

## Moisture in Textiles

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Evidence is presented that for a cotton hair structure of the specific type described, calculations are in such close agreement with many experimental data as to suggest the following tentative conclusions:

1. The moisture content necessary to form a monomolecular layer on all internal surface of the cotton hair appears to be slightly more than 1 per cent of the hair weight.

2. Less than half the internal surface, that termed fibril surface, appears to be involved in moisture adsorption which causes appreciable transverse swelling of the cotton hair. Upon this surface multimolecular chains of water seem to condense, the length of such chains increasing progressively up to saturation with corresponding increases in hair diameter throughout the whole of this range, each hydroxyl group in the cellulose surface being the base of a water chain, with separations between these chains along the surface corresponding to the arrangement of the hydroxyl groups on the cellulose surface.

3. Moisture adsorbed on surfaces within the cellulose aggregates composing the fibrils does not appear to be involved in transverse swelling, but may be responsible for the slight longitudinal swelling exhibited by cotton. The capacity of the cotton hair for this type of adsorption suggests that its locus is the ends of crystallites and therefore within the body of the fibrils. To account for the slight swelling, it is assumed that only a monomolecular layer can be adsorbed on these surfaces.

4. A theory is proposed to explain the dependence of the electrical properties of textiles upon their moisture adsorbing properties, and upon the surface distribution of moisture within the submicroscopic structure.

### 1. INTRODUCTION

A STUDY of the electrical properties of textiles and their dependence on atmospheric conditions and naturally-occurring impurities in the material has resulted in important economies and improvements in the use of textile insulation in the telephone industry. Recently, calculations have been made as to the moisture content and swelling of cotton at various equilibrium conditions, based on assumptions, first as to the structure of the cotton hair,\* then as to the

\* In keeping with recognized terminology, the individual cotton fiber is called a hair, suggestive of its morphological origin.

location and distribution of the internal surface upon which moisture might condense, and finally as to the manner in which moisture may be held upon this internal surface.

From this rather specific picture of the cotton hair structure it has been possible to calculate moisture contents and swelling properties

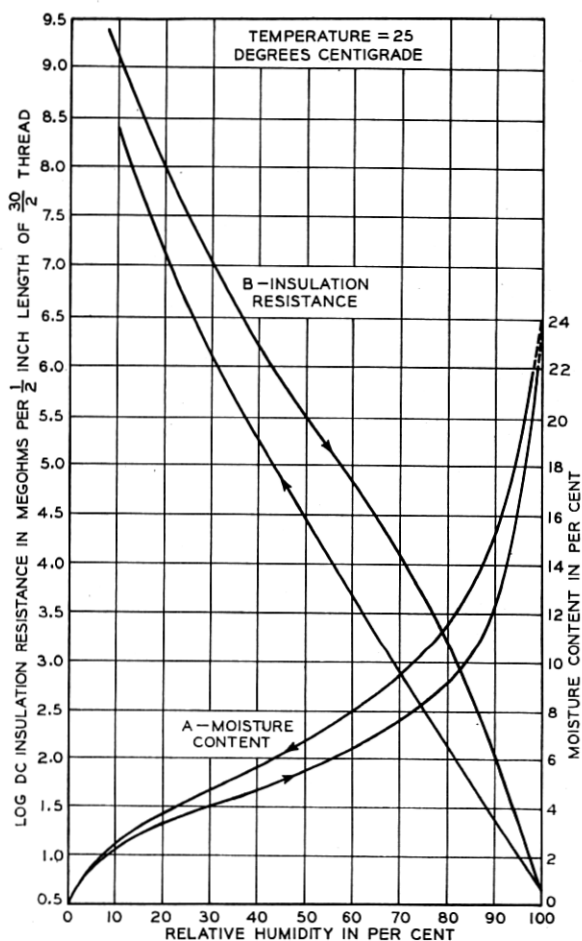


Fig. 1—Moisture sorption and electrical properties of raw cotton.

consistent with experimental data. It has been possible, also, to present a more comprehensive explanation of the change in the relations between electrical resistance and moisture content of cotton over the whole range of atmospheric humidity than that given in

previous publications from these Laboratories.\* It is therefore considered that such a picture should contribute towards a better understanding of the moisture-sorbing † properties, not only of cotton, but also of other similar fibrous materials, despite the hypothetical nature of some of the assumptions upon which the calculations are based.

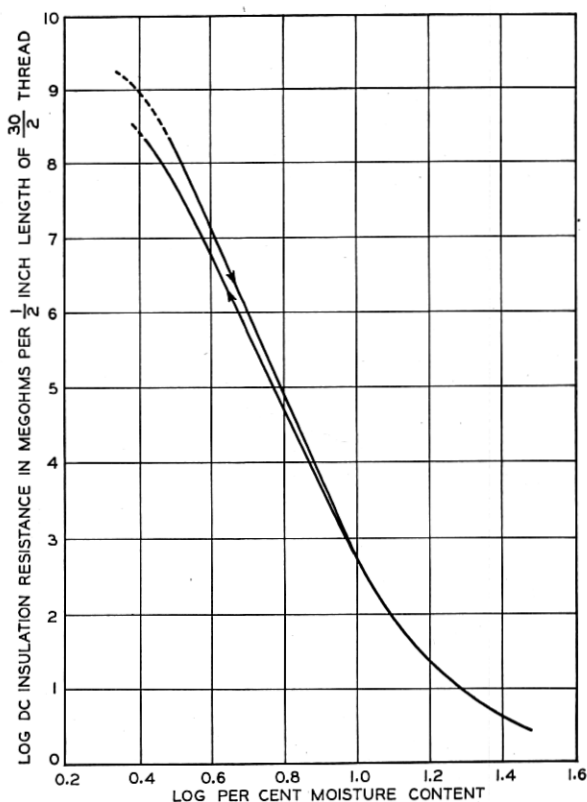


Fig. 2—Effect of previous history on resistance of raw cotton.

