JOURNAL OF APPLIED POLYMER SCIENCE VOL. 20, 2329-2338 (1976)

Analysis of Cotton Fiber Maturity. II. Glycerol Retention Value of Cotton

A. K. KULSHRESHTHA, V. P. CHUDASAMA, and N. E. DWELTZ,
ATIRA, Ahmedabad-380 015, Gujarat, India

Synopsis

The imbibition of glycerol by cotton has been used as a measure of fiber porosity which includes a major contribution from the fiber lumen. Cotton is swollen in glycerol to saturation and subjected to centrifugation until constant weight is attained. The glycerol retention value (GRV) is calculated from the increase in weight of cotton after swelling and centrifugation. This method is applied to determine GRVs and pore space of 12 American cottons which have different wall thicknesses but more or less the same fiber perimeter. A high negative correlation is obtained between GRV and the percentage of mature fibers for various raw and extracted cottons. Effect of fiber wax content on GRV was studied. It has been shown how the average lumen area in swollen state can be calculated from GRV and gravimetric fineness. The significance of pore space is discussed.

INTRODUCTION

Cotton fibers possess a highly porous structure and have been appropriately classified as a "xerogel" by Hermans.[1] The lumen, which is the central hollow cavity within the fiber, is by far the largest single pore in cotton. Apart from the lumen, the cell wall of a cotton fiber contains pores[2,3] which have sizes ranging from about 25 Å upward to those in the submicroscopic range. The existence of pores is not unique to cotton, since pores or cavities are frequently encountered in the outer wall of the epidermis of plants. The pores are presumably the means by which protoplasmic continuity is secured from fibril to fibril and play a very important part in fiber growth.[4,5] They constitute a passage for the materials necessary for the formation and deposition of new fibrils within the cellulosic cell wall. The porosity of cotton decreases with increasing period of fiber growth, as indicated by a progressive decrease[6] in the moisture content of fibers and also by a reduction in lumen extent. This is logical enough, since, as the fiber matures, the need of maintaining a supply line of protoplasm from the cottonseed to the cell wall becomes progressively less and less.

The relationship which exists between fiber porosity and maturity of cotton is particularly interesting to examine, because of the intimate association both these properties have with the performance of the cotton fibers during mechanical[7] and chemical[8] textile processing. Sorption of liquids by cotton may provide[9] a very convenient method of estimating fiber porosity. In fact, the differential dyeing test[10] of fiber maturity is based on differences in the rates of absorption and desorption[8] of direct dyes by immature and mature cotton fibers which are, in turn, controlled by the differences in the pore structure of cottons of extreme maturity. Ono[6] has examined the relationship which exists between moisture absorption and fiber maturity of cotton.

The present paper describes a new method of measuring fiber porosity, based on the imbibition of glycerol by cotton. The glycerol retention value (GRV) is the per cent weight increase of cotton after subjecting it to swelling in glycerol, followed by centrifugation to remove the externally held glycerol. For various cottons investigated in this study, the GRVs have been found to be highly correlated with fiber maturity. The measurement of GRV is not only simple to carry out, but is also very reproducible. It thus offers a new method of estimating the maturity of cotton fibers.

EXPERIMENTAL

Materials

The relationship between GRV and fiber maturity has been investigated for 13 cottons (raw as well as extracted) which included 11 American Upland cottons, one cotton belonging to the Iquitos variety, and Egyptian Karnak. These cottons were selected so as to cover a wide range in maturity, and Table I gives a summary of their physical properties. GRV was also obtained for some other prematurely harvested samples of cotton, as well as for glass wool and viscose.

Purification

All the 13 cottons were subjected to Soxhlet extraction for 24 hr in a mixture of ethanol and benzene, in order to remove oils, waxes, and protoplasmic residue. All cottons were preconditioned at 65% R.H. and 27°C before carrying out the various tests.

