# Effect of the Particle Size of Finishing Chemicals on the Color Assessment of Treated Cotton Fabrics

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**ABSTRACT:** Color change is one of the important side effects of textile treatments to consider. This article evaluates the effect of the particle size of commonly used finishing chemicals (fluorocarbon resins and dimethyloldihydroxylethylene urea reagents) on color assessment by studying instrumental analyses, and it is reported that the smaller the particle size is, the higher the surface reflectance is, and the less the color change can be achieved. On the other hand, the effect of the particle size is not significant on color assessment after abrading cycles. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2587–2594, 2007

**Key words:** crosslinking; fluoropolymers; resins

## INTRODUCTION

Textile fabrics are subjected to various treatments for required finishing effects by specific chemicals. Water/oil repellency and crease recovery are achieved through the most applied treatments, which are also used for products defined as easy-care. Because fluorocarbons are known to have an extremely low surface energy, fluorocarbon resins are the most effective treating agents for water-repellent finishes without impairing a textile's permeability to air and vapor, and considerably more groups of textiles and fiber types are finished with fluorocarbons.[1–3] As for improved crease recovery, mostly an applied approach has been used to introduce crosslinks between individual fiber chains. Crosslinking agents are usually small molecules containing several functional groups capable of reacting with some active groups in the polymer, such as hydroxyl groups in cellulose. *N*-Methylol reagents such as dimethyloldihydroxylethylene urea (DMDHEU) have long been used as durable press finishes producing crease-resistant fabrics.[2,4] The drawbacks of DMDHEU are the well-known formaldehyde problems and the drop in some mechanical properties;[5] thus, there have been efforts to achieve nonformaldehyde alternatives such as multifunctional carboxylic acids,[6–9] glutaraldehyde,[10] and polyisocyanate[1] to replace the traditional *N*-methylol reagents. Crosslinking agents are usually used along with fluorocarbons to improve the washing durability of water repellency.

When we consider the treatment of a textile object, it is important to understand the long-term effects of the treatment and, in addition, any possible side effects. The hand fabric appearance also plays a decisive role; a tendency for changes in the shade or color and yellowing due to the influence of the temperature, light, and environment are to be avoided.[3,11] Changes in the color or shade can be attributed to the structures of the agents along with the deposition process around the fibers. Finishing agents mostly form surface layers on the top of fabrics, and the particle size should designate the distribution and orientation of that film layer and linkage to the fiber. The particle size also plays a vital role in chemicals, paints, pigments, and so forth because, when the inorganic particle size is reduced, the surface area is increased; this leads to good interaction with the matrix polymer, and the highest performance is achieved.[12] When the size of the particles is reduced to a nanometer range, they can substantially alter surface properties in some typical textile finishing applications and do not blur color because they are transparent.[13] The stability/instability of an emulsion system is also very dependent on the particle size, which is dependent on the conditions under which the emulsion has been prepared. The smaller the particle size is, the more stable the emulsion is.[14]

In this study, we evaluated the effect of the particle size of fluorocarbons and DMDHEU reagents on the color assessment of fabrics after treatment. For this purpose, we used two types of commercially available fluorocarbon resins and DMDHEU reagents differing in the particle size, and cotton fabrics were impregnated with them in separate baths. The color differences were instrumentally measured and evaluated after application, repeated launderings, and abrading cycles.

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## EXPERIMENTAL

The commercially available fluorocarbon resins, which we coded F1 and F2 (both were polyoxyalkylene-containing perfluoroalkyl compounds; F1 had 8–12 wt % dipropylene glycol methacrylate and a density of 1.10 g/cm$^3$, and F2 had 8–10 wt % dipropylene glycol methacrylate and a density of 1.02 g/cm$^3$), and the DMDHEU reagents, which we coded C1 and C2 (both were glycolated DMDHEU crosslinking agents containing diethylene glycol; they had densities of 1.21 and 1.22 g/cm$^3$, respectively), were supplied by the producers (Nano-Tex LLC, Emeryville, CA, and Rudolf-Duraner, Bursa, Turkey). One hundred percent cotton knitted rib fabric (15 × 11 course/wale, 235 g/m$^2$) was employed in this study; the fabric was scoured, bleached, and dyed by reactive blue by the supplier (Yeşim Tekstil, Bursa, Turkey).

A PerkinElmer Spectrum 2000 GX Fourier transform infrared (FTIR) apparatus (Wellesley, MA) was used to analyze the spectra of the agents. The resolution for the IR spectra was 4 cm$^{-1}$, and there were four scans for each spectrum. Before the analysis, the agents were dried in an oven under a low pressure at 80°C for 24 h. The FTIR analyses of the chemicals were run between two AgBr plates.