The electrical insulation resistance of textiles, when dry, is enormous compared with the resistance observed under atmospheric conditions. A change of but 1 per cent in atmospheric relative humidity (R. H.), equivalent to between 0.1 per cent and 0.2 per cent change in moisture content (M. C.), causes a change of about 25 per cent in resistance of

\* See references 1 and 2 of the list with which this article concludes.

† "Adsorption" is here defined as the taking up of a gas or vapor by a solid, "desorption" the giving up of a gas or vapor, and "sorption" the general process without special indication of gain or loss. The use of these terms implies no assumptions with regard to the mechanism of the processes they denote.

cotton. With silk the corresponding change in resistance is somewhat greater, and although silk sorbs materially more moisture than cotton at any equivalent atmospheric condition, it is much the better insulating material. Small amounts of naturally-occurring, water-soluble salts in cotton, such as NaCl and  $K_2SO_4$ , seriously impair the resistance of this textile. Traces of acids or alkalies left after degumming have a similar effect on silk. By washing these materials in water, their electrical properties are greatly improved.

Figure 1-A shows the familiar equilibrium relation between relative humidity and moisture content for cotton, including the hysteresis loop. A similar hysteresis characteristic, Fig. 1-B, in the relative humidity-resistance relation has been discussed in previous publications.<sup>1, 2</sup> Figure 2 shows more clearly, as suggested by a comparison of the two types of curves in Fig. 1, that the resistance of cotton is critically dependent upon its moisture content. The curves in Fig. 2 show another important fact. The resistance of cotton may have, not one, but a *range* of resistance values for a single moisture content, depending upon the previous treatment or "history" of the sample.

This fact, which is one of great practical importance, is illustrated in Table I. Eleven samples of cotton, taken successively from the same spool, were dried to constant weight at 100° F., in a current of dry air, then equilibrated together under very carefully controlled conditions, first at 87.7 per cent R. H., then re-dried as before and re-equilibrated at 84.3 per cent R. H. several days later. The moisture contents of these samples were as follows:

TABLE I.

Sample No.	% Moisture Contents	
	at 87.5% R. H.	at 84.3% R. H.
1	10.95	10.1
2	10.8	10.0
3	10.7	9.9
4	10.8	9.8
5	11.1	10.2
6	11.0	9.9
7	11.8	10.8
8	10.7	10.1
9	10.85	9.8
10	11.0	10.0
11	10.7	9.9

The moisture contents of these samples showed small but definite differences, persisting even between tests several days apart. One of the samples had apparently been treated slightly differently from the others in preparation, since it preserved a marked difference in moisture content in both tests. Since a change of only 0.1 per cent in M. C.



may cause a change of about 10 per cent in resistance, these data are considered significant in such testing methods as are used for electrical textiles.

In a previous publication<sup>2</sup> a series of simple equations was formulated to show the quantitative relations between moisture content,

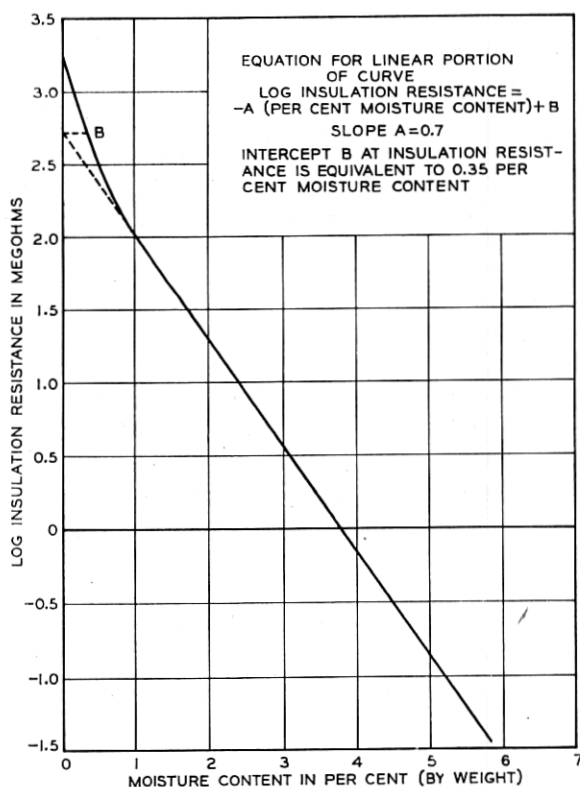


Fig. 3—Moisture content-resistance relation for rag paper.