TABLE I
Physical Properties of Various Raw Cottons

Sr. no.	Sample	Micronaire value M_C	Gravimetric fineness H, 10^{-8} g/cm	Degree of crystallinity, %,[b]
1	American Immature Cotton	2.35	143	53.0
2	American Upland Cotton 947[a]	2.48	146	56.5
3	American Upland Cotton 486	2.80	162	59.9
4	American Upland Cotton 940	3.00	169	—
5	American Upland Cotton 193	3.40	174	55.6
6	American Upland Cotton 934	3.50	200	—
7	American Upland Cotton 805	4.25	207	59.8
8	American Upland Cotton 859	5.08	244	—
9	American Upland Cotton 189	5.40	214	—
10	American Upland Cotton 922	6.00	266	—
11	American Upland Cotton 875	6.50	236	63.7
12	Iquitos Cotton 888	7.40	296	—
13	Egyptian Karnak	3.60	127	—

[a] USDA Code No.
[b] Determined by the x-ray diffraction method of Patil et al.[11]

Determination of Fiber Maturity

Maturity determination for various raw cottons was carried out according to the standard ASTM procedure[12] for randomly selected specimens, in which about 1000 fibers taken directly from a blended laboratory sample were microscopically examined after treatment with 18% (w/w) NaOH. The parameter obtained from this classification is per cent mature fibers (p_M).

Determination of Glycerol Retention Value from Measurement of Liquid Imbibition

About 0.5 g conditioned sample (raw or extracted cotton) was accurately weighed in a weighing bottle and was kept immersed in a beaker containing glycerol for 1 hr. The swollen fibers were then transferred to a glass tube having a false bottom and centrifuged at a speed of 1000 rpm for the time required (usually 30 min) for the attainment of constant sample weight due to removal of superfluous glycerol. The centrifuged sample was weighed again in the weighing bottle. The glycerol retention value (GRV) was obtained from a mean of six measurements, employing the following formula:

$$\mathrm{GRV} = \left[\frac{100(W_3 - W_2)}{(W_2 - W_1)(100 - R)}\right] \times 100$$

where W_1 = weight of empty weighing bottle, W_2 = weight of weighing bottle containing the conditioned sample, W_3 = weight of weighing bottle containing the centrifuged sample, and R is the % moisture content of the sample. The liquid imbibition values of cotton for other liquids (e.g., paraffin and diethanolamine) were determined by a similar procedure.

Determination of Pore Space

In order to eliminate any differences in the observed values due to differences in the density of the liquid used and also to enable a comparison of the uptake of different liquids by cotton, the GRV as well as imbibition values for other liquids can be converted into "pore space" using the formula

$$\text{pore space} = \frac{\text{liquid imbibition value or GRV, cc/g}}{100\rho}$$

where ρ is the actual observed density of the liquid employed in swelling and centrifugation of cellulose.

RESULTS

Figure 1 shows the effect of centrifugation time on the imbibition of glycerol by two cottons, one mature and the other immature. It can be seen that about 30 min of centrifugation time is sufficient for acquiring constant weight by two cottons and has therefore been used throughout this study.

Table II lists the values of pore space for typical raw cottons, calculated from the imbibition of three different liquids, namely, glycerol, diethanolamine, and paraffin. It can be seen that both polar liquids, glycerol and diethanolamine, give almost equal values of pore space for various cottons. Paraf-

TABLE II
Comparison of Pore Space Values Obtained from Imbibition of Glycerol, Diethanolamine, and Paraffin by Different Raw Cottons

Sr. no.	Sample particulars	Per cent mature fibers p_M	Pore space, cc/g, obtained[a] using Glycerol V_G	Diethanolamine V_D	Paraffin V_P
1	American Immature Cotton	29	0.95	0.95	0.06
2	American Upland Cotton 947	45	0.73	0.73	0.61
3	American Upland Cotton 486	60	0.59	0.56	0.40
4	American Upland Cotton 934	77	0.45	0.44	0.31
5	American Upland Cotton 805	83	0.37	0.38	0.27
6	American Upland Cotton 189	92	0.33	0.34	0.25

[a] Pore space values are calculated from a mean of two determinations of liquid imbibition values.

fin, which is a nonpolar liquid, gives consistently lower estimates for pore space. The first two liquids cause a swelling of the cotton fiber lumen, whereas the third is inert and gets physically entrapped in the fiber lumen. However, it has been found that liquid imbibition results are more reproducible when using glycerol than when using liquid paraffin.

