

## Crystalline Character of Native and Chemically Treated Egyptian Cottons. II. Computation of Variance of X-Ray Line Profile and Paracrystalline Lattice Distortions

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### Synopsis

A variance range analysis of the x-ray line profiles for seven cottons (native, urea-treated, and mercerized) has been carried out to get two estimates of the crystallite size from (1) the slope and (2) the variance intercept. Assuming the crystallite length of cellulose to be the same in ramie and native cottons under ideal conditions of growth, the relative fluctuation of the repeat length along the *b*-axis has been calculated for all the samples. This degree of paracrystalline lattice distortions is negatively correlated with the fiber bundle strength at zero gauge and appears to be the same as the imperfections referred to in the weak link theories of fiber strength. While the orientation parameters are also well correlated with strength, the degree of crystallinity does not seem to have any influence. Wilson's rigorous mathematical treatment of the number-average particle size, in relation to the two estimates from the variance slope and intercept as well as the particle size distribution, has been successfully applied for the first time to cotton fibers leading to a clearer understanding of crystallite size-strength relationship.

### INTRODUCTION

In part I of this paper,<sup>1</sup> two aspects of the crystalline character of Egyptian cottons, namely, degree of crystallinity and crystallite orientation, were dealt with in some detail. The results emphasized in particular a greater variation in the x-ray orientation factor from one cotton to another as well as from one treatment to another than that in the degree of crystallinity. Further, the spiral angle obtained from the procedure described by DeLuca and Orr<sup>2</sup> could define the mean inclination of the crystallites to the fiber axis, while Hermans's x-ray orientation factor was apparently based on an angle between the fiber axis and the direction of the molecular chain of cellulose (which need not necessarily coincide with the crystallite axis).

In part II now, it is proposed to discuss the evaluation of crystallite sizes from the very broad x-ray diffraction line profiles. During the last few years, the Fourier transform of the line profile<sup>3</sup> has been applied to polystyrene<sup>4</sup> and cotton.<sup>5</sup> Interpretation of diffraction patterns of poly-

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mers is obstructed by two important difficulties, viz., (i) the presence of a relatively high and not-so-well-defined background and (ii) the absence of higher-order reflections. Wilson<sup>6</sup> described a technique of eliminating the ambiguity of background and estimating the particle size based on the variance range analysis of the line profile. Langford<sup>7</sup> has brought out the advantages of the method, applying it to submicron nickel of particle size hardly larger than 200 Å. Kulshreshtha and co-workers<sup>8</sup> extended the use of the variance range function to Tufcel, a highly oriented polynosic fiber. These authors also obtained an estimate for the degree of paracrystalline distortions in Tufcel<sup>8</sup> and also ramie<sup>9</sup> through an application of Hosemann's theory of paracrystals,<sup>10</sup> making use of the line breadths for three orders of meridional reflections.

In the present work, the variance range method is applied to the line profile of cottons, and the results are interpreted to estimate the degree of paracrystalline lattice distortions in relation to ramie.

### EXPERIMENTAL

Five varieties of Egyptian cottons, viz., Menoufi, Giza 69, Ashmouni, Danderah and Giza 66, were chosen for this study; two more cottons, Sea Island and K6, were included for comparison. The cottons were treated by urea, mercerization, and urea followed by mercerization, as described in part I of this paper.<sup>1</sup>

The equipment consisted of a Philips x-ray generator Model PW 1010, a wide-angle goniometer Model PW 1050, and a diffractometer Model PW 1051. By using a texture goniometer Model PW 1078 for transmission geometry of a fiber bundle, the line profiles of (002) and (040) for cellulose I and (101) as well as (040) for cellulose II were scanned in steps of 0.03° (2 $\theta$ ) using fixed time technique (64 sec.). The other experimental conditions were as follows: Cu K $\alpha$  radiation at 40 kV, 20 mA, with Ni filter, 1° and 4° divergence, and antiscatter slits; 2.2° Soller slits in the incident and diffracted beams; and proportional counter tube with single-channel pulse-height analyzer to give a high peak-to-background ratio.