relative humidity, and the resistance ( $\Omega$ ) of cotton:

$$\log \Omega = -A(\% \text{ M. C.}) + B, \quad (1)$$

$$\log \Omega = -a(\log \% \text{ M. C.}) + b, \quad (2)$$

$$\log \Omega = -\alpha(\% \text{ R. H.}) + \beta. \quad (3)$$

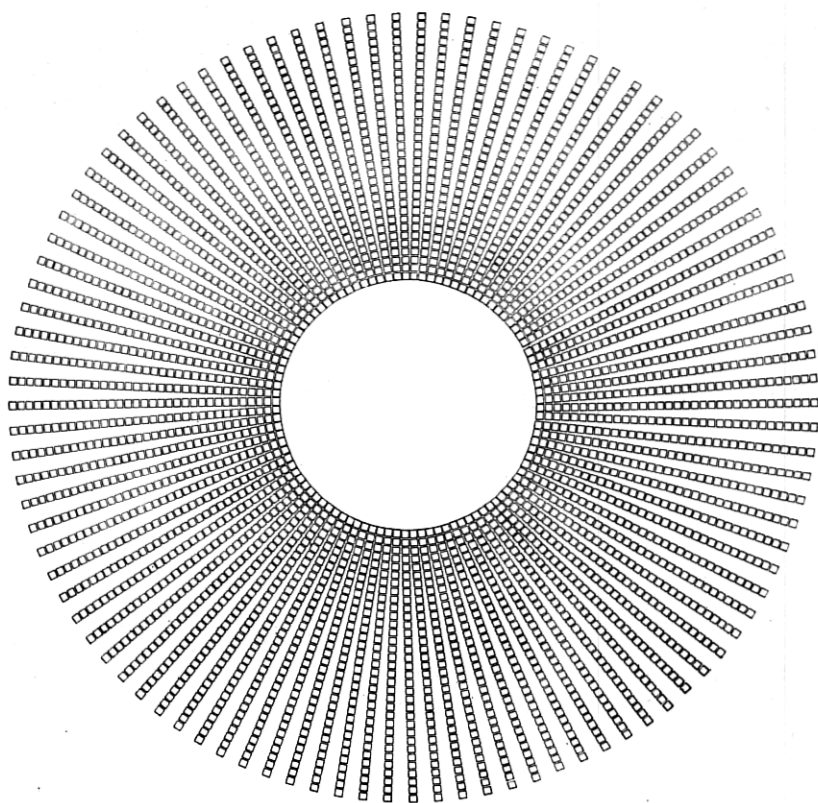
Equation 1 was considered as applying for moisture contents in the vicinity of 3 per cent, Equation 2 between 3 per cent and 10 per cent M. C., and Equation 3 from 10 per cent M. C. to saturation.

The ranges of application of Equations 2 and 3 are evident from Figs. 2 and 1-B, respectively; but since the resistivity of cotton becomes enormously high as the moisture content approaches zero, it has been difficult to verify the application of equation 1 below about 2 per cent. However, a recent study along somewhat different lines has provided us with information on this portion of the moisture content curve down to as low as 0.04 per cent M. C. It will be seen from Fig. 3 that equation 1 holds between 1 per cent and 6 per cent M. C. Below 1 per cent M. C., however, the resistance increases more rapidly with decreasing moisture content than is consistent with equation 1.

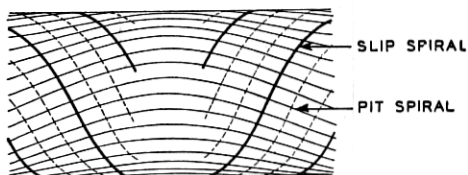
The data from which Fig. 3 was secured completes a chain of evidence upon which is based a theory of moisture adsorption which appears adequate to explain many properties of cotton. This theory involves, in addition to the data just discussed, a rather specific picture of the cotton hair structure.

## 2. STRUCTURE OF THE COTTON FIBER

According to Balls,<sup>3</sup> the cotton hair is formed by the outward extension of a single cell from the epidermis of the seed-coat; this extension, unaccompanied by any cell division may continue until the hair is 2000 times as long as it is broad. Up to about half maturity, the cell wall remains very thin but the hair attains most of its length; during the remaining half of the growth period (about one month) the wall thickens from the outside in until it appears to consist of about 30 to 35 concentric "growth rings" (see Fig. 4). Each growth ring consists, further, of parallel strands of fibrils, which run continuously in spiral form from end to end of the hair making one complete turn around the hair in about three diameters, and with periodic reversals in the direction of this spiral. Balls also suggests that side by side in each growth ring, there are about 100 fibrils, each separated from its neighbor by an air space. These fibrils are described by Balls as "dominoes" laid down one on top of the other in a pile-up of growth rings extending from the wall of the central canal or lumen to the outer wall of the fiber. Thus the front and back of each domino are growth ring boundaries, and each domino is separated from its neighbor by an air space. There are also air spaces between each domino in a growth ring. These air spaces are identified as the so-called pits in the wall structure. They are visible under a microscope, and appear to extend from the outer surface of the cotton hair down to the lumen. These air spaces are far larger in magnitude than those separating the front and back of each domino. Only by swelling the fiber in



(a) CROSS SECTION



(b) SIDE VIEW SHOWING PIT SPIRAL REVERSALS

Fig. 4—The fiber structure of cellulose.