Table III shows the results of the GRV measurements on glass wool, viscose, and Kalyan cotton which was immaturely harvested at various intervals after flowering. In the case of Kalyan, there is a clear indication about the decrease in GRV with increasing age of the boll from which the fibers are picked. Glass wool, which has a diameter about twice that of Egyptian Karnak, shows a GRV of 11%. Obviously, this amount of glycerol is held on the surface of the glass filaments. Viscose has a GRV higher than glass, which can be explained in terms of its porosity, its hydrophilic nature in comparison with glass wool which is inert to glycerol, as well as to its irregular surface. Fully mature Kalyan shows a considerably higher GRV than viscose, which can be explained only if we postulate that glycerol is retained by the fiber

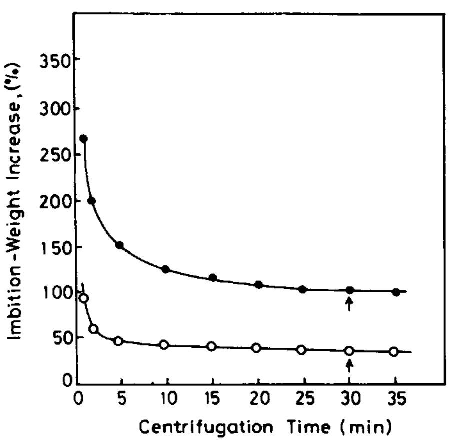

Fig. 1. Effect of centrifugation time on the retention of glycerol by cottons 875 (–O–) (p_M = 98) and 947 (–●–) (p_M = 45).

TABLE III
GRV of Some Typical Fibrous Materials

Sr. no.	Sample particulars	GRV, %
1	Kalyan cotton, harvested 40 days after flowering	177.2
2	Kalyan cotton, harvested 50 days after flowering	148.4
3	Kalyan cotton, harvested 60 days after flowering	138.0
4	Kalyan cotton, harvested 70 days after flowering	62.5
5	Ordinary viscose staple	24.0
6	Viscose cut into a fine powder	18.0
7	Glass wool, fiber diameter 25 μ	11.0

lumen, even after centrifugation. This postulate is supported by the observation that crosslinking of cottons 875 and 947 by the formaldehyde D process did not cause any change in their GRVs. Formaldehyde, being a small molecule, seals off only very fine capillaries or pores in cotton by crosslinking, without significantly affecting the larger pores where glycerol can find access. Glycerol, owing to its high viscosity, does not enter the very fine capillaries in cotton and occupies a considerable volume of the lumen and a few of the other larger pores.

The results of GRV measurements on various raw and extracted cottons are listed in Table IV and plotted in Figure 2. Correlation coefficients between GRV and p_M are linear and have magnitudes of −0.96 and −0.99 for raw and extracted cottons, respectively. It can be seen from Figure 2 that the GRV shows a decreasing linear trend with increase in the percentage of mature fibers. Furthermore, the coefficient of variation of GRV is quite small, usually in the range of 3% to 9%.

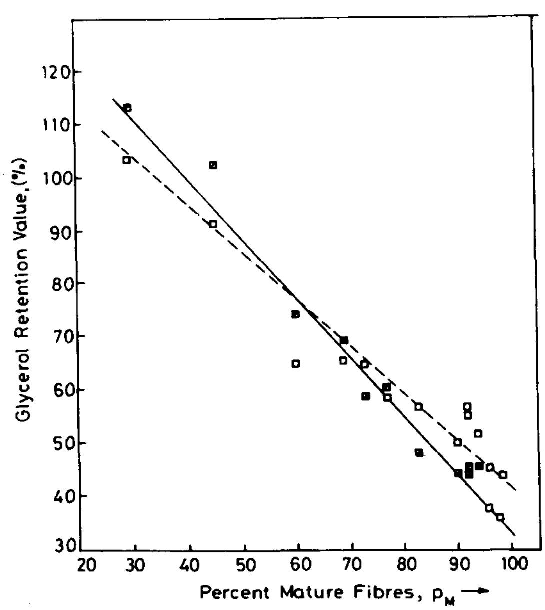

Fig. 2. Relationship between GRV and p_M for various raw (□ - - -) (r = −0.96) and extracted (☒) (r = −0.99) cottons.

However, different relationships are obtained between p_M and GRV for raw and extracted cottons (Fig. 2). For $p_M < 80$, extracted cottons have a higher GRV than raw cottons, whereas for $p_M > 80$, the reverse is the case. This can be explained as follows: cottons having $p_M < 80$ generally have appreciable wax content. For these cottons, extraction with organic solvents helps in removal of waxes and causes an increase in GRV. Highly mature cottons ($p_M > 80$), on the other hand, have a negligible amount of wax. Solvent extraction of these cottons results in some structural collapse, particularly after drying, thereby resulting in lower GRV values obtained.

