The Absorption of Direct Dyes by Crosslinked Cellulose. II. Rate of Dyeing and Diffusivity*

E. CHIANAKWALAM IBE** and EMERY I. VALKO,† *Fibers and Polymers Laboratory, Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

Synopsis

The effect of crosslinking in the dry state on the rate of dyeing of cellophane with two direct dyes, Chrysophenine G and Chlorazol Sky Blue FF, has been studied. Dimethylolethyleneurea and bis(hydroxyethyl) sulfone were the crosslinking agents. It was found that the rate of dyeing was reduced at high degree of crosslinking by more than 90%, whereas the amount of dye absorbed at equilibrium was reduced by only 40%. It was concluded that the major factor in the practical un-dyeability of the crosslinked cellulose fibers in commerce is the reduction of the rate of dyeing rather than that of the absorption at final equilibrium. The average diffusivities of the dyes in the cellulose film were calculated from the rate data. The diffusion coefficients as functions of the dye concentration in the films were estimated from the diffusivity values. The two models of swollen cellulose, the pore model and the gel model, were applied to explain the effect of crosslinking on the diffusion coefficients. The pore model offers a satisfactory explanation by assuming that crosslinking reduces the average pore diameter and therefore increases the drag and also the tortuosity. The gel model offers an equally satisfactory explanation by assuming that crosslinking reduces the free volume by increasing the rigidity and concentration of the cellulose chains in the cellulose gel.

INTRODUCTION

In order to understand the effect of crosslinking on the dyeing behavior of cellulosic fibers, we need to know both the ultimate distribution equilibrium of the dye between bath and fiber and the rate at which this absorption equilibrium is approached. Using cellophane film as a model for cellulosic fibers, we reported in the first paper of this series[1] on the absorption equilibrium of these films crosslinked to various degrees with two direct dyes, Chrysophenine G and Chlorazol Sky Blue FF. The crosslinking was imparted by reacting the cellulose with dimethylolethyleneurea (DMEU) or with bis(hydroxyethyl) sulfone (BHES) by the pad-dry-cure method. The present paper reports on the rate at which the dye was absorbed by the films from the dye bath. As has been frequently done in the treatment of the kinetics of dyeing, the diffusivities of the dyes in the swollen polymer were calculated from these results.

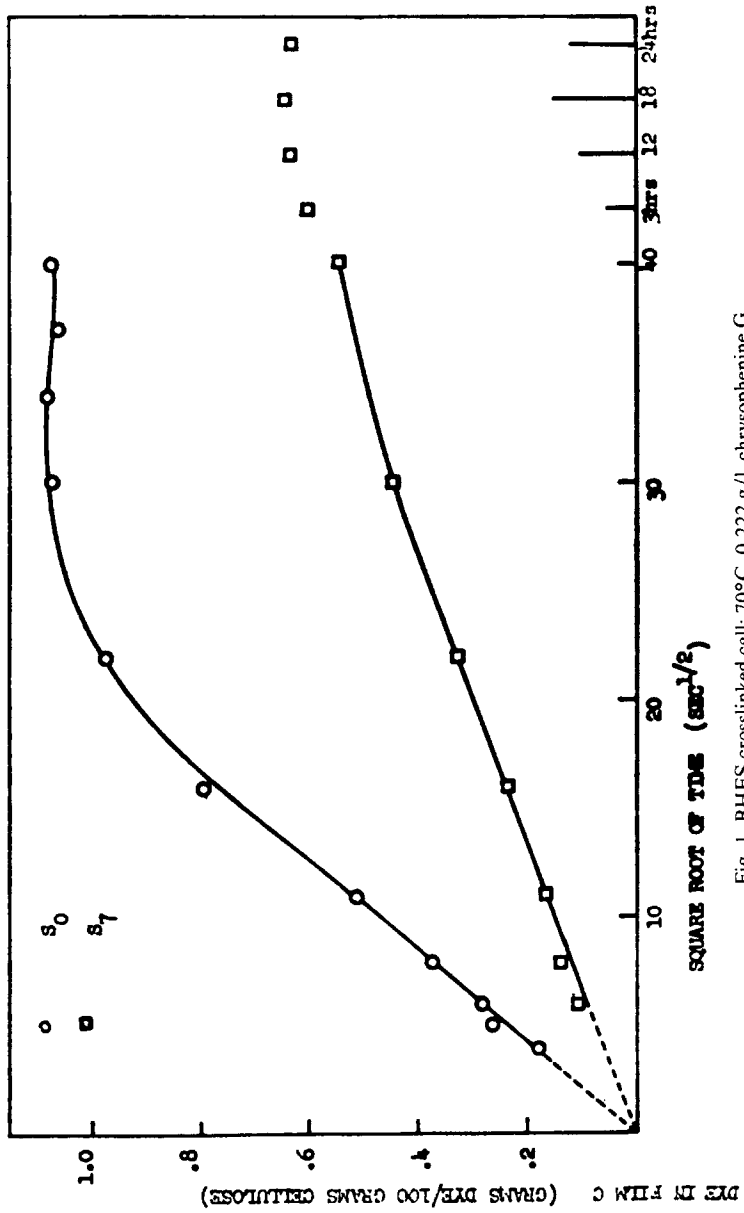Several models of the swollen polymer structure were proposed in the past for