(a) An idealized cross-section of the cotton hair. The domino-like blocks shown in cross-section are arranged according to Ball's conception.

(b) The spiral arrangement of these domino-like blocks or fibrils is shown, together with the separating pits in the wall, and the slip-spiral effect along the fibrils.

Obviously these conventional type figures do not represent the true shape of the cotton of commerce, but they approximate the shape during the growth period, before the boll is opened. As the hair dries out, the central lumen collapses and the hair twists.

caustic soda can a differentiation be detected in the cross-sectional structure of the fiber to indicate this growth-ring character. Thus the fibrils are considered as being separated by air spaces on all sides, the whole cotton hair is spongy, and the surfaces of cellulose bounding these air spaces are internal surfaces of the fiber.

Slip spirals are visible in the hair surface at high magnification. Though decidedly irregular, they appear to cross the pits at approximately right angles, suggesting that there are additional internal surfaces at these points.

Cellulose from all sources appears to consist of definitely arranged crystallites or micellae.\* Haworth<sup>9</sup> suggested that cellulose is composed of an elementary group consisting of two  $C_6H_{10}O_5$  units, called cellobiose (Fig. 5-A). Figure 5-B indicates how these cellobiose units are joined together end to end to provide the fibrous structure of native cellulose.

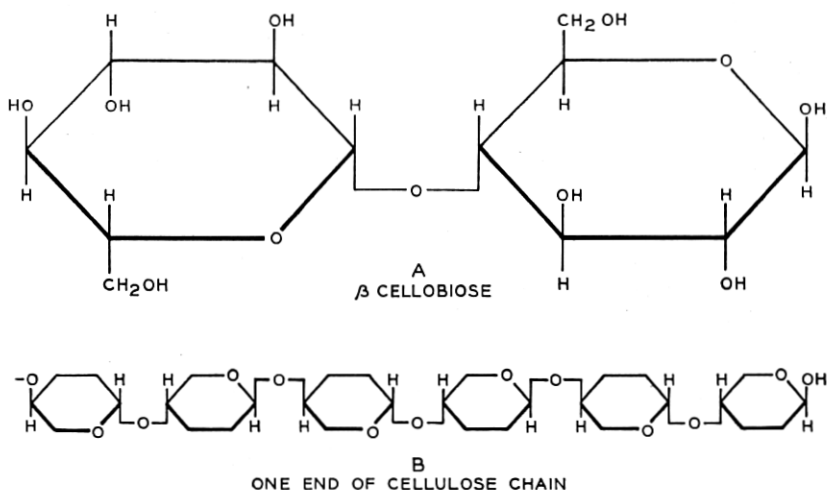


Fig. 5—Molecular structure of cellulose.

Diffraction and chemical evidence indicate that the cellobiose units are arranged parallel to the *b*-axis of the unit cell, with one cellobiose group at each common edge of adjacent cells and one through the center of each cell. These form long primary valence chains arranged parallel to the fiber axis and are held together laterally by cohesive forces. Figure 6 shows this conception of the unit cell as given by Meyer and Mark.<sup>5</sup>

\* Sponsler and Dore,<sup>4</sup> Meyer and Mark,<sup>5</sup> Freudenberg,<sup>6</sup> Herzog,<sup>7</sup> Polanyi.<sup>8</sup>

## 3. MOISTURE ADSORPTION ON FIBRIL SURFACES

It appears reasonable to assume that moisture will first adsorb on dry cotton on the outer surface of the hair, and by diffusion in the vapor state will penetrate into the pits and adsorb on the pit walls. Since cotton swells appreciably in a transverse direction, but hardly at all lengthwise, it is further assumed that moisture in the pits will next penetrate between the fibrils which are contiguous to one another in the radial direction. At equilibrium with any humidity below that required to form a monomolecular layer, it is assumed that the water molecules will be distributed at random on active points over all of the internal surface. For humidities above this value, polymolecular chains of uniform thickness are assumed to adsorb at active points on the fibril surfaces only, since moisture on the growth ring surfaces of these fibrils appears to be responsible for the transverse swelling of the cotton.

The equilibrium moisture content of cotton is reduced if the hydroxyl groups on the cellulose molecules are acetylated or otherwise esterified. Consequently it seems reasonable to assume that each water molecule adsorbed on the cellulose surface is held by a force originating in the oxygen atom of a surface hydroxyl group. As may be seen from Fig. 5-A, there are six hydroxyl groups per cellobiose unit, and the percentage moisture equivalent to a monomolecular layer covering the surface of the fibril structure with each water molecule satisfying forces of a surface hydroxyl oxygen will now be estimated.