#### Standard for Instrumental Line Breadth

For the determination of the crystallite sizes, the observed line breadths have first to be corrected for instrumental line broadening obtained from a standard substance. It is also desirable that the standard used and the specimens whose crystallite sizes are to be evaluated be of similar chemical composition and be analyzed under identical experimental conditions. Thus, Langford<sup>7</sup> employed with success a solid annealed specimen of nickel for his study on annealed nickel powder. Apparently, because quartz is a widely used standard in x-ray crystallography and because it is a far more powerful scatterer than cellulose, Kulshreshtha and co-workers<sup>8</sup> used a thin film of quartz powder in collodion. Recently, Buchanan and Miller<sup>4</sup> as well as Viswanathan and Venkatakrishnan<sup>11</sup> have found that hexamethylene-

tetramine,  $(\text{CH}_2)_6\text{N}_4$ , could serve well as a standard for correcting the line profiles from cellulosic fibers. Accordingly, a specimen of this material (0.4 mm thick) compacted at  $80^\circ\text{C}$  was used in this study and found satisfactory.

### Variance Range Analysis

The centroid of the x-ray line profile is calculated according to the expression given by Pike and Wilson<sup>12</sup> and used in the variance range function of Langford and Wilson<sup>13</sup> who have shown that the linear portion of the variance-versus-range curve is very sensitive to the assumed background. The additive property of variance has been used in the present work to correct the observed intensities for instrumental line broadening. The variance range analysis was carried out for six levels of background (in order to get the true one) through a program written in FORTRAN II for a CDC 3600 computer, after making some alterations, especially with a view to saving further computer time, to the one published by Hilleard and Webster<sup>14</sup> in ALGOL.

The slope  $k_s$  and the intercept  $W_s$  of this variance range function arising from the particle size of the specimen under investigation are given by the differences between the corresponding quantities of the broadened and standard profiles, as in eqs. (1) and (2):

$$k_s = k_b - k_t \quad (1)$$

and

$$W_s = W_b - W_t. \quad (2)$$

The  $k_s$  and  $W_s$  values give two independent estimates  $\epsilon_k$  and  $\epsilon_w$  of the "apparent" particle size,<sup>7</sup> given by

$$\epsilon_k = \frac{\lambda}{\Pi^2 k_s \cos \theta} \quad (3)$$

$$\epsilon_w = \frac{\lambda}{2\Pi(-W_s)^{1/2} \cos \theta}. \quad (4)$$

From the relation established by Wilson<sup>15</sup> between the two estimates, an upper limit to the number-average crystallite size  $\langle p \rangle$  could be obtained from eq. (5):

$$\langle p \rangle \leq \left( \frac{L}{K} \right) \frac{\epsilon_w^2}{\epsilon_k} \quad (5)$$

where  $L$  and  $K$  are the taper parameter and variance Scherrer constant, respectively. The values for  $L$  and  $K$  for different shapes of crystallites and for the various  $(hkl)$  reflections from crystals of cubic symmetry have been calculated by Wilson<sup>16</sup> and Lele and Anantharaman.<sup>17</sup>

The crystallites in cellulose are generally considered to be lamellar in shape, a form closest to parallelepiped. The values given by Wilson for

the parameters  $L$  and  $K$  seem, however, to be inapplicable to cellulose, because the cellulose crystallites are perhaps lamellar but are definitely known to spiral irregularly about the fiber axis, thereby assuming a distorted shape. Since the precise shape of the crystallites is thus indeterminate and the intention of the present study is only to estimate the relative sizes of the crystallites in different cottons,  $L$  and  $K$  are assumed as a first approximation to be equal. Further, with another assumption made that the crystallites within a cotton are all of uniform size, the sign of inequality in eq. (5) disappears. Thus the crystallite size, say,  $t$ , could be estimated directly from the quotient of  $\epsilon_w^2/\epsilon_k$  and would correspond to the upper limit of Wilson's number-average crystallite size  $\langle p \rangle$ .