---

Fig. 1   BHES crosslinked cell: 70°C, 0.222 g/l. chrysophenine G.
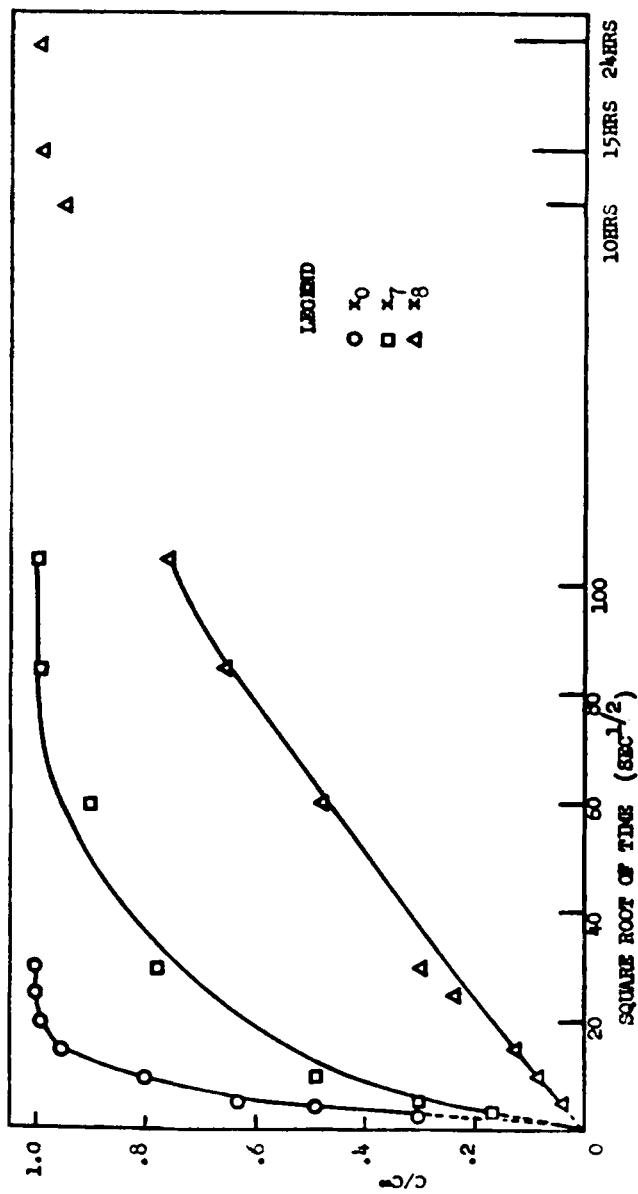
Fig. 2 DME(: crosslinked cell: 100°C, 0.196 g/l. chrysophenine G.

the purpose of explaining observed diffusivities of the dyes in the polymers.   The
effect of crosslinking on the diffusivity should serve us to test the usefulness of
these models.

EXPERIMENTAL

   The preceding paper gave the experimental details for the preparation of the
crosslinked cellulose samples, the determination of the degree of crosslinking,
the dyeing procedure, and the determination of the dye absorption.   In contrast
to the equilibrium determinations, the dyeing time ranged from as little as a few
seconds to no more than a few minutes.   Therefore, care was exerted to fix the
beginning and end of the dyeing period.   Prior to immersion in the dye bath, the
film samples were equilibrated with the appropriate buffer solution at the dye
bath temperature; and upon removal from the dye bath, the samples were
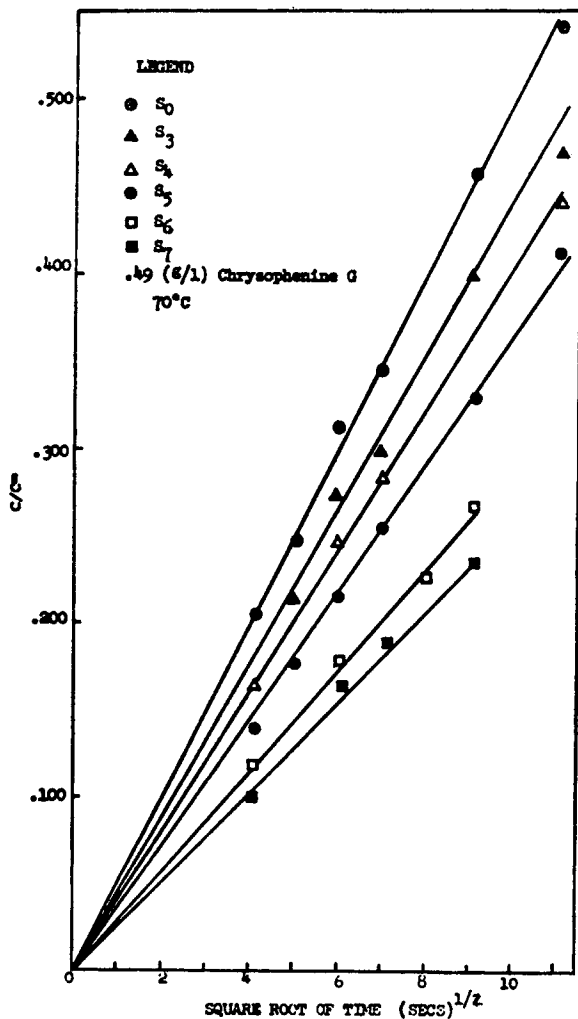

