

# Modification of the Surface Characteristics of Cotton by the Introduction of Anionic Groups, and the Mechanism of Ion Binding<sup>1</sup>

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## ABSTRACT

The introduction of carboxymethyl, phosphate and sulfate groups into cotton cellulose considerably modifies the capacity of the cellulose to bind cationic systems. The ion-binding characteristics of these anionic derivatives have been quantitatively studied using the cationic dye methylene blue. Diffuse reflectance spectral measurements demonstrate that two types of sulfated and phosphorylated celluloses can be produced, which differ considerably in the interaction of their anionic groups with the dye. Anionic systems are, in contrast, repelled by the anionic substituents. In this way the resistance of the cotton cellulose to wet soiling can be considerably increased. The mechanism of ion binding to anionic celluloses has been examined and the information utilized to predict methods of modifying the surface characteristics of cotton cellulose.

## INTRODUCTION

One important method of modifying the surface characteristics of cotton cellulose, which has received little study, is by the introduction of anionic groups into the cellulose molecule. Nevertheless, some significant improvements in certain physical characteristics have been achieved in this way. Phosphate (1-3) and allied groupings (4) confer notably flame-proofing qualities. Carboxymethylation has been investigated as a method of stiffening cotton fabrics (5). More recently Schofield and Lawton (6) have described methods of preparing a variety of polyanions from cotton and rayon, which can be utilized to confer a bactericidal finish. Other cellulosic polyanions, generally water soluble, which have been reported are sulfomethyl (7), sulfoethyl (8), tartrate (9) and sulfate (10).

The vital property of such cellulosic polyanions, which confers upon them a unique quality, is their ability to strongly bind cations, either inorganic or organic. This behavior cannot be regarded as a trivial electrostatic attraction which any ion exerts towards a suitable counterion, since the individual monomeric units substituted with the same anionic groups show no such ion-binding characteristics. Only polyanions (or polyelectrolytes as they are also called) show this behavior (11). Considerable practical use has been made of this effect in the use of polyanions as stabilizers in the food and pharmaceutical industry (referred to here as hydrocolloids).

Whereas the mechanism of the ion-binding shown by polyanions in aqueous solution is understood (12), there is little information about solid state systems which would be applicable to anionic celluloses. It is our view that if significant progress is to be made in exploiting the ion-binding characteristics of anionic celluloses, then more information must be obtained about the factors and forces

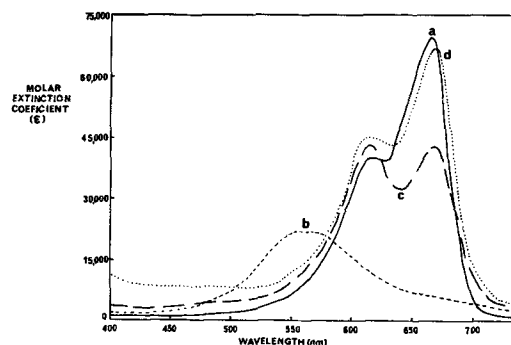


FIG. 1. Interaction of methylene blue and dextran sulfate in aqueous solution. ( $MB^+$ )  $2 \times 10^{-5}M$ . Site-dye (a) 0:1, (b) 100:1, (c) 8000:1, (d) 40,000:1.

which control such interactions. Therefore, we have selected a model organic counterion, the cationic dye methylene blue, and shall describe a spectral study of the interaction of this cation with sulfated, phosphorylated and carboxymethylated cellulose. The information obtained is relevant to other more practical ionic systems, e.g., water borne soils which are negatively charged. Indeed, we shall demonstrate that increasing the surface charge of the substrate and modifying the nature of the anionic site increases its resistance to the deposition of wet soil and hence, improves the washing characteristics.