The particle size and multimodal size distribution measurements of the chemicals were performed with a Brookhaven Instruments 90 Plus (Holtsville, NY) with a dynamic light scattering technique, which was based on simply passing a beam of light through a colloidal dispersion. When this happens, the particles or droplets scatter some of the light in all directions. When the particles are very small compared with the wavelength of the light, the intensity of the scattered light is uniform in all directions (Rayleigh scattering); for larger particles (above ca. 250 nm in diameter), the intensity is angle-dependent (Mie scattering). If the light is coherent and monochromatic, as from a laser, for example, it is possible to observe time-dependent fluctuations in the scattered intensity with a suitable detector such as a photomultiplier capable of operating in a photon-counting mode. These fluctuations arise from the fact that the particles are small enough to undergo random thermal (Brownian) motion, and the distance between them is therefore constantly varying. The constructive and destructive interference of light scattered by neighboring particles within the illuminated zone gives rise to the intensity fluctuation at the detector plane, which, as it arises from particle motion, contains information about this motion. An analysis of the time dependence of the intensity fluctuation can therefore yield the diffusion coefficient of the particles, from which, via the Stokes–Einstein equation, with knowledge of the viscosity of the medium, the hydrodynamic radius or diameter of the particles can be calculated.[15]

To determine the particle size and distribution parameters of the fluorocarbon resins, an emulsion was prepared by the dilution of the fluorocarbon resin (F1 or F2) in 1 m*M* KCl in a ratio of 1 : 10; then, a polyacrylic measuring cell of the Brookhaven 90 Plus was filled with approximately 4 mL of the emulsion, and it was located in the measuring cuvette of the instrument without shaking or mixing to get a laser beam to pass through it. The same procedure was carried for the DMDHEU reagents (C1 and C2), but they were diluted in distilled water in the same ratio. The instrument applied a dynamic light scattering technique (see the appendix);[16] the duration of the measurement was around 5 min for fluorocarbon resins and 9 min for DMDHEU reagents, and it was repeated four times for each emulsion. The wavelength of the laser light was 670 nm. The size distributions were determined at a scattering angle of the laser beam of 90°C, and the measurements were carried out at room temperature (25°C).

For the color assessments, fabric samples were padded to about 80% wet pickup with aqueous solutions comprising 40 g/L chemical (fluorocarbon resin or DMDHEU), then dried at 130°C for 5 min, and subsequently cured at 170°C for 1 min in the laboratory to complete the condensation of the chemical with the fiber. The color coordinates of the control (dyed but not treated) and treated samples were measured on a Macbeth MS 2020+ reflectance spectrophotometer

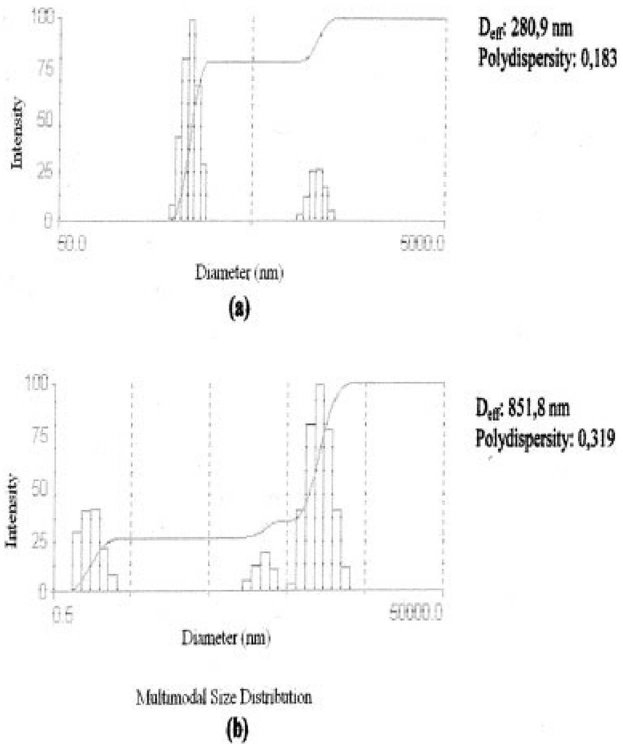

**Figure 1** Multimodal size distribution of DMDHEU reagents (a) C1 and (b) C2 and their $D_{\mathrm{eff}}$ values by intensity.