Fig. 3

plunged into ice-cold water and blotted. Vigorous stirring of the dye bath prevented the formation of a stagnant layer next to the surface of the film.

The thicknesses of the films swollen in the buffer solutions were determined with a Pratt-Whitney Supermicrometer Model B (courtesy of Van Keuren Instrument Company) at room temperature and at a pressure of 0.5 psi.

RESULTS

Rate of Dyeing

As in the determination of the equilibrium, the variables were the dye, its concentration in the bath, the bath temperature, the crosslinker, and the degree of the crosslinking. The absorption of the dye by the film as a function of the square root of the exposure to the dye bath is shown in form of graphs in Figures 1–10. The first two figures record, in addition to the short time determinations, the approach to the equilibrium, on which the results reported in the preceding paper were based. In Figure 1, the absorption is expressed in grams on the weight of the cellulose; in all other figures, it is expressed as a fraction of the equilibrium absorption.

DIFFUSIVITY OF THE DYE IN THE FILM

Ever since the pioneering work of Garvie, Griffiths, and Neale,[1a] the data on the rate of dyeing have been used to derive the value of diffusivity of the dye in the fiber or film. The McBain[1b] equation, which is based on Fick's law and the assumptions that the diffusion coefficient in the film is constant and the surface

Fig. 4

Fig. 5

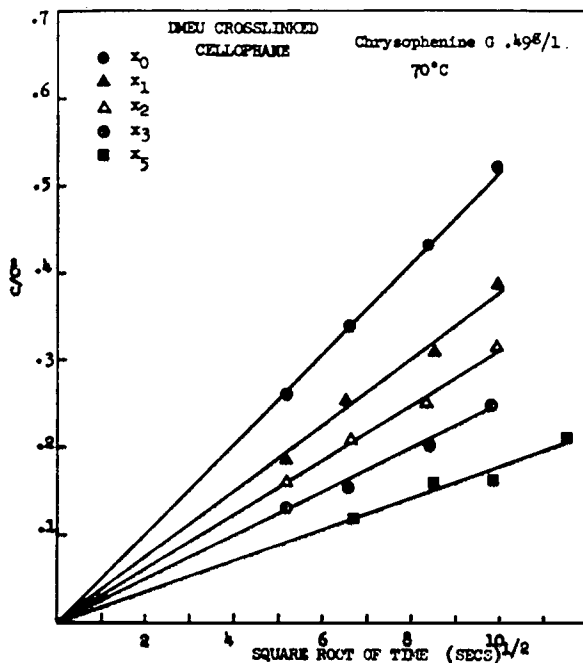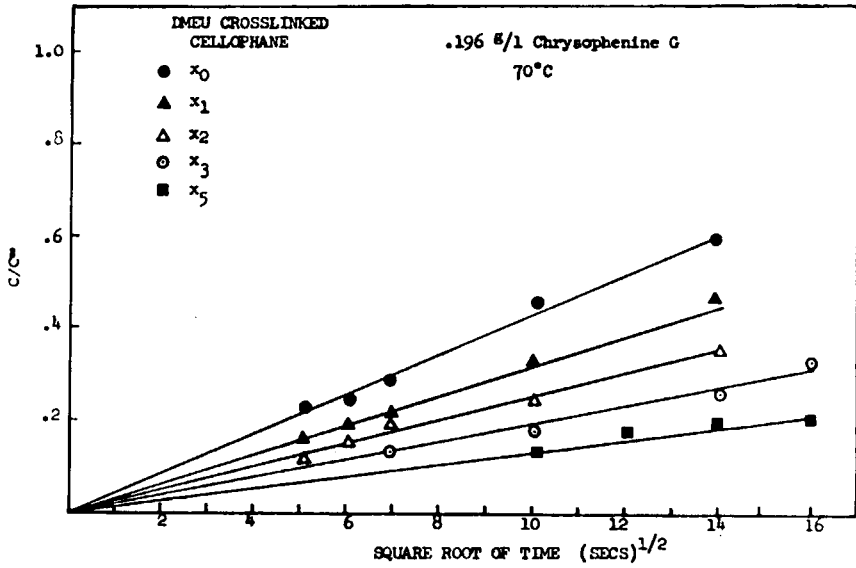layer of the film attains and maintains an instantaneous absorption equilibrium with the surrounding bath containing a constant concentration of the dye ("infinite" dye bath), serves this purpose. Accordingly,

$$C/C_\infty = 4 \left(\frac{Dt}{l^2}\right) \frac{1}{2} \left[\frac{1}{\pi^{1/2}} + 2 \sum_{n=o}^{\infty} (-1)^n i\,\mathrm{erfc}\, \frac{nl}{2(Dt)^{1/2}} \right] \qquad (1)$$