### Paracrystalline Lattice Distortions

According to the treatment of Hosemann,<sup>18,19</sup> real crystal structures are subject to two kinds of distortions, referred to as of the first kind, which does not, however, affect the long-range order, and of the second kind, which contributes to increasing line breadth for higher orders of reflection. Bonart and co-workers<sup>20</sup> have suggested a means of separating the line breadths  $\beta_P$  and  $\beta_D$  due to particle size and lattice distortions of the second kind from the observed line breadth  $\beta_{PD}$  from the equation

$$\beta_{PD}^2 = \beta_P^2 + \beta_D^2 = \frac{1}{L_{hkl}^2} + \frac{(\Pi gn)^4}{d_{hkl}^2} \quad (6)$$

where  $L_{hkl}$  and  $d_{hkl}$  are, respectively, the ideal crystallite size and the repeat distance in the direction perpendicular to  $(hkl)$  planes, and  $g$  is the relative fluctuation of  $d_{hkl}$ .

Equation (6) could be used for the estimation of both the "ideal" crystallite size in the  $(hkl)$  direction and the degree of paracrystalline lattice distortion  $g$ , if the experimental data are available for different orders of reflection  $(hkl)$ . However, a minimum of three orders is necessary to decide uniquely whether the line broadening is due to paracrystalline distortions or microstrains, for Wilson (ref. 16, p. 5) has shown that the line breadth  $\beta_M$  due to a strain  $e$  is given by

$$\beta_M = 4e \frac{\sin\theta}{\lambda} = \frac{2en}{d_{hkl}} \quad (7)$$

which, like the line breadth due to paracrystalline distortions, is related to the experimental line profile by the equation

$$\beta_{PM}^2 = \beta_P^2 + \beta_M^2 = \frac{1}{L_{hkl}^2} + \frac{(2en)^2}{d_{hkl}^2}. \quad (8)$$

Thus, the square of the observed line breadth varies linearly with  $n^2$  for microstrains and with  $n^4$  for paracrystalline distortions. Since Kulshreshtha and co-workers<sup>9</sup> have already established the paracrystalline character of cellulose through a linear relation between  $\beta_{PD}^2$  and  $n^4$  from the

three reflections (020), (040), and (080) for ramie, in the present work attention is confined only to the reflections from the (020) and (040) planes with comparable intensities for ramie.<sup>21</sup> Using the procedure due to Jones,<sup>22</sup> Kulshreshtha and co-workers<sup>8,9</sup> reported the values of  $g = 1.66\%$  for Tufcel and  $g = 0.8\%$  for ramie. In extending this study of paracrystalline lattice distortions to cottons, where only the (040) reflection is obtained in practice, it is assumed that cellulose being the constituent of both ramie and cottons, the ideal crystallite length in cottons would have been equal to that in ramie but for the different degrees of lattice distortions.

## RESULTS

The results of the variance range analysis of the (020) and (040) reflections from ramie are indicated in Table I. The subscripts  $b$  and  $i$  refer to the observed line profiles for ramie and the standard substance hexamethylenetetramine, respectively;  $k_s$  and  $W_s$  are the corrected slope and variance intercept, respectively, for ramie;  $\epsilon_k$  and  $\epsilon_w$  are the resultant estimates of the "apparent" particle sizes, respectively. Given that the estimate from the slope is less susceptible to residual strain in the reference material and by definition is identical with that given by the Fourier method,<sup>23</sup> the ideal crystallite length in ramie in the direction perpendicular to the (0*k*0) planes is estimated to be 220 Å, and  $g = 1.44\%$  from eq. (6) by substitution of the values of  $1/\epsilon_k$  for  $\beta_{PD}$ .