## SPECTRAL ASPECTS OF CATIONIC DYE BINDING

Cotton cellulose invariably contains small numbers of carboxyl groups which increase considerably during bleaching (oxycellulose). Interaction of methylene blue with such groups is the basis of the standard method for the carboxyl content of cotton cellulose (13,14). X-ray studies reveal that the x-ray diagram of crystalline methylene blue is superimposed on that of the oxycellulose (15,16). However, only Gavrilov and Ermolenko (17) and Patel (18) have noted that spectral changes accompany such interactions in the solid state. Spectral shifts which accompany the interaction of polyanions and cationic dyes in solution (metachromasia) are well known and are the basis of a wide range of histological methods for identifying polyanions in biological systems, particularly in tissue sections (19). This behavior is illustrated in Figure 1 for the interaction of methylene blue with dextran sulfate. Curve a shows the main absorption band (665 nm) of methylene blue ( $\alpha$ - or M-band) which is due to monomeric dye molecules (or ions) and the shoulder (615 nm) due to dimers ( $\beta$ - or D-band). Addition of the polyanion leads to a decrease in the intensity of the  $\alpha$ - and  $\beta$ -bands and the appearance of a new (metachromatic) band ( $\gamma$ - or H-band) at shorter (hypsochromic) wavelength (curve b), which is also hypochromic to the  $\alpha$ -band. Addition of excess polyanion causes the

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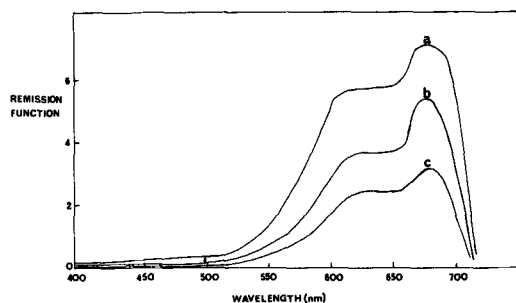


FIG. 2. Solid state absorption spectra of untreated cotton cellulose yarn dyed with methylene blue: mM dye/100 g cotton (a) 0.75, (b) 0.56, (c) 0.28; sites-dye (a) 0.94, (b) 1.25, (c) 2.54.

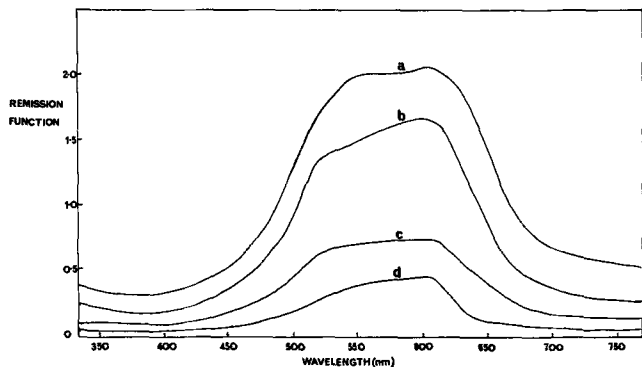


FIG. 3. Solid state absorption spectra of methylene blue-magnesium oxide mixtures: Mole fraction dye (a)  $1.25 \times 10^{-3}$ , (b)  $0.84 \times 10^{-3}$ , (c)  $0.63 \times 10^{-3}$ , (d)  $1.25 \times 10^{-4}$ .

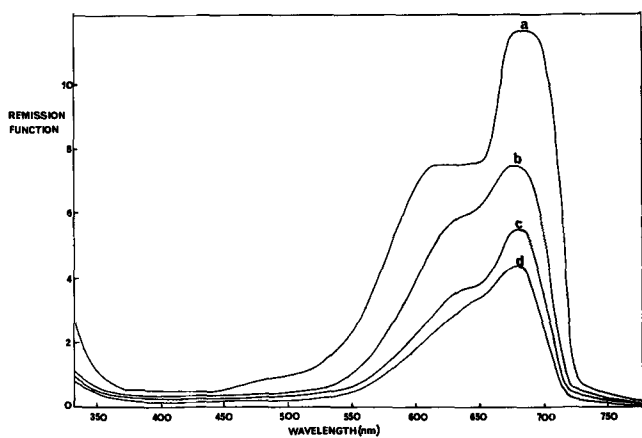


FIG. 4. Solid state absorption spectra of cellulose phosphate-methylene blue complexes: mM dye/100 g (a) 0.50, (b) 0.25, (c) 0.16, (d) 0.12; sites-dye (a) 2000, (b) 4000, (c) 6000, (d) 8000.