Fig. 6

DMEU CROSSLINKED CELLOPHANE   .298/1 Chrysophenine G
                                           90°C

● x_0
▲ x_1
△ x_2
◉ x_3
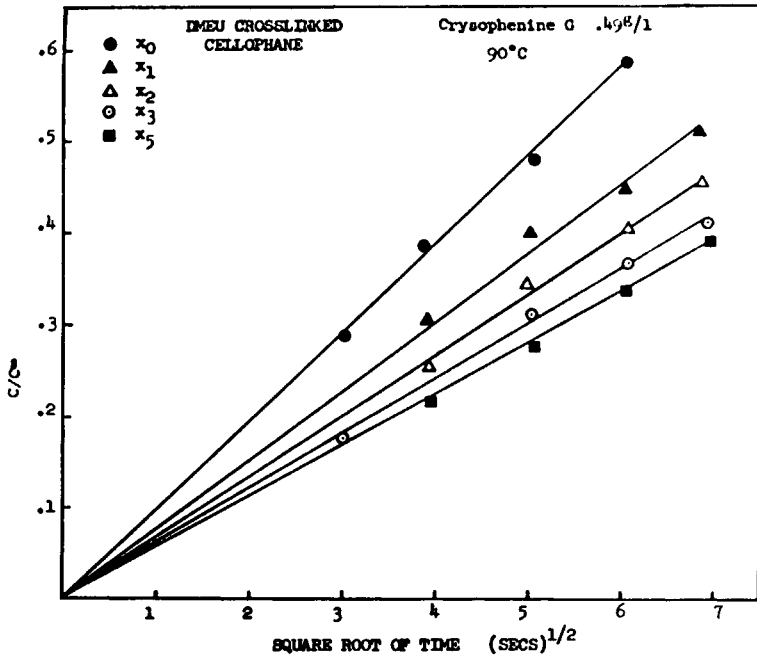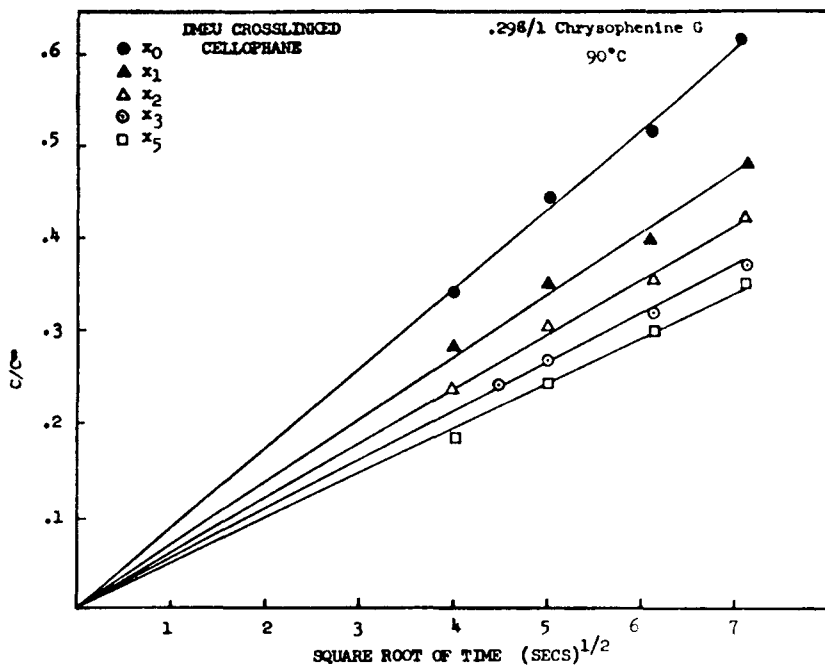□ x_5

C/C∞

SQUARE ROOT OF TIME (SECS)$^{1/2}$

Fig. 7

where D is the diffusion coefficient, C is the concentration of dye in the film at the time t, C_∞ is the equilibrium concentration of the dye in the film, and l is the thickness of the film. By neglecting the second term in the right-hand bracket of the equation, one obtains

$$\bar{D} = \frac{\pi l^2}{16t} \left(\frac{C}{C_\infty}\right)^2 \qquad (2)$$

as a reasonably good approximation for the initial period of dyeing, i.e., small t values. In order to utilize the above equation for the conversion of the rate of dyeing data into diffusivities, we must know the values of l, the thickness of the film in the dye bath.