TABLE I  
Slopes<sup>a</sup> and Intercepts<sup>b</sup> from the Variance Range Function for Ramie and Corresponding Crystallite Lengths

(0 <i>k</i> 0)	Instrumental		Observed		Corrected		$\epsilon_k$ , Å	$\epsilon_w$ , Å
	$k_i$	$W_i$	$k_b$	$W_b$	$k_s$	$W_s$		
(020)	4.1	-54	8.3	-103	4.2	-49	215	203
(040)	3.9	-34	9.1	-107	5.2	-73	180	171

<sup>a</sup>  $k$ , in degrees  $(2\theta) \times 10^2$ .

<sup>b</sup>  $W$ , in degrees  $(2\theta)^2 \times 10^4$ .

The particle sizes for the various cottons—native and treated—estimated according to eq. (5) are given in Tables II and III for the meridional and equatorial reflections, respectively. These values are derived from the slopes and intercepts of the variance range function without taking the paracrystalline lattice distortions into account. Substituting in eq. (6), the values of  $1/\epsilon_k$  for  $\beta_{PD}$  (the experimental line breadth for cottons after correction for instrumental line broadening) and the value  $1/\beta_P = 220$  Å for the ideal length that would have been obtained as in ramie, the degree of paracrystalline distortions  $g$  could be estimated. The values thus obtained for  $g$  in the case of (040) reflections are also included in Table II. The mean value of  $g$  is found to be 2.59%, varying from 2.37% to 2.81% for the different cottons and treatments.

TABLE II  
Crystallite Length and Degree of Paracrystalline Distortion Derived from Slope and Variance Intercept for Cottons

	$k_s$	$W_s$	$\epsilon_k, \text{\AA}$	$\epsilon_w, \text{\AA}$	$t, \text{\AA}$	$g, \%$
Raw (040)						
Menoufi	8.43	-203	111	105	99	2.37
Giza 69	9.93	-218	94	100	105	2.63
Ashmouni	10.76	-223	87	99	111	2.61
Dandarah	10.76	-226	87	98	110	2.61
Giza 66	10.60	-223	88	99	110	2.73
Sea Island	9.93	-216	94	100	106	2.63
K6	9.43	-203	99	103	107	2.55
Urea (040)						
Menoufi	9.26	-208	101	102	103	2.52
Giza 69	10.76	-231	87	97	108	2.61
Ashmouni	10.26	-223	91	99	106	2.68
Dandarah	10.76	-223	87	99	111	2.61
Giza 66	9.76	-213	97	101	105	2.60
Sea Island	10.60	-226	88	98	108	2.73
K6	9.43	-213	99	101	102	2.55
Mercerization (040)						
Menoufi	9.76	-218	96	100	104	2.60
Giza 69	10.76	-238	87	95	104	2.76
Ashmouni	10.43	-228	90	97	106	2.71
Dandarah	10.76	-233	87	96	107	2.76
Giza 66	10.10	-228	84	97	112	2.81
Sea Island	9.66	-218	97	100	102	2.59
K6	9.26	-213	101	101	100	2.52
Urea and Mercerization (040)						
Menoufi	9.10	-208	103	102	101	2.49
Giza 69	8.50	-205	110	103	96	2.38
Ashmouni	9.33	-210	100	102	104	2.53
Dandarah	9.93	-219	94	99	105	2.63
Giza 66	9.60	-218	98	100	102	2.60
Sea Island	8.77	-204	107	103	100	2.42
K6	8.43	-203	111	103	96	2.37