DISCUSSION

Since cellulose is a xerogel, it has a marked capacity to undergo sorption and swelling when allowed to interact with different liquids. The volume of the gel, or the "pore volume" of cotton, increases when sorption is accompanied by swelling. The structure and properties of the liquid to a great extent determine the sites occupied by liquid molecules in the pore spectrum of cotton cellulose and the increase in pore volume due to its swelling action. In general, polar liquids such as water or glycerol have a high affinity for cellulose and are taken up excessively by fibers resulting in a swelling of the cell wall. The sorption of these liquids by cotton is facilitated by its porosity as well as by the hydrophilic nature of cellulose. The swelling action of liquids on cellulose causes an increase in pore volume due to two mechanisms: (i) expansion of existing pores, and (ii) reopening of some pores which had closed earlier during drying of the cotton hair from its biologically wet state. These changes in pore volume are associated with changes in the state of aggregation of the microfibrils.[18]

From the foregoing, it is evident that there is no liquid which can give a true estimate of total pore volume of cotton in the collapsed state. Nonpolar liquids are incapable of penetrating and being imbibed by the entire pore structure of cotton, whereas polar liquids cause an expansion of the pore structure to different extents. Liquid imbibition studies of cotton yield a measure of "pore volume in the swollen state," which varies from liquid to liquid. In the present study, imbibition of glycerol by cottons of different maturity has been examined. The choice of glycerol over other liquids as the liquid of imbibition is based on its following merits: (i) it has the same affinity for the hydroxyl groups of cellulose as water,[14] (ii) like water, it possesses high values of dielectric constant and surface tension, (iii) like water, it does not affect the crystal lattice of native cellulose,[15] (iv) it does not vaporize easily and has a higher boiling point than water, (v) it has a high viscosity compared to water and other liquids and as a result would occupy only the lumen and a few large pores ("large" in comparison with pores occupied by water, which have dimensions in the range of 25 Å to about 300 Å) and, what is more important, would not desorb easily, (vi) it has a relatively high density and, therefore, causes a larger weight increase upon imbibition than other liquids.

It has been discussed by Stone and Scallan[3] that the pore volume in dry cotton is likely to be less than 0.02 cc/g, although wet pulp shows a pore volume of about 0.15 cc/g. Even water retention measurements on a mature cotton[16] give a pore volume of 0.17 cc/g. Therefore, a pore volume of about

TABLE IV
Results of Determination of GRV for Various Raw and Extracted Cottons

Sr. no.	Cotton	Per cent mature fibers p_M	Glycerol retention value, %[a] Raw cotton Mean	Raw cotton C.V., %	Extracted cotton Mean	Extracted cotton C.V., %
1	American Immature Cotton	29	104	3.8	113	6.8
2	American Upland Cotton 947	45	91	7.2	102	6.2
3	American Upland Cotton 486	60	65	5.1	74	4.6
4	American Upland Cotton 940	69	65	4.9	69	9.4
5	American Upland Cotton 193	73	64	4.3	59	9.3
6	American Upland Cotton 934	77	58	5.1	60	3.0
7	American Upland Cotton 805	83	57	3.5	48	4.4
8	American Upland Cotton 859	92	56	7.9	45	7.0
9	American Upland Cotton 189	92	55	2.8	44	7.1
10	American Upland Cotton 922	94	51	4.9	43	2.5
11	American Upland Cotton 875	98	49	5.6	36	4.6
12	American Iquitos Cotton 888	96	45	13.2	38	5.7
13	Egyptian Karnak	90	50	9.1	44	5.4
14	Mercerized Egyptian Karnak	—	—	—	32	4.8

[a] Determined from six measurements on each sample.

0.3 cc/g for mature cottons (Table III) can be explained on the basis that glycerol is retained by the fiber lumen. Thus, the "pore space" calculated from GRV measurements mainly comprises the volume of the fiber lumen in its swollen state (see Appendix). This also accounts for the high magnitudes of GRV and pore space for immature cottons, because they possess a considerably wider lumen than mature cottons. Further, this assumption explains the decrease in GRV observed after slack mercerization in 24% (w/w) NaOH solution (Table IV).