TABLE I
Thickness of Cellophane Films Swollen in Water

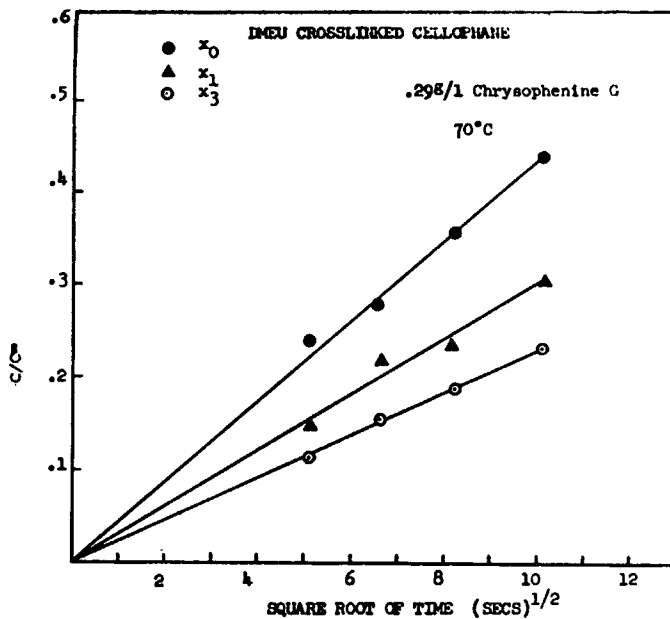| Film	M_c	Thickness, microns
S_0, X_0 (uncrosslinked)		52.1
Crosslinked with BHES		
S_3	6,700	48.0
S_4	4,400	45.7
S_5	2,900	42.9
S_6	1,640	38.1
S_7	940	35.0
Crosslinked with DMEU		
X_5	5,300	40.1
X_7	2,400	37.8
X_8	950	33.0

Fig. 8

The thickness of the films was found to be the same within experimental error whether it was swollen in water or in the dye bath, and it decreased significantly with increased degree of crosslinking. The reduction of the moisture absorption more than compensated for the volume of the added crosslinker. The results are listed in Table I.

The graphs in Figures 3–10, representing the fractional dye absorption *versus,* the square root of time, are straight lines and, therefore, eq. (2) can be applied to calculate $\bar{D}$ from their slopes. They are listed in Tables II and III. A possible source of error of several per cent is that the thickness was measured at room temperature, whereas the dyeing experiments were done at elevated temperatures.

The McBain equation is valid only if the diffusion coefficient is independent of the concentration of the dye in the polymer. In fact, however, the diffusion coefficient of direct dyes in cellulosic polymers has been found to increase with the concentration. The increase of our $\bar{D}$ values with the concentration of the dye in the bath reflects this fact. In such a case, $\bar{D}$, which we will call the "apparent diffusivity," is thought to represent some kind of mean value of the concentration-variable diffusion coefficients, but its precise meaning is uncertain. In any case, $\bar{D}$ can be used to characterize the rate of dyeing for a given dye bath concentration by a single figure, and it serves this purpose in Tables II and III.

Crank[2] suggested that $\bar{D}$ be considered the weighted average of diffusion coefficients in accordance with eq. (3):

$$\bar{D} = 5/3 \cdot C_{\infty}^{5/3} \cdot \int_{0}^{C_{\infty}} D_{C} \cdot C^{2/3} \cdot dC \qquad (3)$$

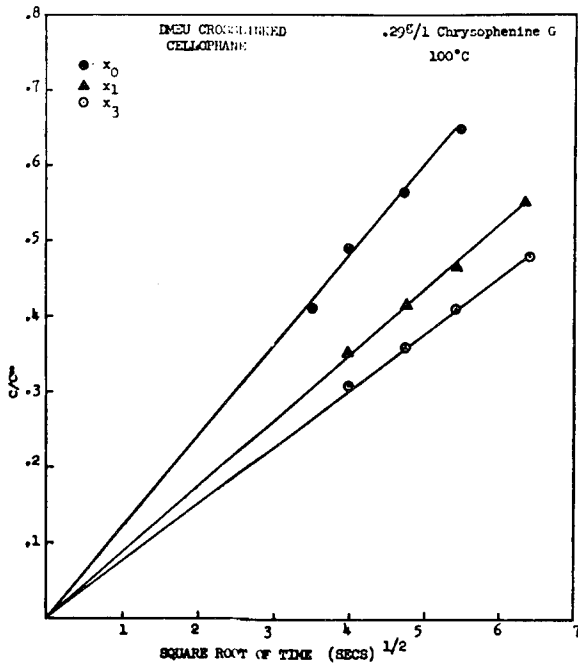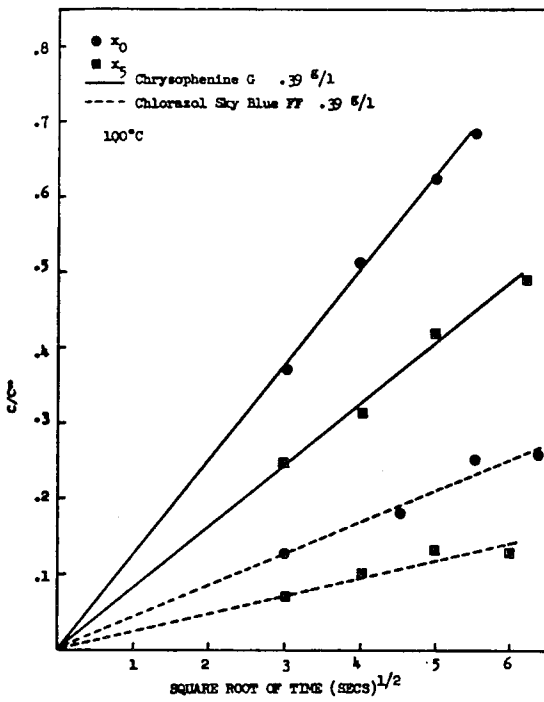where D denotes the concentration-dependent diffusion coefficient. By using