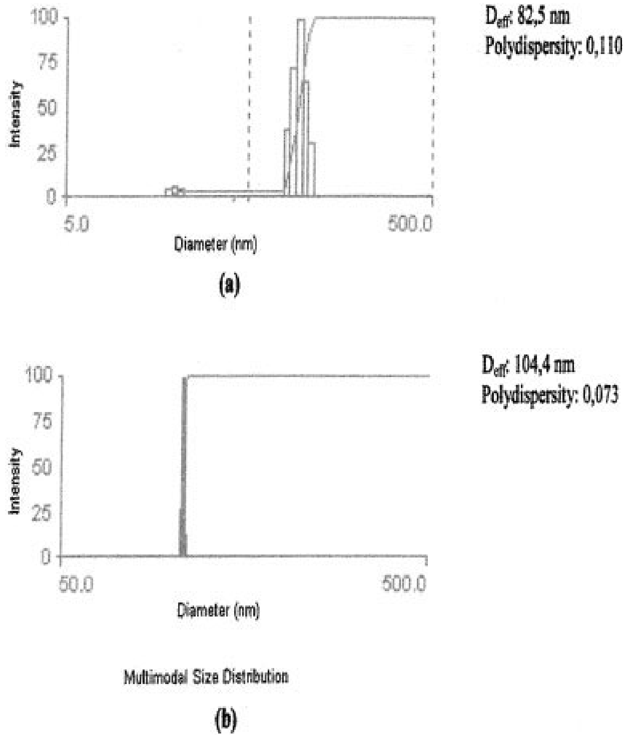

**Figure 2** Multimodal size distribution of fluorocarbon resins (a) F1 and (b) F2 and their $D_{eff}$ values by intensity.

coupled to a personal computer under a $D65/10^0$ illuminant according to AATCC 173. Four reflectance measurements were made on each sample; the samples were rotated 90° before each measurement, and the averages of the reflectance values (%) at wavelengths between 400 and 700 nm were recorded. Color differences according to the CIELAB (1976) equation were also obtained from color measuring software and reported as $\Delta E$ (or DE); the control sample was taken as the standards, and the treated fabrics were taken as the trials, when the color differences were calculated. This procedure was repeated after 5 and 10 repeated home launderings carried out at 40°C as described in the AATCC standard ''Standardization of Home Laundry Test Conditions''. The abrading cycles of the treated and control fabric samples were performed on a Nu-Martindale abrasion tester (Halifax, UK) according to ASTM D 4966 with four different abrasion cycles (2500, 5000, 7500, and 10,000). The reflectance measurements were taken for the samples after abrasion with each abrasion cycle; three abraded samples were measured for each sample (control and treated), and the averages of three measurements were reported as the color differences.

## RESULTS AND DISCUSSION

### Particle size measurements

Figures 1 and 2 show the results of the effective diameter ($D_{eff}$) of the chemicals. $D_{eff}$ is the diameter that a sphere would have to diffuse at the same rate as the particle being measured. It can also be called the *equivalent sphere diameter*. If the system is polydisperse, $D_{eff}$ is an average diameter, and if weighted by the intensity, it is an averaged intensity of scattered light by each particle. The most important pieces of information obtained in multimodal size distribution analysis are the positions of the peaks and ratio of their areas, but not their widths. Unfortunately, it is difficult to determine the particle concentration with a dynamic light scattering technique, but the relative changes can be well monitored.[14] Some details about the instrument software, used for calculations of the diameter and multimodal size distribution from the scattered laser, are given in the appendix.[16]

$D_{eff}$ may result from one or more populations of the particles present in the emulsions. From the multimodal size distribution, it appears that in the investigated DMDHEU reagents (C1 and C2), there was more than one remarkable population of particles, and only one was large (Fig. 1). The distributions of the diameters and $G(d)$ functions (see the appendix) for C1 and C2 are also given in Table I. For C1, the

**TABLE I**
**Distribution of Diameter $d$ (nm) and Function $G(d)$ for the Measured DMDHEU Reagents (C1 and C2)**

| C1 | | | | | | C2 | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *d* | *G*(*d*) | *d* | *G*(*d*) | *d* | *G*(*d*) | *d* | *G*(*d*) | *d* | *G*(*d*) | *d* | *G*(*d*) |
| 167.2 | 0 | 371.9 | 0 | 827.1 | 0 | 1.0 | 29 | 16.2 | 0 | 330.8 | 10 |
| 179.8 | 0 | 400.0 | 0 | 889.5 | 0 | 1.3 | 39 | 23.7 | 0 | 430.7 | 0 |
| 193.4 | 8 | 430.1 | 0 | 956.5 | 11 | 1.7 | 39 | 30.8 | 0 | 560.6 | 3 |
| 208.0 | 41 | 462.5 | 0 | 1028.6 | 24 | 2.2 | 20 | 40.1 | 0 | 729.8 | 38 |
| 223.6 | 80 | 497.4 | 0 | 1106.1 | 25 | 2.9 | 7 | 52.2 | 0 | 950.0 | 81 |
| 240.5 | 100 | 534.9 | 0 | 1189.5 | 16 | 3.7 | 0 | 68.0 | 0 | 1236.7 | 100 |
| 258.6 | 67 | 575.2 | 0 | 1279.1 | 4 | 4.9 | 0 | 88.5 | 0 | 1609.8 | 78 |
| 278.1 | 27 | 618.5 | 0 | 1375.5 | 0 | 6.3 | 0 | 115.2 | 0 | 2095.6 | 39 |
| 299.1 | 0 | 665.1 | 0 | 1479.2 | 10 | 8.2 | 0 | 150.0 | 4 | 2728.0 | 10 |
| 321.6 | 0 | 715.3 | 0 | 1590.7 | 0 | 10.7 | 0 | 195.2 | 12 | 3551.1 | 0 |
| 345.9 | 0 | 769.2 | 0 | 1710.6 | 0 | 14.0 | 0 | 254.1 | 18 | 4622.7 | 0 |