## DISCUSSION

### Crystallite Size

The results confirm the findings of an earlier study<sup>24</sup> that the crystallite sizes hardly vary from one cotton to another in the direction perpendicular to the fiber axis. It was found that the mean crystallite size estimated from (002) reflections for 15 cottons of different origin was  $55 \text{\AA} \pm 3 \text{\AA}$ . It is seen from Table III that the mean crystallite size estimated from the slope (which is less susceptible to residual strain) is of the same order, namely,  $58 \text{\AA} \pm 3 \text{\AA}$ , for all the seven cottons, native and treated, reported in this study. These results seem to be in fair agreement with the recent work of Heyn<sup>25</sup> who by electron staining as well as small-angle x-ray scat-

TABLE III  
Crystallite Size from Slope and Variance Intercept of  
Equatorial Reflections from Cottons

Cotton	$k_s$	$W_s$	$\epsilon_k, \text{\AA}$	$\epsilon_w, \text{\AA}$	$t, \text{\AA}$
Raw (002)					
Menoufi	14.82	-388	62	73	86
Giza 69	15.70	-413	58	71	86
Ashmouni	16.50	-423	55	70	89
Dandarah	15.54	-408	59	71	85
Giza 66	15.86	-418	58	70	84
Sea Island	14.98	-398	61	72	85
K6	16.82	-428	54	69	88
Urea (002)					
Menoufi	15.06	-393	61	72	85
Giza 69	15.22	-398	60	72	86
Ashmouni	13.86	-378	66	74	83
Dandarah	15.46	-403	59	71	85
Giza 66	17.14	-448	53	68	87
Sea Island	14.58	-388	62	73	85
K6	15.06	-394	61	72	85
Mercerization (101)					
Menoufi	16.09	-421	56	69	85
Giza 69	14.68	-406	61	70	80
Ashmouni	15.91	-416	57	69	85
Dandarah	15.91	-391	57	72	90
Giza 66	16.26	-418	55	69	86
Sea Island	15.91	-421	57	69	84
K6	14.68	-401	61	71	81
Urea and Mercerization (101)					
Menoufi	15.74	-416	57	69	84
Giza 69	15.10	-398	60	71	84
Ashmouni	15.21	-404	59	70	84
Dandarah	16.61	-433	54	68	85
Giza 66	16.17	-418	56	69	86
Sea Island	16.26	-421	55	69	86
K6	16.09	-418	56	69	86

tering estimated the size of the cellulose microcrystallites in cotton fiber to be of the order of about 50 Å. It may be mentioned in passing that the crystallite size  $t$  estimated from  $\epsilon_w^2/\epsilon_k$  (last column of Table III) remains fairly constant ( $85 \text{ \AA} \pm 2 \text{ \AA}$ ) for all the cottons, native and treated. The significance of the crystallite sizes  $t$  estimated from the variance slopes and intercepts in this study is discussed in the concluding paragraph.

In contrast to the lateral size, the crystallite length, that is, the dimension of the crystallites in the direction best aligned with the fiber axis, shows significant variation from cotton to cotton, irrespective of whether these estimates of length are made from the slope or the intercept or from both. Just as was the case with crystallinity, the effect of urea treatment is not so clear-cut, in the sense that the changes in crystallite length do not

reflect any definite trend. On mercerization, however, there is a consistent decrease in the crystallite length  $l$  as estimated in Table II. The crystallite lengths for the raw and chemically treated samples are seen to range from 84 Å to 112 Å.

### Paracrystalline Lattice Distortion

It is interesting to note from Table II that for all the Egyptian cottons (raw), the degree of paracrystalline distortion increases on mercerization and there is only a marginal effect on the other two cottons, K6 and Sea Island. In the context of the recent observation<sup>1,11</sup> that disorder increases on mercerization, the present results on lattice distortion of the second kind could, as suggested by Ruland,<sup>26</sup> form part of the disorder in the fine structure of cottons. Besides, the relative fluctuation of the repeat length along the fiber axis  $g$  is less for all the urea-treated and subsequently mercerized samples than for those not so treated prior to mercerization.