Fig. 9

Fig. 10

TABLE II
Diffusivities of Chrysophenine G in Cellophane Crosslinked with DMEU

Film	M_c	Apparent Diffusivity, at .2g dye/l.	$\bar{D} \times 10^9$, cm²/sec at .5g dye/l.	Diffusion Coefficient $D = A_x c^B$ (cm²/sec) $A \times 10^9$	B
		70° C			
X_0	00	9.75	14.1	1.45	1.1
X_1	16,900	4.67	6.59	8.96	0.79
X_2	11,000	2.66	4.20	5.41	0.87
X_3	9,000	1.29	2.95	2.903	0.96
X_5	5,300	0.56	0.67	1.202	0.91
		80° C			
X_0	00	22.3	26.6	4.52	0.3
X_1	16,900	11.0	13.2	1.99	0.94
X_2	11,000	7.74	9.06	1.67	0.07
X_3	9,000	5.55	6.82	1.00	0.80
X_5	5,300	4.15	4.04	8.77	0.98
		90° C			
X_0	00	43.1	54.2	9.86	1.2
X_1	16,900	22.9	27.0	5.40	0.89
X_2	11,000	14.6	18.2	3.81	0.98
X_3	9,000	11.1	12.6	2.84	0.99
X_5	5,300	8.83	9.40	2.60	1.02
		100° C			
X_0	00	69.00	81.6	1.60	0.67
X_1	16,900	37.8	45.6	8.3	0.61
X_2	11,000	25.0	33.1	6.1	0.62
X_3	9,000	17.5	26.3	4.6	0.59
X_5	5,300	13.0	18.6	3.6	0.64
X_7	2,400	7.86	11.0	2.29	0.64
X_8	950	0.18	0.85	1.3	0.95

the values of $\bar{D}$, determined for various concentrations of the dye in the bath and assuming that the diffusion coefficient depends on the concentration in accordance with eq. (4),

$$D = AC^B \tag{4}$$

we calculated the values for the two parameters by a computer-aided iterative method and listed them in Tables II and III.

TABLE III
Diffusivities of Chrysophenine G in Cellophane
at 70°C and 0.5 g Dye/l. Crosslinked with BHES

Film	M_c	Apparent diffusivity $\bar{D} \times 10^9$, cm²/sec
S_0	00	11.3
S_3	6,700	8.94
S_5	2,900	4.86
S_6	1,640	2.47
S_7	940	1.26

DISCUSSION

Rate of Dyeing

From the point of view of this study, the important finding is the reduction of the dyeing rate and the diffusivity brought about by crosslinking. The extent of reduction allows the conclusion that the obstacle to dyeability of crosslinked fibers observed in commercial practice is mainly due to a decrease in the rate of dyeing rather than to a reduction of the equilibrium absorption. Figure 1 shows that, at 70°C, the crosslinking has reduced the equilibrium absorption by 40%, but it increases the time needed to reach the equilibrium within experimental error from 15 min to some 5 to 10 hr. The time to accumulate 0.2% dye in the film is increased from 10 sec to 100 sec. Figure 2 shows that, at 100°C, the uncrosslinked film required only 5 sec to reach half of the equilibrium absorption, but the highly crosslinked film X_8, containing approximately 10% DMEU, required 1 hr. The intermediate degrees of crosslinking lie between these extremes in order of their content of crosslinker.