The fibril cross-section is estimated to be  $1240 \times 1300$  AU, based on average dimensions of the cotton hair.\* Assuming the cellobiose units arranged with the  $a$ -axis parallel to the fibril width (Fig. 6), there will be  $1240/8.3 = 150$  unit cells across the fibril, and  $1300/7.9 = 165$  unit cells down through the fibril. Therefore the total number of oxygen atoms per unit cell length in the four fibril surfaces is:

$$6 \times 150 \times 2 + 6 \times 165 \times 2 = 3780.$$

From this the moisture content equivalent to a monomolecular layer is:

$$\frac{3780}{2 \times 150 \times 165} \times \frac{18}{324} \times 100 = 0.42\%.\dagger$$

\* The considerations upon which these and subsequent calculations are based are given in detail in separate publications which will appear in the April and May issues of *Textile Research*.

† The Angström unit AU is  $10^{-8}$  cm. From Fig. 6 it appears that only the equivalent of one cellobiose unit may be available for surface adsorption per unit cell in the fibril surface. Furthermore, since molecules in solid or liquid surfaces are subject to unbalanced forces (surface tension) it is assumed that all surface cellobiose units are so oriented that all 6 hydroxyl groups have surface forces capable of adsorbing water molecules.

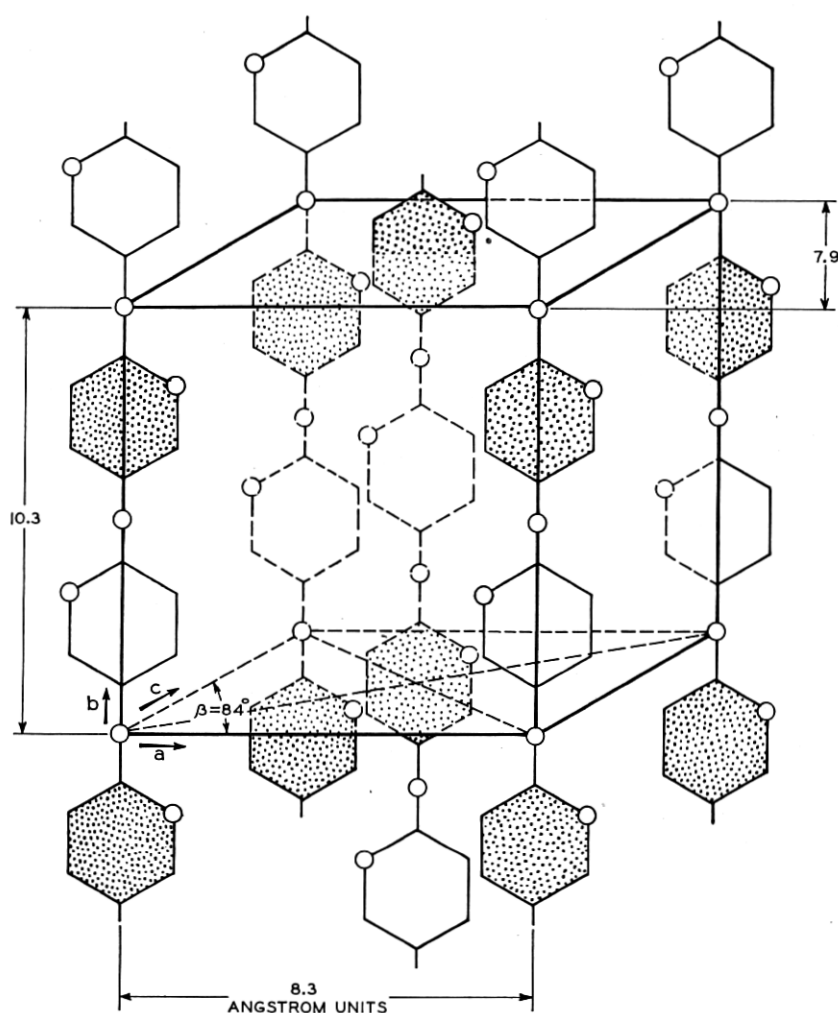


Fig. 6—The cellulose unit cell or crystallite structure.

#### 4. HAIR SWELLING DUE TO FIBRIL SURFACE MOISTURE

The diameter of the water molecule is reported as 3.8 AU. The surfaces of adjacent fibrils along growth ring boundaries must be separated at least  $2 \times 3.8 = 7.6$  AU when a monomolecular layer of water is present on each contiguous surface. This corresponds to a total increase in hair diameter of  $33 \times 2 \times 7.6 = 500$  AU. The percentage diameter increase in the hair is:

$$(500/125000) \times 100 = 0.4\%.$$

where 125000 AU is taken as the mean diameter of the dry cotton hair.

According to Collins,<sup>10</sup> the coefficient of hair diameter increase with humidity is about 0.11 per cent per 1 per cent R. H. Therefore, an increase of 0.4 per cent in hair diameter is found at  $0.4/.11 = 3.6$  per cent R. H. From adsorption data (Fig. 7) by Urquhart and Williams,<sup>11</sup> this relative humidity corresponds to between 1.1 per cent and 1.2 per cent moisture content. The difference in this value and that