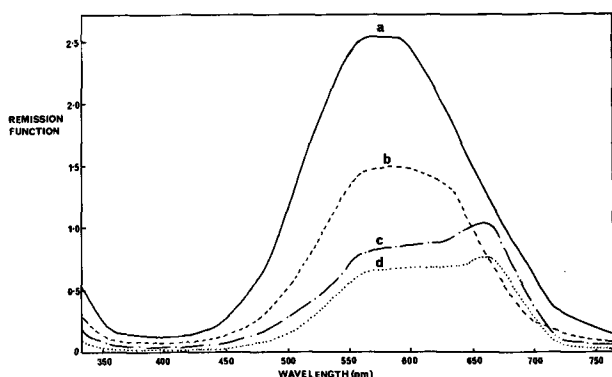


FIG. 5. Solid state absorption spectra of potassium metaphosphate-methylene blue complexes: mM dye/100 g (a) 0.40, (b) 0.20, (c) 0.12, (d) 0.09; sites-dye (a) 2000, (b) 4000, (c) 6000, (d) 8000.

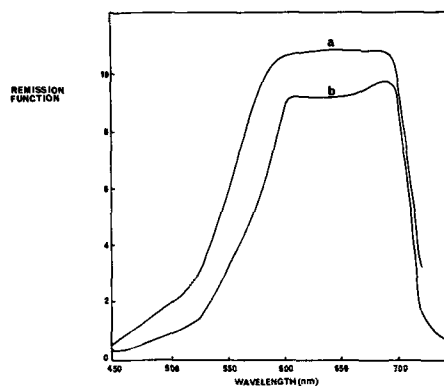


FIG. 6. Solid state absorption spectra of carboxymethyl cellulose-methylene blue complexes: mM dye/100 g (a) 0.89, (b) 0.41; sites-dye (a) 14, (b) 76.

spectrum to gradually revert to that of the monomeric dye (curve c). At very high ratios of anionic sites to dye (40,000:1), a slight bathochromic shift (to longer wavelengths) in the main band (curve d) relative to the monomeric dye absorption can be observed. On the basis of this behavior it has been suggested that the  $\gamma$ -band is due to aggregates higher than dimers. As the ratio of anionic sites to dye is increased, the probability of such aggregates forming is reduced and eventually monomeric dye bound to the polyanion results. The spectrum of such a monomeric-bound dye state approximates that of the free monomeric dye in solution, but the slight bathochromic shift and reduced extinction coefficient have been attributed to perturbation of the electron distribution in the dye because of the dye-substrate interaction (11,12,35). However, it should be pointed out that there is still considerable controversy whether dye-dye interaction or dye-site interaction is dominant in producing the hypsochromic spectral shift (11). Recent work, however, points to the former (12).

We have sought to similarly investigate the spectral changes, for cellulosic polyanions but in the solid state on which practical interest centers and not in aqueous solution. For this purpose we have developed diffuse reflectance spectral methods which will be given in detail elsewhere (20). Throughout we have used the Kubelka-Munk theory (21-23). Assuming that only diffusely reflected light is collected the relationship between the reflectance ( $r_{\infty}$ ) of the solid (measured against a suitable standard such as magnesium oxide), the absorption coefficient ( $k$ ) and the scattering coefficient ( $s$ ) is

$$f(r_{\infty}) = \frac{(1 - r_{\infty})^2}{2r_{\infty}} = \frac{k}{s}$$

Where  $f(r_{\infty})$  is the Kubelka-Munk (or remission) function. For a mixture of nonabsorbing solid and a dye

$$f(r_{\infty}) = \frac{k}{s} = \frac{2.303 \epsilon c}{s}$$

where  $\epsilon$  is the molar extinction coefficient and  $c$  the molar concentration of absorbing material. It has been shown that the scattering coefficient is constant for cellulose con-