DIFFUSIVITY AND DIFFUSION COEFFICIENTS

According to eq. (2), the calculated diffusivities reflect not only the reduction of the rate of dyeing, but also the reduction of the thickness of the films by crosslinking. This is seen in Tables II, III, and IV for various dye concentrations and temperatures. In each of the series, the diffusivity decreases strongly with increasing degree of crosslinking. This must be due to the reduced diffusion coefficients. The values of the diffusion coefficients are given in the form of the two parameters of eq. (3). In each case, the parameters were calculated on the basis of only two or three diffusivity values. They must be considered rough approximations with validity limited to the medium range of dye concentrations encountered. The exponent B shows no systematic trend, but the factor A decreases at each given temperature with increasing degree of crosslinking of the polymer.

Garvie and Neal,[3] McGregor,[4] and McGregor and Peters[5] studied the diffusion of the same dyes through uncrosslinked cellophane as reported here. Although differences in the films and in the dyeing conditions preclude direct comparisons, if these differences are taken into account a general agreement of their results and ours with the uncrosslinked film can be observed not only in regard to the diffusivities, but also, within the limits mentioned above, the diffusion coefficients. We are not aware of any previous attempt to determine the rate of dyeing

TABLE IV
Diffusivities of Chlorazol Sky Blue FF in Cellophane
at 100°C and 0.5 g Dye/l. Crosslinked with DMEU

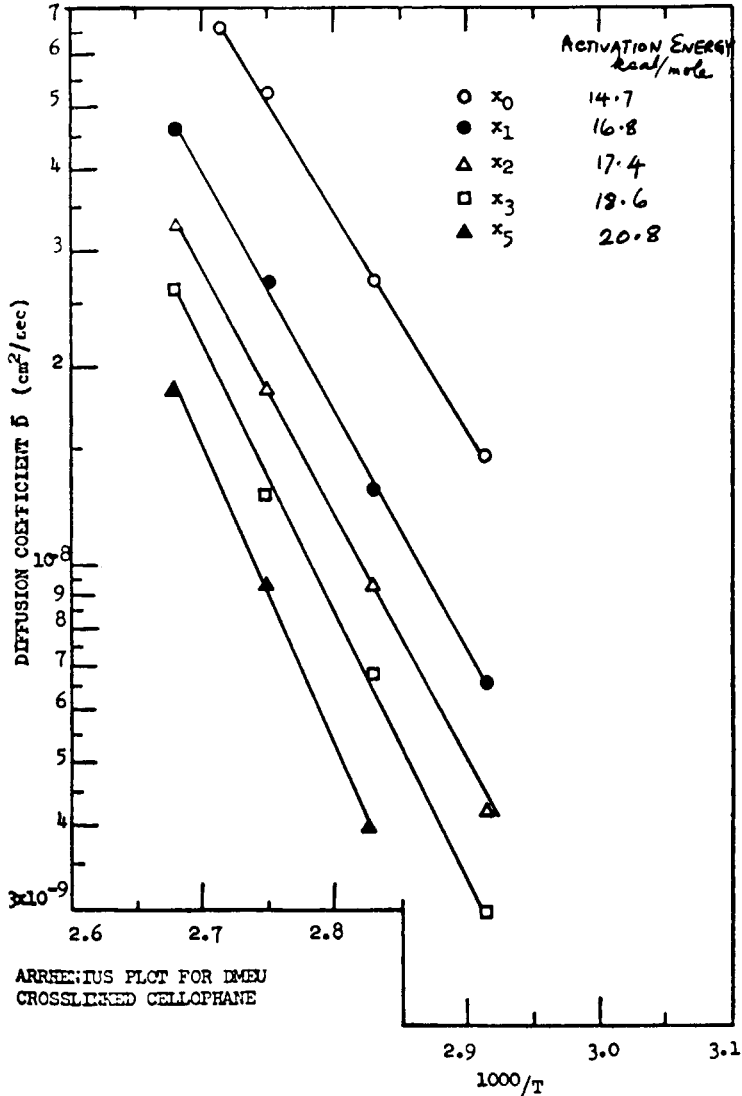| Film	M_C	Apparent diffusivity $\bar{D} \times 10^9$, cm²/sec
X_0	00	9.2
X_5	5,300	1.7
X_7	2,400	0.99
X_8	950	0.072

Fig. 11

of crosslinked cellulose or the diffusivity of dyes in it.   However, Kärrholm[6] used
used her observations of the rate of reaction of sodium periodate with regenerated
cellulose fibers to calculate the average diffusion coefficient of this reagent in
uncrosslinked fibers as well as in those crosslinked with formaldehyde by the
pad-dry-cure process.   She found that the diffusion coefficient at $23°C$ was 7.6
$\times 10^{-8}$ cm^2/sec in the uncrosslinked fiber, 3.4×10^{-8} cm^2/sec in the fiber con-
taining 0.7% fixed formaldehyde, and 1.0×10^{-8} cm^2/sec in the fiber containing
2.7% fixed formaldehyde.