The present paper serves to establish a new and reliable method of estimating fiber porosity. The estimates of pore space calculated from glycerol retention measurements have been shown to be highly correlated with the maturity of various cottons. The GRV can therefore be used as a reliable, highly reproducible estimate of the maturity of cotton fibers.

The authors wish to thank the Director, ATIRA, for his permission to present this work. This research has been financed in part by a grant made by the United States Department of Agriculture under P.L.-480. A part of this paper was presented at the 15th Joint Technological Conference of ATIRA, BTRA, and SITRA held at BTRA, Bombay on January 8th, 1974.

Appendix

Physical Significance of GRV and Pore Space

Glycerol causes a swelling of the cotton fiber lumen and is retained inside the lumen after centrifugation. Pore space, which is GRV/100ρ, can be assumed to be the volume of the lumen in the swollen state, per unit weight of fibers:

$$\text{lumen volume} = \text{GRV}/100\rho = V_G,\ \text{cc/g} \quad (1)$$

TABLE V
Calculation of Maturity Index and Area of Cross Section of (Swollen) Cotton Fibers from GRV

Sr. no.	Sample particulars	Per cent mature fibers p_M	Gravimetric fineness H, 10^{-8} g/cm	Measured perimeter p, μ	Pore space $V_G = \frac{GRV}{100\rho}$, cc/g	Wall area $0.66H$, μ^2	Swollen lumen area $V_g \cdot H$, μ^2	Total area $(V_G + 0.66)$ H, μ^2	Area of circle with perimeter p, $\mu 2$	Maturity index I
1	American Immature Cptton	29	143	53.1	0.84	94	120	214	225	0.44
2	American Upland Cotton 947	45	146	49.9	0.74	96	108	204	198	0.47
3	American Upland Cotton 486	60	162	49.1	0.52	107	85	192	192	0.56
4	American Upland Cotton 940	69	169	50.6	0.53	112	83	195	204	0.56
5	American Upland Cotton 193	73	174	48.1	0.52	115	90	205	184	0.56
6	American Upland Cotton 934	77	200	52.1	0.47	142	94	226	216	0.58
7	American Upland Cotton 805	83	207	61.2	0.46	137	96	233	298	0.59
8	American Upland Cotton 859	92	244	54.8	0.46	161	112	273	239	0.59
9	American Upland Cotton 189	92	214	50.5	0.45	141	96	237	203	0.60
10	American Upland Cotton 922	94	266	50.8	0.42	176	111	287	205	0.61
11	American Upland Cotton 875	98	236	49.8	0.39	156	93	249	197	0.63
12	American Upland Cotton 888	96	296	57.0	0.37	195	108	303	259	0.64
13	Egyptian Cotton	90	127	45.1	0.40	84	51	135	162	0.62

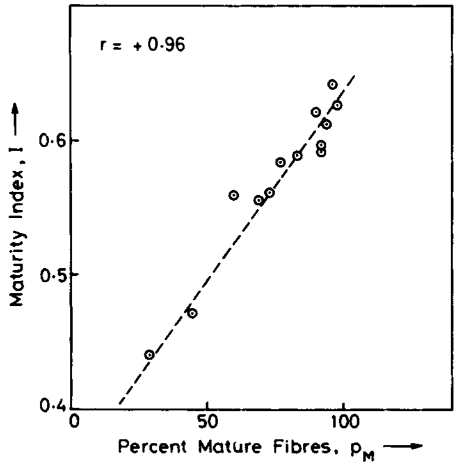

Fig. 3. Relationship between p_M and maturity index I.

If H is the gravimetric fineness, i.e., the mean fiber weight per unit length, in 10^{-8} g/cm, then

$$\text{total length of fibers/g} = \frac{1}{H}, \text{cm}/10^{-8}\text{g}. \tag{2}$$

The average area of the cross section of the fiber lumen (in the swollen state) is obtained by dividing eq. (1) by eq. (2):

$$\text{average lumen area} = V_G \times H,\ 10^{-8}\,\text{cm}^2, \text{ or } \mu^2 \tag{3}$$

where $\mu = 10^{-4}$ cm. The average area of the cross section of the cell wall is given by Lord[17] as

$$\text{average wall area} = 0.66H,\ \mu^2 \tag{4}$$

$$\therefore \text{total area of cross section} = \text{wall area} + \text{lumen area}$$

$$= (V_G + 0.66)H,\ \mu^2. \tag{5}$$

The maturity index I can be defined as

$$I = \frac{\text{wall area}}{\text{wall area} + \text{lumen area}}$$

$$= \frac{0.66}{V_G + 0.66}. \tag{6}$$

From eqs (1) and (2) it can be seen that the maturity index I is inversely related to GRV through V_G. For all cottons used in practice, $I < 1$; and in the hypothetical case when the lumen is absent, $I = 1$, indicating a completely mature cotton.