**TABLE II**
**Distribution of Diameter *d* (nm) and Function *G*(*d*) for the Measured Fluorocarbon Resins (F1 and F2)**

| F1 | | | | F2 | | | |
|---|---|---|---|---|---|---|---|
| *d* | *G*(*d*) | *d* | *G*(*d*) | *d* | *G*(*d*) | *d* | *G*(*d*) |
| 3.2 | 0 | 69.2 | 42 | 27.4 | 0 | 128.6 | 0 |
| 5.3 | 0 | 75.1 | 71 | 32.7 | 0 | 134.5 | 0 |
| 9.2 | 0 | 82.3 | 100 | 38.9 | 0 | 142.4 | 0 |
| 14.5 | 6 | 87.1 | 64 | 45.4 | 0 | 149.6 | 0 |
| 19.2 | 8 | 92.6 | 32 | 54.3 | 0 | 158.2 | 0 |
| 24.2 | 5 | 98.5 | 0 | 65.2 | 0 | 169.4 | 0 |
| 35.2 | 0 | 106.2 | 0 | 77.5 | 24 | 179.3 | 0 |
| 42.2 | 0 | 111.6 | 0 | 84.6 | 82 | 189.2 | 0 |
| 48.1 | 0 | 118.2 | 0 | 103.4 | 100 | 202.3 | 0 |
| 56.3 | 0 | 125.3 | 0 | 108.1 | 11 | 209.1 | 0 |
| 64.9 | 0 | 135.2 | 0 | 117.4 | 0 | 217.2 | 0 |

fluctuation around 250 nm was larger than that around 1000 nm; thus, $D_{\mathrm{eff}}$ was measured to be 280.9 nm. However, for C2, the main fluctuation was around 1250 nm, which caused a bigger $D_{\mathrm{eff}}$ value (851.8 nm). The polydispersity values for C1 and C2 were 0.183 and 0.319, respectively, and this means that the emulsion prepared with C1 had a narrower distribution.

There were fluctuations around 20 and 80 nm for the emulsion of fluorocarbon resin F1 ($D_{\mathrm{eff}}$ = 82.5 nm), with a polydispersity value of 0.110. However, in the emulsion of F2, there was only one population of particles, around 100 nm, and this caused a bigger $D_{\mathrm{eff}}$ value (104.4 nm), but the system had a very narrow distribution, with a polydispersity value of 0.073. Table II shows the distribution of the diameters and *G*(*d*) functions for the fluorocarbon resins, and Figure 2 shows the multimodal size distributions.

FTIR analyses of the chemicals are shown in Figure 3. The main difference that one can observe between the spectra of the fluorocarbon resins is the stretching peaks in the carbonyl region; there are two absorbing intensities around 1730–1690 cm$^{-1}$ in the spectrum of F1, whereas F2 gives a strong characteristic ester (C=O) peak around 1730 cm$^{-1}$. It is known that additional groups are introduced into fluorocarbon resins to achieve sufficient stability during use and to develop chemical bonds to the textile substrate,[1] and it is possible to assume that F1 comprises anhydride functional groups to react with hydroxyl in the fiber. In the fluorocarbon resin spectra, there are also characteristic peaks of O—H stretching (ca. 3300 cm$^{-1}$), aliphatic C—H stretching (ca. 2900–2850 cm$^{-1}$), and