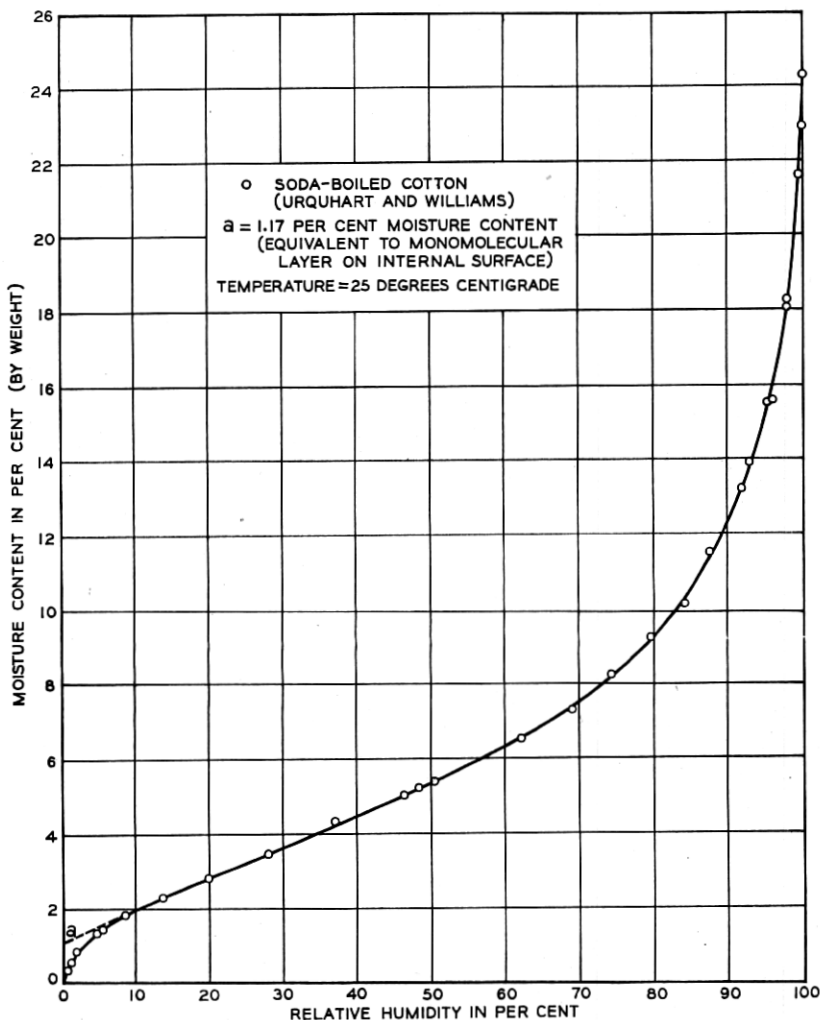


Fig. 7—Moisture adsorption-humidity relation for cotton at 25° C.

calculated under Section 3 is between 0.7 per cent and 0.8 per cent, suggesting that there is additional internal surface within the hair structure upon which moisture may be held without manifesting itself by an increase in diameter. This suggestion appears to be confirmed by quite different considerations.

Brunauer and Emmett<sup>12, 13</sup> consider it likely that the linear portion of van der Waals adsorption isotherms for nitrogen on the surface of ammonia catalysts indicates the building up of additional layers of adsorbed molecules. They state that extrapolation of this linear portion to zero pressure indicates the amount of gas needed to form a monomolecular layer upon this surface. Between 3 per cent and 50 per cent relative humidity the adsorption isotherm for cotton in Fig. 7 is very nearly linear. Applying this method to cotton the intercept ( $a$ ) has values between 1.4 per cent and 0.35 per cent, depending on temperature. The average value is about 1 per cent being of the same order as that estimated from swelling data.

Since the estimated moisture content equivalent to a monomolecular layer on the internal surface of the cotton hair is so nearly the same when determined by two independent methods, it seems reasonable to postulate an additional internal surface in the cotton hair, amounting in extent to somewhat more than that corresponding to the fibril surfaces.

Slip spirals along the hair, crossing the pits at approximately right angles (see (b) of Fig. 4) suggest that there are discontinuities in the length of the fibril structure, hence further internal surface. Since the additional internal surface suggested by the preceding calculations and estimates does not appear to be involved in the transverse swelling of the cotton hair, it is suggested that this may be held upon the ends of crystallites or micellae which compose the fibril structure.

It is considered of much less importance to pursue the detailed calculations of this possibility than it is to point out that some such distribution of surface within the body of the fibril structure may be involved in adsorption of a small amount of moisture, and this picture is of material value in accounting for some of the properties of cotton.

## 5. MULTIMOLECULAR LAYERS

It is further assumed that above 1.5 per cent moisture content, addition of moisture simply increases the thickness of the moisture layer upon the surfaces of the fibrils. The thickness ( $n$ ) of the moisture layer on each fibril, expressed in number of water molecules, and the percentage moisture content at 50 per cent R. H. may readily be obtained. At 50 per cent R. H. the hair diameter increase is 5 per cent