From eqs (1), (3), and (4), we obtain

$$\text{GRV} = \text{k} \times \frac{\text{average swollen lumen area}}{\text{average wall area}} \tag{7}$$

where k is a constant equal to 66ρ, ρ being the density of glycerol. Equation (7) thus explains the physical significance of GRV and the fact that it is inversely related to p_M (Fig. 2).

Table V gives the values of the wall area, lumen area, total area, and maturity index for all cottons, calculated using equations (3)–(6). For comparison with the total area, the area of a circle with perimeter p (measured on raw cotton) is also given in some cases. The agreement between the two is quite fair within the limits of experimental error. In this comparison, allowance should also be made for the fact that the total area may be larger than the area of the *uncollapsed* fiber cross section on account of swelling by glycerol. With increasing maturity of cotton, the wall area increases but the total area does not change appreciably. This is on account of the fact that glycerol swells the fiber lumen in all cottons irrespective of their maturity, so that the total area represents the area of more or less circular cross section of glycerol swollen fibers.

Since the cottons in Table V do not have very different perimeters, the total area for most cottons has a value ≈200 μ^2, which would give a value of ≈50 μ for fiber perimeter. The actually measured values of fiber perimeter listed in Table V are not very different from this.

Finally, Figure 3 gives a plot of maturity index I against p_M. The relationship between these two is linear, giving a correlation coefficient of +0.96.

References

1. P. H. Hermans, in *Colloid Science,* Vol. II, H. R. Kruyt, Ed., Elsevier, Amsterdam, 1949, Chap. XII.

2. Y. Fahmy and F. Mobarak, *Svensk Papperstidn.,* **74,** 2 (1971).

3. J. E. Stone and A. M. Scallan, in *Consolidation of the Paper Web,* Technical Section of the British Paper and Board Makers' Association, London, 1965.

4. A. K. Kulshreshtha, K. F. Patel, A. R. Patel, M. M. Patel, , and N. T. Baddi, *Cellulose Chem. Technol.,* **7,** 307 (1973).

5. A. K. Kulshreshtha, K. F. Patel, A. R. Patel, M. M. Patel, and N. T. Baddi, *Cellulose Chem. Technol.,* **7,** 343 (1973).

6. Y. Ono, *Proc. 1st Sirtec Symp.,* 157 (1969).

7. B. Maron, G. Schnitzler, M. Aubry, and M. Vautier, *Bull. Inst. Text., France,* **22,** 197 (1968).

8. N.-B. Furvik, *J. Soc. Dyers Colour.,* **74,** 29 9 (1958).

9. L. Rebenfeld, Systematic Investigation of Non-Aqueous Swelling Agents for Cotton Cellulose, Report No. ARS 72-33, U.S. Dept. of Agriculture, Washington, D.C., 1965.

10. J. Boulton and W. Armfield, *J. Text. Inst.,* **40,** T445 (1945).

11. N. B. Patil, N. E. Dweltz, and T. Radhakrishnan, *Text. Res. J.,* **32,** 460 (1962).

12. ASTM Test D-1442-70, *Annual Handbook of ASTM Standards,* American Society for Testing Materials, Philadelphia, 1971.

13. B. R. Porter and M. L. Rollins, *J. Appl. Polym. Sci.,* **16,** 217 (1972).

14. R. Mykolajewycz, E. Wellisch, R. N. Lewis, and O. J. Sweeting, *J. Appl. Polym. Sci.,* **2,** 236 (1958).

15. E. Wellisch, L. Hagan, L. Marker, and O. J. Sweeting, *J. Appl. Polym. Sci.,* **3,** 331 (1960).

16. A. K. Kulshreshtha, A. R. Patel, N. T. Baddi, and H. C. Srivastava, *J. Polym. Sci.,* in press.

17. E. Lord, *The Characteristics of Raw Cotton,* The Textile Institute, Butterworth, Manchester and London, 1961, p. 103–138.

Received July 23, 1975