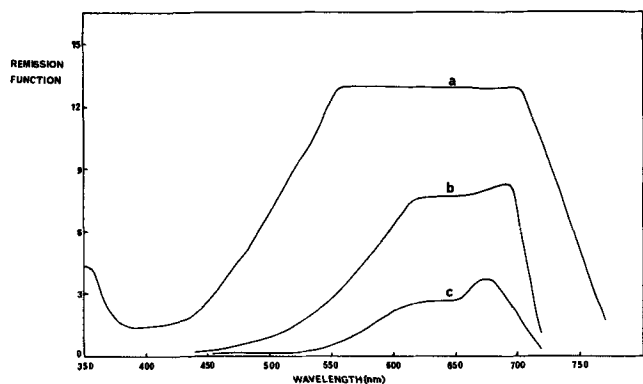


FIG. 7. Solid state absorption spectra of cellulose phosphate-methylene blue complexes: mM dye/100 g (a) 6.58, (b) 0.61, (c) 0.76; sites-dye (a) 1.1, (b) 14.7, (c) 13.3.

taining small quantities of dye (24). Thus for dyed cotton  $f(r_{\infty})$  is proportional to  $\epsilon$  and a plot of  $f(r_{\infty})$  against wavelength gives a true absorption spectrum of the dyed cellulose.

Untreated cotton yarn containing various concentrations of methylene blue ( $MB^+$ ) gave spectra shown in Figure 2. The spectra of mixtures of methylene blue ground with magnesium oxide are shown in Figure 3. Figures 4 and 5 show typical spectra of complexes of  $MB^+$  with cellulose phosphate [prepared by an aqueous method (12,25)] and potassium metaphosphate. Figure 6 shows typical spectra of carboxymethyl cellulose complexes. The behavior of cellulose phosphate samples of low D.S. (0.017-0.0059) is given in Figure 7 and cellulose sulfate in Figures 8 and 9.

Certain general features become apparent from these spectra. On untreated cotton there is a small bathochromic shift in the spectrum of the monomeric  $MB^+$  band (Fig. 2) compared with aqueous solution (Fig. 1). This behavior would be anticipated, since the spectrum is influenced by the refractive index surrounding medium (26,27). The shoulder, due to dimer, is again apparent on cotton. The spectra, however, are quite different from that of solid  $MB^+$  (Fig. 3). Here the main band is centered at 560 nm, which is more closely related to the metachromatic ( $\gamma$ -band) peak which we have previously related to aggregated dye. This conclusion receives additional support from our present comparison with the spectra of solid  $MB^+$  where intermolecular interaction between adjacent dye molecules would be at a maximum. No such evidence of aggregation is observed with cellulose phosphate prepared under aqueous conditions (Fig. 4). When the phosphate groups are demonstrably close as in potassium metaphosphate the metachromatic peak due to aggregation is again evident (Fig. 5), and the complexes are definitely violet to the naked eye. Cellulose phosphate prepared under anhydrous (1,28) conditions (Fig. 7a), although less highly substituted (D.S. 0.017) than the samples in Figure 4 (D.S. 0.41), showed a similar behavior giving a broad absorption extending to the  $\gamma$ -band near 550 nm. Cellulose sulfate prepared under aqueous conditions (6) (Fig. 8) gave a range of behavior showing the monomer  $MB^+$  band at site-dye = 26 and the band broadening as the site-dye ratio is decreased to 2.16. It should be noted that the cellulose sulfate, prepared under anhydrous conditions, with chlorosulfonic acid in pyridine also gave complexes which were violet (metachromatic) (Fig. 9).

Therefore, it can be seen that cellulose sulfates, phosphates and carboxymethyl cellulose complexes with  $MB^+$  show similar spectral characteristics when prepared under aqueous conditions. The absorption due to monomeric  $MB^+$  as well as the dimer absorption are observable. Despite the appearance of broad bands, which vary in width from sample to sample, these complexes are not truly metachro-

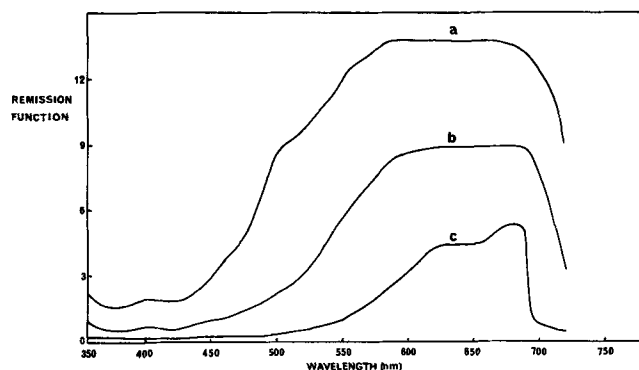


FIG. 8. Solid state absorption spectra of cellulose sulfate-methylene blue complexes: mM dye/100 g (a) 7.28, (b) 4.54, (c) 0.60; sites-dye (a) 2.16, (b) 3.4, (c) 26.