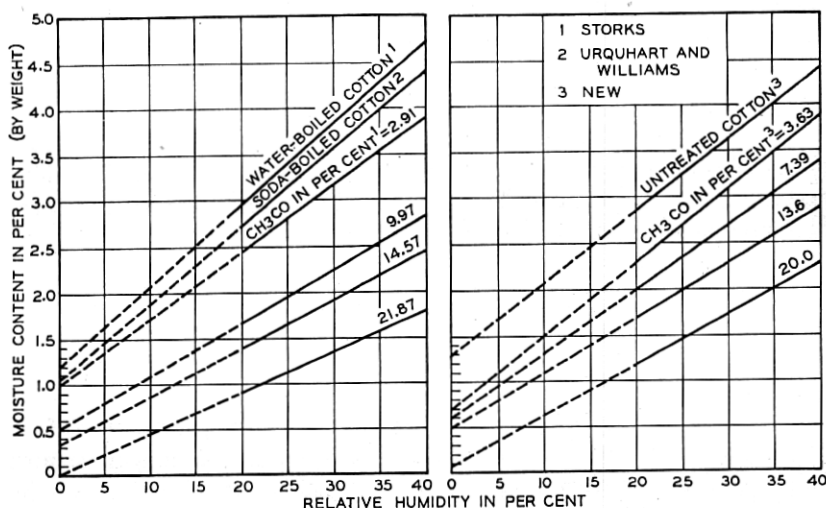


Fig. 8—Moisture adsorption intercepts for acetylated cottons indicating amounts of internal surface.

#### 8. THEORY OF CONDUCTION OF ELECTRICITY THROUGH COTTON

It now appears possible to provide a more comprehensive theory for the conduction of electrical current through the moisture paths in a textile than has been suggested previously.<sup>1, 2</sup>

Below 1 per cent moisture content it is likely that equation 1 fails to hold, due to obvious discontinuities in the moisture paths over surfaces containing less than a monomolecular layer of water.\* Above 1 per cent, it is not to be concluded, however, that a continuous moisture film exists. It appears that some space is still available between certain water molecules, and the space pattern of water distribution is determined by the type of solid surface and the arrangement of active points or zones upon which each water molecule is held. In the case of cotton, such active points are considered to be hydroxyl groups; for silk they may be amino or carboxyl groups or both, and from Astbury's discussion<sup>16</sup> of the chain structure of these two materials it seems likely that their space patterns for moisture adsorption are different. Furthermore, it is assumed that each of these active points may be anchorage not only for a single water molecule, but for a chain of such molecules, the length of the chain being deter-

\* It is of interest to note that if the linear portion of the curve shown on Fig. 3 is extrapolated to the insulation resistance axis, the insulation resistance corresponding to this intercept is found at 0.3 per cent M. C. (see *a*—Fig. 3), this being of the same order of magnitude as that estimated to cover fibril surfaces with a monomolecular layer, suggesting that the linear portion of the curve is specifically related to moisture adsorption on the fibril surfaces.

mined by the relative humidity. This conception is much like the picture of acid or oil molecules standing as a film on a water surface, with the polar end in the water.

Some such function as equation 1 may apply since simply increasing the length of the water chains will not cause a proportionate decrease in the resistance. It seems evident from Fig. 5-a that small increments of water might be expected to sufficiently lengthen water chains of minimum separation so as to establish contacts between them along the current path, but that larger increments of water are necessary to accomplish the same result between more widely separated anchorage points. This would explain the gradual change from the relation of equation 1 at low moisture contents to equation 2 at intermediate moisture contents. At some point along the humidity curve it is conceivable that capillary condensation occurs in the pits so that at progressively higher humidities the increasing cross-section of these pits plays a more important part in current conduction than the adsorbed chains of water molecules. This may explain why equation 3 is found to apply at highest humidities.

Adsorption, however, appears to continue throughout the whole of the humidity range, consistent with the hair swelling relations. Thus it is shown that adsorption and capillary condensation need not be considered separately but may go along together with a gradual shifting in importance from one to the other in the current conduction process.

Evershed<sup>17</sup> explained the decrease in resistance of a textile with increasing applied potential as being due to elongation of pools of water in the material under electrical stress forming more continuous current paths. This deviation from Ohm's law may be explained also as being due to the influence of increasing electrical stress upon the oscillation of the free ends of moisture chains, bringing more of them into orderly alignment along the line of applied potential, and establishing shorter current paths through the structure.

The difference in electrical behavior of different textile fibers may be illustrated by a comparison of the adsorption of moisture on cotton and silk surfaces. From Astbury's pictures of the structure of protein molecules as compared with cellulose molecules it appears that although there may be more points per unit surface for moisture to condense upon on protein surface, there are also possibilities of separation of adjacent moisture chains in a manner similar to that discussed for cellulose, and furthermore, there appear to be side chains of hydrocarbons interspersed in the protein chain which may act as barriers to the ready contact of adsorbed water chains on either side

of these hydrocarbon chains. This may explain why silk has a higher resistance than cotton for a given moisture content. It might be expected that silk, due to these hydrocarbon barriers in the current path might also have a higher dielectric breakdown under potential stress.