### Strength-Crystalline Character Relationship

In the introduction to part I of this paper,<sup>1</sup> it was indicated how a study of the crystalline character of the Egyptian cottons in relation to their strength would help understand their widest use in fabrics of superior quality. Table IV gives the tenacities of the seven cottons, before and after treatment with urea and/or caustic soda, expressed in g/tex units for zero gauge test specimen lengths. Here again, the effect of urea treatment alone on strength does not show any definite trend, but mercerization reduces the strength in all cases by 7.6 to 11.7 g/tex and by 8.0 to 13.8 g/tex with and without prior urea treatment, respectively. This is quite in conformity with the widely reported results on slack mercerization at zero gauge length.<sup>27</sup>

As pointed out by Warwick and co-workers,<sup>27</sup> "it seems anomalous that slack mercerized fibers are slightly more oriented, yet have a lower tenacity at 'zero' test length, than unmercerized fibers." This behavior could per-

TABLE IV  
Intrinsic Strength of Cottons at "Zero" Test Specimen Length<sup>a</sup>

	Raw	Urea	Mercerization	Urea and mercerization
Menoufi	49.6	50.1	35.8	37.9
Giza 69	47.0	46.3	33.5	35.9
Ashmouni	40.0	41.8	32.0	32.4
Dandarah	43.1	41.5	32.8	34.1
Giza 66	41.5	40.0	31.5	32.8
Sea Island	41.7	40.9	32.6	33.0
K6	43.5	43.5	34.9	33.8

<sup>a</sup> Expressed in g/tex measured on a Stelometer. Tex is a measure of the linear density used in textile science and corresponds to the weight in grams of a filament 1 km long. Gram/tex is at times indicated in length units and referred to as Breaking Length R Km.



haps be due to the increase in paracrystalline lattice distortions on mercerization. It is well known that a reduction in strength is caused by imperfections or flaws in solids, crystalline or amorphous.<sup>28</sup> Incidentally, the degree of imperfections referred to by Pillay<sup>29</sup> in his study on "fiber strength at finite gauge lengths for raw and mercerized cottons" seems to be none other than that of paracrystalline lattice distortions. Such a view is strongly supported by a correlation coefficient of  $-0.688$ , significant at the 1% level, for cellulose I between fiber bundle strength at zero gauge length and degree of paracrystalline lattice distortions.

Table V gives a complete picture of the correlations between fiber strength at zero gauge and the various crystalline characteristics investigated in the present study. It is seen that the correlation in general is significant at a higher level for cellulose I than for cellulose II. This could be attributed to the greater precision possible in practice in the identification of line profiles for the (002) and (040) reflections for cellulose I. For cellulose II, the (040) reflection is known to be contaminated by other reflections, and (002) and (101) overlap considerably.

TABLE V  
Coefficients of Correlation  $r$  between Strength and Crystalline Characteristics

Crystalline characteristics	Cellulose I		Cellulose II	
	$r$	Significance level	$r$	Significance level
Degree of crystallinity $X_{cr}$	0.048	N.S. <sup>b</sup>	-0.428	N.S.
Hermans's orientation factor $f_x$	0.654	2%	0.638	2%
Spiral angle $\phi^a$	-0.714	1%	-0.638	5%
Crystallite orientation angle $\alpha^a$	-0.814	1%	-0.203	N.S.
Apparent crystallite length $\epsilon_k$	+0.621	2%	+0.491	10%
Apparent crystallite length $\epsilon w$	-0.374	N.S.	+0.449	N.S.
Crystallite length $t$	-0.649	2%	-0.525	10%
Paracrystalline distortion $g$	-0.688	1%	-0.505	10%

<sup>a</sup> Results are based on six cottons only.

<sup>b</sup> N.S. = not significant.