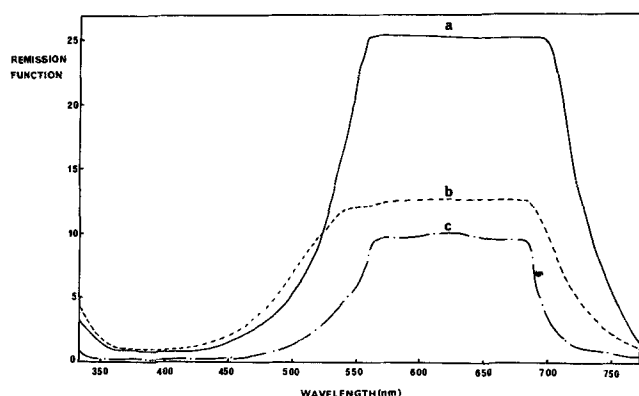


FIG. 9. Solid state absorption spectra of cellulose sulfate-methylene blue complexes: mM dye/100 g (a) 3.21, (b) 2.81, (c) 0.60; sites-dye (a) 1.3, (b) 1.5, (c) 6.8.

matic. However, when the sulfate (Fig. 9) or phosphate groups (Fig. 7a) are introduced under unhydrous conditions, even at very low D.S. ( $<0.0059$ ), the band is considerably broader and extends to the metachromatic  $\gamma$ band; the complexes consequently show a distinct purple color and can be easily distinguished from the normally nonmetachromatic blue complexes.

Data relating to the influence of the nature and density of the site is given in Table I. It can be seen that the extent of the hypsochromic shift increases in the following order: carboxymethyl < phosphate < sulfate. This is in agreement with the order of the spectral shifts found for metachromasia of polyanions in aqueous solution (29,30). The magnitude of the shift depends on the distribution of the sites and increases as the intersite distance decreases, which is also in good agreement with observations in solution (31).

The pronounced effect of the medium used for the preparation of the cellulose phosphates and sulfates can be understood on the basis of the observations of Jeffries et al. (32) that whereas 25% of the hydroxyl groups in cellulose are accessible to aqueous solutions, only 13% are accessible to nonswelling solvents. Thus on the basis of the recent fibrillar model of cellulose (32), the anionic groups would be located at fewer interfibrillar surfaces and junctions for the polyanions prepared in pyridine solution. The anionic groups, despite the lower overall D.S. could, therefore, be considerably closer and the resulting dye-dye interaction, and hence the spectral shift would be greater. Indeed, examination of two sulfated samples of similar D.S. prepared in aqueous and nonaqueous systems from cotton yarn showed that only the latter was metachromatic.

On the basis of our observations three basic types of interaction can be seen to contribute to the spectral

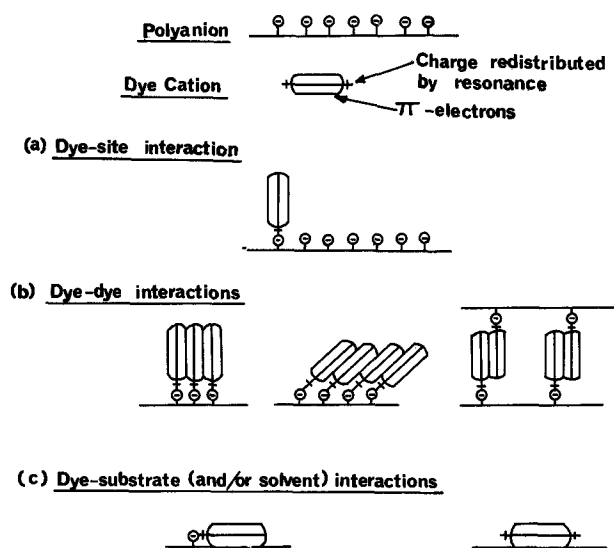


FIG. 10. Interactions between dye cations and a polyanion which contribute to spectral changes.