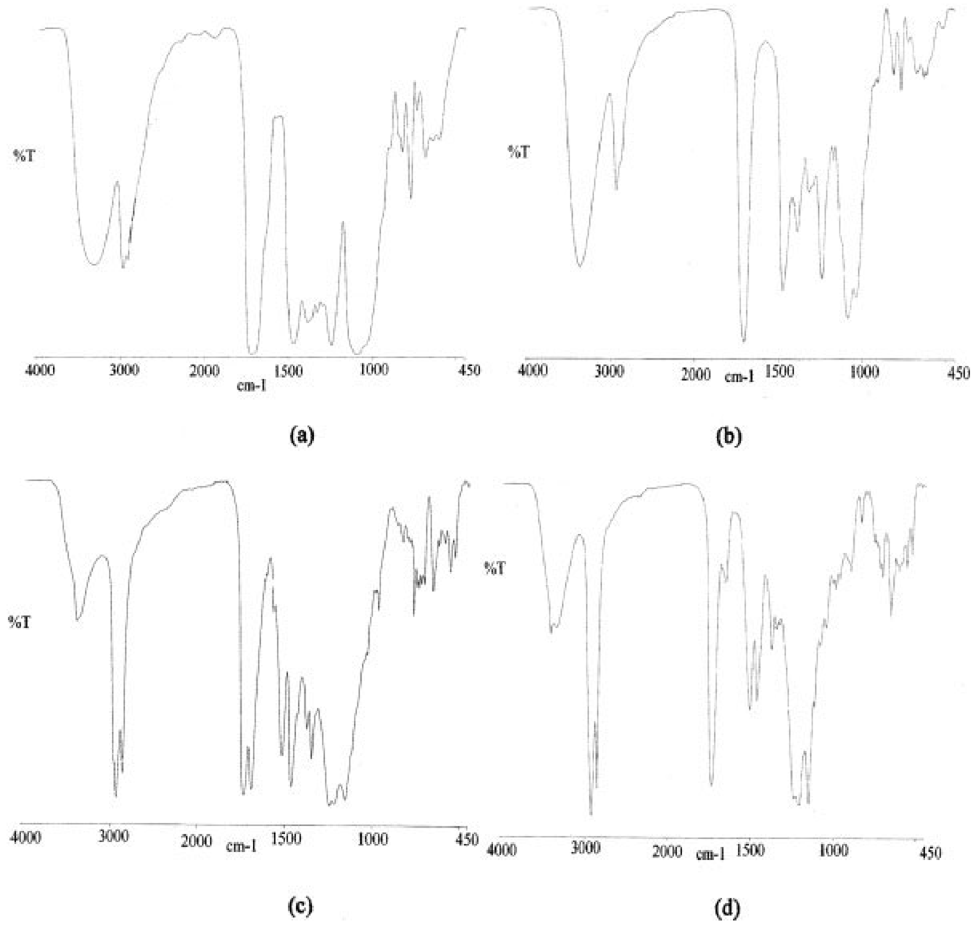

**Figure 3** FTIR spectra of DMDHEU reagents (a) C1 and (b) C2 and fluorocarbon resins (c) F1 and (d) F2 (fully dried).

**TABLE III**
**Reflectance Values of the Treated Samples and Control Sample (CS)**

| Wavelength (nm) | Reflectance (%) | | | | |
|---|---|---|---|---|---|
| | CS | F1 | F2 | C1 | C2 |
| 400 | 57.21 | 56.17 | 54.95 | 58.37 | 58.33 |
| 420 | 61.91 | 60.73 | 59.18 | 62.59 | 62.58 |
| 440 | 64.62 | 63.46 | 61.70 | 65.04 | 64.99 |
| 460 | 63.01 | 62.11 | 60.48 | 63.55 | 63.45 |
| 480 | 57.03 | 56.50 | 55.23 | 57.89 | 57.89 |
| 500 | 50.65 | 50.34 | 49.34 | 51.89 | 51.81 |
| 520 | 41.80 | 41.58 | 40.90 | 43.13 | 43.38 |
| 540 | 34.88 | 34.70 | 34.22 | 36.27 | 36.59 |
| 560 | 29.24 | 29.07 | 28.72 | 30.95 | 30.59 |
| 580 | 25.02 | 24.84 | 24.59 | 26.68 | 26.34 |
| 600 | 22.03 | 21.92 | 21.75 | 23.25 | 23.66 |
| 620 | 22.76 | 22.73 | 22.53 | 24.45 | 24.06 |
| 640 | 21.10 | 20.96 | 20.81 | 22.27 | 22.36 |
| 660 | 26.45 | 26.82 | 26.57 | 28.37 | 28.76 |
| 680 | 45.19 | 46.17 | 45.38 | 47.21 | 46.49 |
| 700 | 66.22 | 66.71 | 65.28 | 67.17 | 66.94 |

C—F stretching (ca. 1200 cm$^{-1}$) visible as certain similarities. The IR spectra for both DMDHEU reagents showed also the characteristic peaks of O—H stretching (ca. 3300 cm$^{-1}$), aliphatic C—H stretching (ca. 2940 cm$^{-1}$), C=O stretching (ca. 1700 cm$^{-1}$), and C—N stretching (ca. 1380 cm$^{-1}$). Besides, the fingerprint region between 400 and 1000 cm$^{-1}$ of the spectra exhibited similar peaks for either the fluorocarbon resins or DMDHEU reagents, and the correlation factor between the spectra of both F1 and F2 and C1 and C2 exceeded 0.90, which means that the agents differ mainly in particle size, not in chemical composition; therefore, we believe that color assessment after application could be studied to evaluate the effect of the particle size.