A pertinent remark may be made in this context that the degree of crystallinity has absolutely no influence on strength, justifying thereby an earlier observation<sup>30</sup> that "the degree of crystallinity by itself does not enable a definite conclusion to be drawn regarding the relation between fiber structure and physico-chemical properties." On the other hand, the orientation parameters are all well correlated with the fiber strength. The reason for the disparity in the correlations involving crystallite orientation angle  $\alpha$  must be sought in the irregular dispersion, on mercerization, of the crystallites about the spiral angle, as mentioned in part I of this paper.

Finally, the correlations of the different estimates for the crystallite length deserve some closer scrutiny. The slope estimate of the crystallite

length  $\epsilon_k$  is also well correlated with the fiber strength, which is however independent of the variance intercept estimate  $\epsilon_w$ . Now, the positive correlation (0.621) with the slope estimate of the apparent crystallite length and the negative correlation (-0.649) with the estimate  $t$  of the crystallite length require some explanation. The estimate  $t$  in the foregoing was based on the assumption that the crystallites were all of the same size. In practice, there is a finite distribution of crystallite sizes within each cotton and even within a fiber. Consequently, the sign of inequality has to be retained in eq. (5), and, according to Wilson,<sup>15</sup> the more general relation governing  $\epsilon_w$ ,  $\epsilon_k$ , and  $\langle p \rangle$  is given by

$$\frac{\epsilon_w^2}{\epsilon_k} = \langle p \rangle + \frac{W_p}{\langle p \rangle} \quad (9)$$

where  $W_p$  is the variance of the crystallite size (within a cotton). Equation (9) can be rearranged and further reduced to eq. (10) by definition of variance:

$$\begin{aligned} t &= \frac{\epsilon_w^2}{\epsilon_k} = \langle p \rangle \left[ 1 + \frac{W_p}{\langle p \rangle^2} \right] \\ &= \langle p \rangle \left[ 1 + \left\{ \frac{\sum (p_i - \langle p \rangle)^2}{\langle p \rangle} \right\} \right] \end{aligned} \quad (10)$$

where  $p_i$  is the individual crystallite size and the summation covers all the individual crystallites.

The second term within the brackets in eq. (10) is nothing but the square of the coefficient of variation of the crystallite sizes within a cotton. Thus, the crystallite size estimate  $t$  is not only a function of the number-average crystallite size  $\langle p \rangle$  but also of the distribution of the individual crystallites within a given cotton. (Unfortunately, the x-ray diffraction line profile does not give any information on the size distribution.) It has already been shown that the strength of a fiber bundle is positively correlated with the slope estimate of the apparent crystallite length. This then leads to the inference that it is the coefficient of variation of the individual crystallite sizes which is really negatively correlated with strength. This is of course understandable, since the strength of a fiber, which is a chain of crystallites, is decided by its weakest link, namely, the shortest crystallite. Thus, although two cottons might have nearly the same average crystallite size, the one exhibiting a smaller variation in individual sizes is bound to be stronger than the one with a wider variation. In other words, the results obtained in this study may be interpreted to mean that the variation of the crystallite lengths within a cotton is greater than the variation between cottons. The application of Wilson's mathematical treatment of the average crystallite size to cotton fibers has thus been clearly brought out for the first time in this work.

## CONCLUSIONS

From the foregoing, it may be concluded that the application of variance range analysis to the broad experimental x-ray line profiles from macromolecules such as cotton cellulose is advantageous to estimate not only the crystallite dimensions but also paracrystalline lattice distortions making use of Hosemann's theory. The crystallite lengths thus determined are well correlated with the fiber bundle strength at zero gauge length. So also is the degree of paracrystalline distortion, which varies from 2.37% to 2.81%. Of the other crystalline characteristics considered in the work,<sup>1</sup> all the three orientation parameters, viz., x-ray orientation factor  $f_x$ , spiral angle  $\phi$ , and crystallite orientation angle  $\alpha$ , are highly correlated with the strength. However, in the case of mercerized cottons, due to the high dispersion of the crystallites, the crystallite orientation angle  $\alpha$  is not significantly associated with strength.

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