changes which can be observed when cellulosic polyanions interact with  $MB^+$ , namely, dye-anionic site, dye-dye and dye-substrate. These are illustrated in Figure 10. The effects illustrated in Figure 10a and b are clearly the most pronounced influences at low site-dye ratios. We have seen (Table I) that even under conditions of low dye concentration, where there is no significant dye-dye interaction, there is still an observable hypsochromic band broadening, which is considerably influenced by the nature of the site increasing carboxymethyl < phosphate < sulfate. However, when the ratio of dye-anionic sites is increase, very pronounced hypsochromic shifts occur due to enhanced dye-dye interaction. This effect is maximized in potassium metaphosphate. Due to the small distance between anionic sites here (0.37 nm) considerable dye-dye interaction is possible and metachromasia is also observable here. Sylven(33) has indicated that an intersite distance of <0.5 nm is necessary before metachromasia is possible and, in this connection, it is significant that even in our most highly substituted cellulose phosphate samples the average intersite distance is not less than 1.18 nm. As noted previously, special considerations apply to the phosphated and sulfated celluloses prepared in pyridine, such that the anionic sites could occupy more localized regions in the

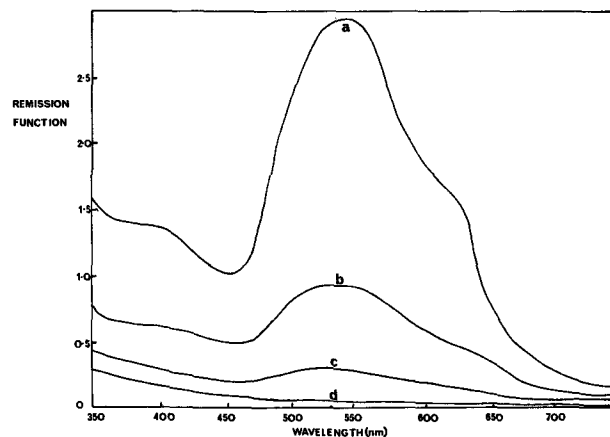


FIG. 11. Solid state absorption spectra of cotton cellulose and polyanionic celluloses after soiling: (a) carboxymethyl cellulose, (b) untreated cotton, (c) cellulose sulfate, (d) unsoiled cotton.

cellulose making dye-dye interactions, and hence metachromasia, possible. Finally, some perturbation of the dye spectrum is possible due to the presence of the cellulose substrate. Comparison of the spectrum of  $MB^+$  on cotton cellulose and in solution illustrates the bathochromic shift which is probably due to the change in the refractive index of the surrounding medium as first suggested by Kundt (34). This behavior has been considered on a more quantitative basis recently (26,27).

The ion pair hypothesis of metachromasia (35-37) (Figure 10a) has been presented in conflict to the dye aggregation hypothesis (38-40), although it is clearly apparent that there is some merit in each point of view (11). Our results indicate that each type of interaction shown in Figure 10 could contribute to the spectral change, but, as we have previously demonstrated for polyanions in aqueous solution (12,30), the appearance of the metachromatic  $\gamma$ -band is almost certainly dependent on significant dye-dye interaction. From our solid state studies we can now add that dye-site interactions can nevertheless exert an influence on the spectral characteristics of the dye.

#### INTERACTION OF CELLULOSIC POLYANIONS WITH SOIL

Several methods are available for testing the antiredeposition properties of textiles (41-43). Although several complex soil mixtures have been proposed, it has been established that a simple soil model which is negatively charged will serve to assess either the antiredeposition