## Color-difference measurements

Color change is defined as a change in color of any kind, whether in hue, chroma, or lightness.[17] Color and color-difference evaluation with the CIELAB color space is based on the surface reflectance in the visible waveband (400–700 nm); any effects that change the reflectance cause a color difference. Table III shows the reflectance values of treated and control fabric samples at wavelengths of 400–700 nm. The results reveal that the fabric treatment changes the reflectance values (%) of the fabric, depending on the chemical type before the application, and samples treated with the chemicals that are smaller in particle size (F1 and C1) generally give higher reflectance values (%). For a randomly rough surface for which the distribution of surface heights is defined by a Gaussian probability distribution, the reflectance can be related by the following relation:[18]

$$R_r = R_s \exp[-(4\pi\sigma \cos i/\lambda)^2] \qquad (1)$$

where $R_s$ and $R_r$ are specular reflectances of perfectly smooth and rough surfaces, respectively; $\sigma$ is the standard deviation of the surface from its mean level as a function of the surface roughness; and $i$ and $\lambda$ are the incident angle and wavelength of light, respectively. The equation shows that surface roughness reduces the specular reflectance of a wavelength of light, particularly at a high angle of incidence. It has also been shown that the surface reflectance depends on the roughness because surface roughening increases the scattering of light and decreases surface reflectance,[19] or vice versa. When a similar relation between the reflectance values of the control (as $R_s$) and treated samples (as $R_r$) of the study is assumed, higher reflectance values (%) of the samples treated with chemicals that are smaller in particle size can be explained by a smoother reflecting surface; therefore, it is concluded that a smaller particle size allow the chemicals to have a high surface area and obtain a uniform dispersion in the textile medium to give a smoother reflecting surface.

The reflectance difference between control and treated samples was obtained by the subtraction of the reflectance (%) of the treated fabrics by that of the control, as shown in Figure 4. Samples treated with fluorocarbon resins exhibited a decrease in the reflectance (%), and this points out that those agents have a lower refractive index than the fabric itself and may

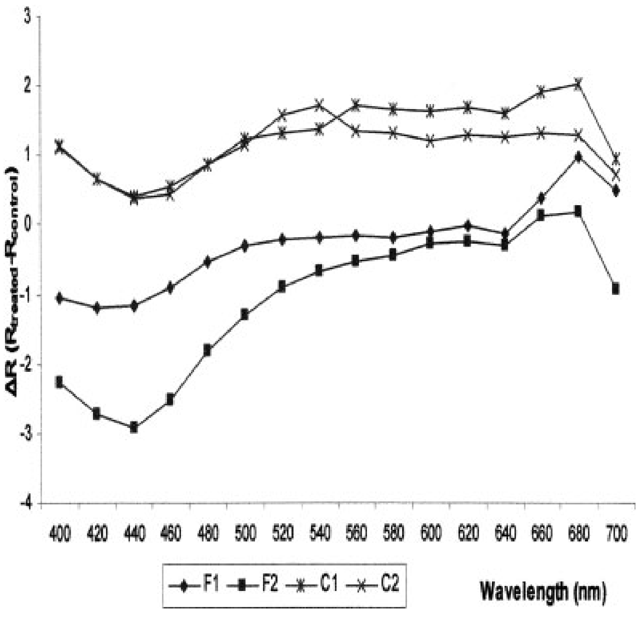

**Figure 4** Reflectance changes ($\Delta R$) of the treated fabrics. The samples were treated with fluorocarbon resin F1, fluorocarbon resin F2, DMDHEU reagent C1, or DMDHEU reagent C2.

be used for nonreflective coatings;[19] in contrast, the DMDHEU reagents were found to cause an increase. However, there was a minimum in the range of 400–440 nm for all treated samples. The pronounced decrease may be related to the height of the surface roughness, which can scatter short wavelength of the visible spectrum. From this point of view, the distribution of the height profile of a treated fabric surface may be correlated to the profile of the reflectance-difference graphs of the samples, as presented in Figure 4. Although the difference in the measured $D_{\mathrm{eff}}$ values of the tested DMDHEU reagents was much higher than that of the fluorocarbon resins, the reflectance-difference profiles were found to be similar, especially at the short wavelengths of visible light. This may be explained by the contribution of the particle size distribution of DMDHEU emulsions, the polydispersity values of which were high, suggesting that the variations in the particle size could also be important when the surface reflectance of a treated fabric is predicted. However, there should be several complicating factors influencing the reflectance difference, such as the incident angle of light, the horizontally not planar surface of the fabric,[19] and even the color coordinates of fabric. The reflectance change of the treated fabric seems to be related to the particle size and distribution of the chemical applied.

