentially space-charge limited or trapped-charge limited to ohmic when as little as five percent polyethylene glycol of molecular weight 20,000 is added to the fiber. In some cases, commercial nylon fibers containing only delustrants and stabilizers were also ohmic. All except one of the commercial antistatic fibers examined, which probably also contained tensides, were also ohmic. The charge transport mechanism in poly(ethylene terephthalate) fibers was found to be space-charge limited.

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