TABLE I

Influence of Nature of Anionic Site and Site Density on Metachromasia

Anionic site	Distribution, glucose units/site	mM Dye/ 100 g	Sites-dye	Absorption band, nm	
				Width	Center
Carboxymethyl	16.7	0.47	75.5	690-700	695
	16.7	2.14	16.6	610-697	653
	48.5	0.89	14.2	620-690	655
Phosphate	170	0.60	12.0	615-688	652
	170	6.58	1.10	556-700	628
	224	0.60	9.1	611-684	646
	224	5.48	1.0	559-703	631
Sulfate	150	0.60	6.80	588-687	638
	150	3.21	1.27	556-696	626
	116	0.60	8.85	588-680	636
	116	5.34	1.00	526-651	590
	11.5	0.60	85.3	575-633	603
	11.5	5.00	10.2	500-664	582

TABLE II

## Wet Soiling Properties of Cellulose Polyanions

Polyanion	Soil resistance index <sup>a</sup>	Anionic Sites mM/100 g
Cellulose sulfate	+ 41	39.9 <sup>b</sup>
	+ 29	34.0
	+ 16	51.2 <sup>c</sup>
	+ 10	30.4 <sup>b</sup>
	+ 5	15.7
Cellulose phosphate	+ 31	5.4 <sup>b</sup>
	+ 21	7.2 <sup>b</sup>
	- 7	59.4
	- 10	90.5
	- 14	10.1
Carboxymethyl cellulose	- 26	9.0
	- 17	3.6
	- 27	12.6
	- 43	25.4
	- 44	30.5
Cotton, slack mercerized	- 55	57.9
	- 24	2.96
	0	0.67

$$^a\text{Soil resistance index} = \frac{R_s - R_{us}}{R_u - R_{us}} \times 100 \text{ (reflectance measured at 535 nm.)}$$

at 535 nm.

<sup>b</sup>Polyanion prepared under anhydrous conditions.

<sup>c</sup>Partially soluble in water.

properties of a detergent or the soil resistance of a surface (J.B. Lawton, unpublished work). To this end an aqueous suspension of the vat dye, Caledon Printing Purple 4RS, can be successfully used to compare the wet soiling properties of various substrates (44). The cellulosic polyanions were immersed in an aqueous suspension of dye (5 g/liter) for 10 min at 60 C with stirring and then rinsed in deionized water (3 x 200 ml). The degree of soiling can then be assessed by measuring the diffuse reflectance spectra of the soiled cellulosic polyanions.

Figure 11 shows typical plots of  $f(r_{\infty})$  against wavelength for untreated cotton, cellulose sulfate and carboxymethyl cellulose, compared with unsoiled cotton. The soil resistance may be expressed as follows:

$$\text{Soil resistance index} = \frac{R_s - R_{us}}{R_u - R_{us}} \times 100$$

where  $R_s$  is the reflectance of soiled polyanionic cotton;  $R_{us}$  is the reflectance of soiled untreated cotton;  $R_u$  is the reflectance of unsoiled untreated cotton. For the perfect material the index would have a value of 100, when  $R_s$  is equal to  $R_u$ . Untreated cotton has an index value of 0 ( $R_s = R_{us}$ ). Negative values indicate that polyanion picks up more soil than untreated cotton. Table II shows a summary of the results obtained for a variety of cellulosic polyanions.

Sodium carboxymethyl cellulose has been used for a number of years to reduce wet soiling during laundering. The results in Table II show that the carboxymethyl celluloses soil worse than untreated cotton. The method of preparation involved treating cotton in a slack condition with sodium monochloroacetate and a concentrated solution of sodium hydroxide. In effect, therefore, cotton was "slack mercerized" during the reaction, and Table II further shows that slack mercerized cotton soiled badly. Thus the poor soiling properties of these yarns is probably caused by soil being mechanically trapped in the highly twisted structure of the yarn.

The cellulose phosphates prepared under anhydrous conditions show better soil resistance than those prepared from aqueous solution. All the phosphates tend to show increased soil resistance as the degree of substitution is increased.

All the cellulose sulfates resist wet soiling better than the untreated cotton and one of the samples prepared in anhydrous conditions is particularly good. Visually, the yarns with a soil resistance index greater than 20 appear clean.

It is significant that the factors which influence cationic dye binding govern also the resistance towards anionic soil. In this way, therefore, cottons can be tailored to resist wet soiling. In each instance the nature and distribution of anionic sites are the critical factors.

## ACKNOWLEDGMENTS

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