The color-difference values of treated samples after applications (0 laundry) and 5 and 10 laundries are presented in Figure 5. Figure 5 first shows that samples treated with the DMDHEU reagents exhibited higher color differences than those treated with the fluorocarbon resins, and repeated laundries increased the color difference, as expected. The chemicals with smaller particle sizes were found to produce less color difference, which was calculated from changes in the color coordinates as a function of the surface reflectance; when this result is connected with the reflectance values (%), it is concluded that the smaller the particle size is of the chemical, the less the change is in the surface morphology of the fiber and the less the effect is on the color change.

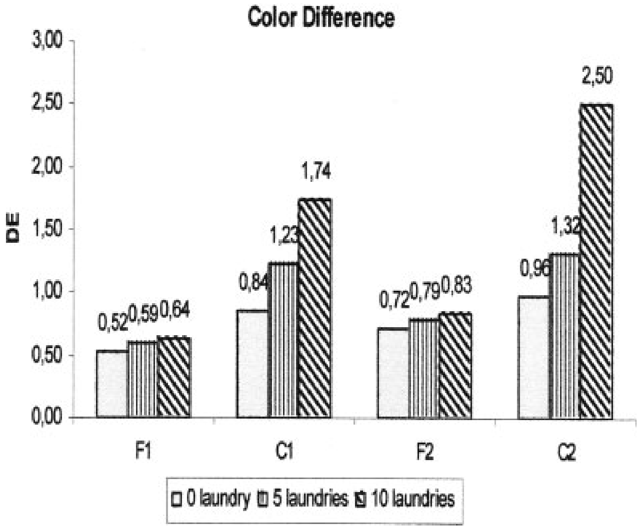

**Figure 5** Color differences of the treated fabrics. The fabrics were treated with fluorocarbon resin F1, fluorocarbon resin F2, DMDHEU reagent C1, or DMDHEU reagent C2.

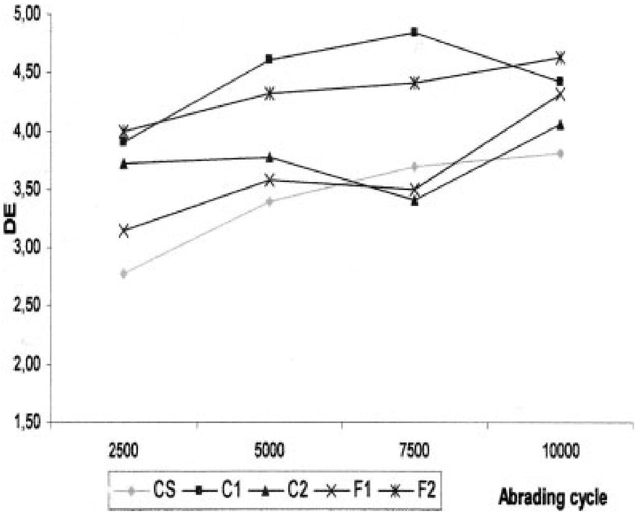

**Figure 6** Color differences of the abraded fabrics. CS was a control sample (dyed but not treated). The other fabrics were treated with fluorocarbon resin F1, fluorocarbon resin F2, DMDHEU reagent C1, or DMDHEU reagent C2.

However, when the samples were subjected to abrading to evaluate the effect of mechanical deformation at very high level on color assessment, the effect of the particle size was nonsignificant. As seen in Figure 6, the color-difference values of the abraded samples increased as the abrading cycle increased, and the treated samples exhibited generally higher color differences due to abrading. The main differences in the color-difference values were observed between 0 and 2500 cycles of abrasion. Increasing the abrasion cycles after 5000 did not change the color-difference values of the samples significantly because the rubbing motion of the Martindale instrument made the fabric sample surface more regular because of a combing effect on the fibers of the fabric surface and avoided greater color differences.[20]

## CONCLUSIONS

Color assessment after various textile treatments is an important analysis, and it is known that a change in color can be observed that depends on the finishing chemical type after the treatment. This study has shown that the particle size and distribution of the chemicals have an effect on the color assessment of treated fabrics by evaluating commercially available fluorocarbon resins and DMDHEU reagents. Fabrics treated with the chemicals that are smaller in particle size give higher reflectance values (%), and it is concluded that a smaller particle size allows the chemicals to have a high surface area and obtain a uniform dispersion in the textile medium to give a smoother reflecting surface. Also, the chemicals with a smaller particle size produce less color difference, which is calculated from changes in the color coordinates as a function of the surface reflectance. The variations in the particle size can also be important when the surface reflectance of a treated fabric is predicted. However, the effect of the particle size is nonsignificant when the treated fabrics are subjected to abrading to evaluate the effect of mechanical deformation at a very high level on color assessment; abrading motion is only designative.