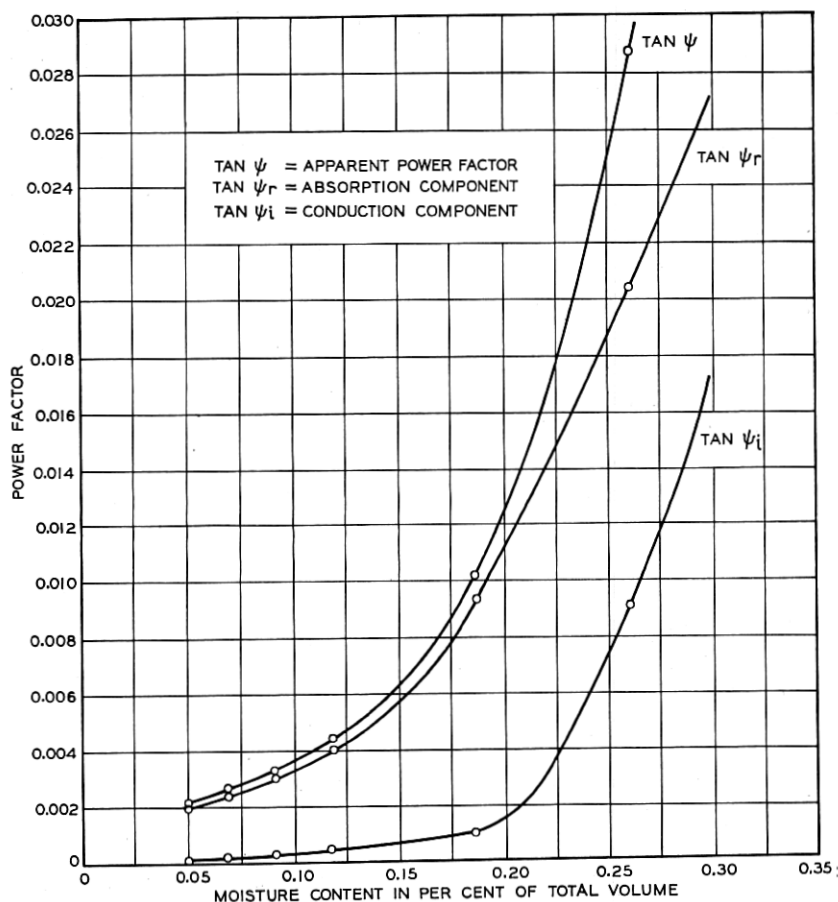


Fig. 9—Relation between power factor components of cable paper and moisture content.

Whitehead,<sup>18</sup> in a study of the effects of moisture on power cable paper insulation, obtained data on the change of power factor with increasing moisture content. Figure 9 shows this relation. It will be noted that the conduction component ( $\text{tan } \psi_i$ ) of the power factor rises sharply as the moisture content of the paper exceeds 0.2 per cent

by volume (about 0.3 per cent by weight). This increase occurs in the range consistent with the completion of the monomolecular layer of moisture on the internal surface of the material, particularly since the internal surface of paper and cotton appears to be of the same order of magnitude.

#### 9. GENERAL DISCUSSION OF THEORY

Peirce<sup>19</sup> proposed a two-phase theory for the adsorption of moisture by cotton, based upon the facts that a small quantity of water is adsorbed by dry cotton very much more rapidly than the same amount added to cotton with a moderate water content, that it has much greater effect on the elastic properties, evolves more heat, and is more difficult to remove. He regards the moisture attached to the hydroxyl points as in phase (*a*) while that in phase (*b*) consists of an indefinite number of molecules adsorbed in a looser fashion over all available surfaces, limited only by the conditions of space and of equilibrium with the external concentration of aqueous vapor.

The differentiation between fibril and other internal surfaces is considered as giving a more definite explanation of such two-phase adsorption than that proposed by Peirce. The (*a*) phase may be pictured as moisture added to the active hydroxyls which lie on the fibril surfaces where such surfaces are readily available for moisture adsorption, while the (*b*) phase is associated with a definite number of active hydroxyls but within the body of the fibrils and therefore less accessible than those on the surface. As has been pointed out, it is quantitatively reasonable to suppose these available internal hydroxyls to be located at the ends of the crystallites.

According to the cotton hair structure presented in this paper, there is actually more than twice as much internal surface available for moisture adsorption from the dry state as there is in cotton already in equilibrium with a 1 per cent moisture content. The slow diffusion of moisture to those surfaces most deeply buried in the fibrils may account for the fact that while cotton very nearly reaches equilibrium with any given humidity in a relatively few minutes, the final establishment of equilibrium conditions, involving a change of less than 1 per cent in moisture content, may take more than 24 hours. The first water molecule to attach itself to an active hydroxyl might be expected to evolve more heat than subsequent molecules in the chain since the interaction is between water and cellulose hydroxyls, not between water and water. Also, water held within the fibril structure no doubt is the most difficult to remove since it must diffuse out through this fibril structure.

This picture of moisture adsorption seems to provide a reasonable explanation for a variety of practical problems.

Thus it is known that if fibrous materials, such as wood, paper or fiber board are dried below a certain critical moisture content, permanent changes may be expected in the structure; even serious damage may result from too thorough drying at low temperatures. It seems evident that when the moisture content of such more or less dense structures is reduced to a point where the outer layers have less than 1 per cent of moisture, the internal surfaces of these layers may begin to lose the monomolecular layer of water. The valence forces of surface hydroxyl groups are now no longer satisfied by water molecules, so that such hydroxyls on contiguous surfaces may stick together. On readsorption of moisture, portions of these surfaces may be so permanently attached to one another that swelling will no longer occur in just the same way as originally, and cracking and warping may result.

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