## APPENDIX

Dynamic light scattering has been applied for almost 3 decades for studying dispersed systems. The software applied in the apparatus from Brookhaven Instruments gives multimodal size distributions based on the autocorrelation functions for the dispersed light of the laser beam (670 nm) along with the polydispersity and $D_{\text{eff}}$. The polydispersity is a measure of nonuniformity in the particle size distribution in the studied system. It results from the method of cumulant analysis. In this method, no assumption is needed about distribution functions.[16] The basic equation is

$$g(t) = \int G(\Gamma) e^{-\Gamma t} \partial\Gamma \tag{A.1}$$

where $g(t)$ is measured data, $t$ is the delay time,[16] and $G(\Gamma)$ is dependent on the distribution of the particles. $\Gamma$ is defined as follows:

$$\Gamma = Dq^2 \tag{A.2}$$

where $D$ is the translational diffusion coefficient, which is determined from the scattered light. Equation (A3) describes quantity $q$:

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \tag{A.3}$$

where $n$ is the refraction index of the suspending liquid, $\theta$ is the scattering angle, and $l$ is the wavelength of the laser light. Finally, $D$ is related to particle diameter $d$:

$$D = \frac{kT}{3\pi\eta d} \tag{A.4}$$

where $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $\eta$ is the suspending liquid viscosity. The exponential in eq. (A.1) is expanded in a Taylor series about the mean value and then integrated, giving a general result. Then, the logarithm of the autocorrelation function can expressed as a polynomial in delay time $t$. The $t$ powers in a Taylor series are called the *cumulants of the distribution*, and they are identical to the *moments of distributions*. It appears that practically only the first two of them are of reliable meaning. Equation (A.2) expresses the first cumulant, and the second is given by[16]

$$\mu_2 = (D^2 - D^{*2})q^2 \tag{A.5}$$

where $D^*$ is the average diffusion coefficient. Thus, $D_{\text{eff}}$ is calculated from eq. (A.4), and the $\mu_2$ moment allows the calculation of the variance of the intensity weighed distribution of the diffusion coefficient. It gives information about the width of the size distribution; more practical is the use of the relative width, that is, the reduced second moment, which is called the *polydispersity*:[16]

$$\text{Polydispersity} = \mu 2/\Gamma^2 \tag{A.6}$$

This is a dimensionless magnitude and is close to zero for an almost monodisperse sample. For a narrowly distributed sample, it is about 0.02–0.08 and becomes higher for more broadly distributed samples.

As mentioned previously, the analysis is based on the intensity of scattered light, which is proportional to the number of particles, $N$, present in the suspension that have diameter $d$ and mass $M$. Moreover, the particle shape (if not spherical) factor, $P(q,d)$, has to be taken into account [for $q$, see eq. (A.3)]. The factor is equal to 1 for particles much smaller than the wavelength (<60 nm) and if the measurements are extrapolated to a 0° angle. The diffusion coefficient distribution can be expressed as follows:

$$D = \sum NM^2 P(q,d) D \Big/ \sum NM^2 P(q,d) \tag{A.7}$$

The sums deal with all particles in the sample. Because mass $M$ (or the volume) is related to diameter $d$ in the third power, the average, called $D_{\text{eff}}$, is[16]

$$D_{\text{eff}} = \sum Nd^6 \Big/ \sum Nd^5 \tag{A.8}$$

if $P(q,d) = 1$ has been assumed. Similarly, the number-average diameter ($d_n$) can be defined:

$$d_n = \sum Nd \Big/ \sum N \tag{A.9}$$

The area-average diameter ($d_a$) can be defined:

$$d_a = \sum Nd^3 \Big/ \sum Nd^2 \tag{A.10}$$

The weight-average diameter ($d_w$) can be defined:

$$d_w = \sum Nd^4 \Big/ \sum Nd^3 \tag{A.11}$$

According to eqs. (A.8–A.11), $d_n \leq d_a \leq d_w \leq D_{\text{eff}}$, and equality occurs only for a monodisperse sample. The bigger differences between the calculated diameters are the broader distributions of the particles in the sample. However, although the values are relative, for the same sample, all the diameters can be used to characterize the sample. Moreover, the software has an option for a multimodal size distribution, which applies a nonnegatively constrained least-squares algorithm, with which the solution of eq. (A.1) is more general. It applies the approach of Grabowski and Morrison.[21] With this algorithm, the weight (or volume), surface and number fractions from the intensity fractions, and first scattering factors have to be calculated. They are obtained by the Mie method, but here, in addition to the suspending liquid refractive index, the complex refractive index of the particles has to be taken into account.

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