ACTIVATION ENERGY OF DIFFUSION

Figure 11 represents the effect of the temperature on the diffusivity of Chry-
sophenine G in DMEU-crosslinked films in the form of Arrhenius plots.   From

TABLE V
Activation Energy of Diffusion Chrysophenine G.
Cellophane Crosslinked with DMEU

Film	M_c	Energy of activation, kcal/mole
X_0	00	14.7
X_1	16,900	16.8
X_2	11,000	17.4
X_3	9,000	18.6
X_5	5,300	20.8

the slopes of the lines, the energies of activation were calculated and listed in Table V. The value for the uncrosslinked film is of the same order of magnitude as reported for another direct dye. The significance of the increase of the energy of activation with increasing degree of crosslinking will be discussed in the context of the diffusion models proposed.

DISTANCE OF JUNCTIONS IN UNCROSSLINKED CELLULOSE

For BHES-crosslinked cellulose, the diffusivity at 70°C as a function of the degree of crosslinking can be expressed by the equation

$$\bar{D} = a \cdot \exp \left(- \frac{b}{M_c} \right) \tag{5}$$

where a and b are empirical constants and M_c is the average molecular weight of the cellulose chain between the crosslink junctions of the ladder model. This can be seen in Figure 12, in which the results are plotted on a semilogarithmic scale. Since the value of $\bar{D}$ for the uncrosslinked cellophane is known, the corresponding value of M_c can be estimated, and one obtains a value of 20,000. According to the ladder model, this represents the average molecular weight of the cellulose chains between the crystallites. We ascribe here to the crystallites the role of junctions between the cellulose to molecules analogous to that of the chemical crosslinks. In view of the fact that osmotic and viscosity determinations give an average molecular weight of regenerated cellulose in the order of several hundred thousand, the value of 20,000 between crystallites appears reasonable. More accurate values could be obtained by extrapolating from diffusivities at lower crosslink densities.

PORE MODEL AND GEL MODEL OF DIFFUSION

Two kinds of models of the fine structure of polymers have been used to explain the diffusion of dyes through them. The pore model as proposed by Morton[7] and Valko[8] in 1935 visualizes the swollen cellulose as a system of interconnected water-filled channels traversing the impenetrable regions of the polymer. As the dye diffuses through these channels, a portion of it is absorbed to the cellulose chains, which form the walls. The distribution between free and absorbed dye molecules in any portion of the channel corresponds to the macroscopic absorption equilibrium and the diffusion coefficient of the free dye molecule and is the same as its diffusion coefficient in the bulk aqueous solution. However,
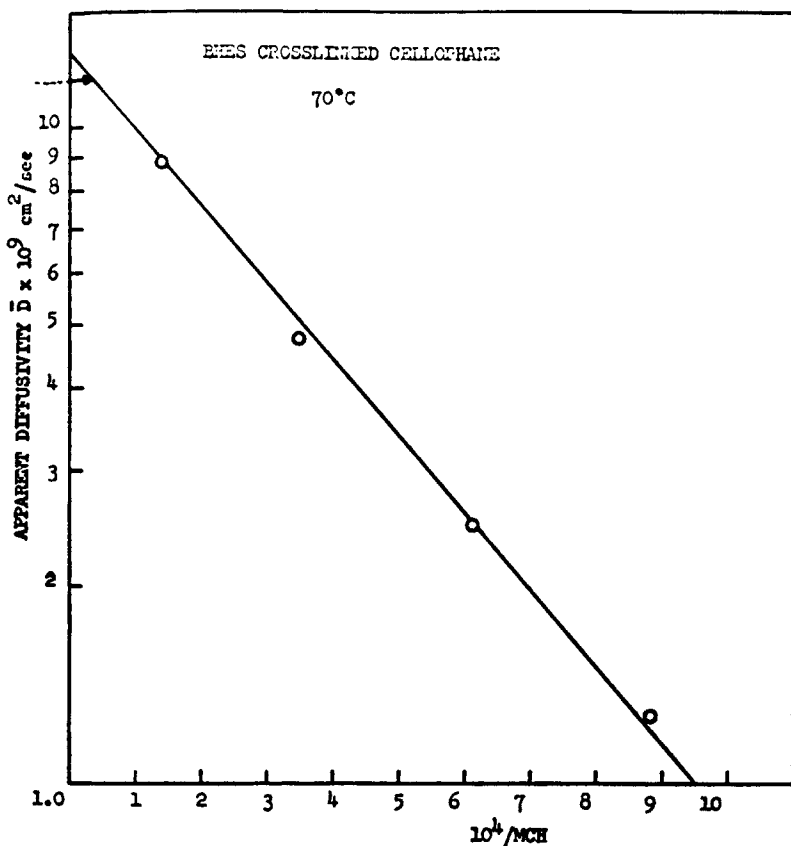
Fig. 12

due to the immobilization of the absorbed fraction of the dye, its average diffusivity in the polymer is much lower than in the solution. Crank,[2] Morton,[7] Standing, Warwicker, and Willis,[9] and Warwicker[9b] established quantitative relationships of the diffusivity of direct dyes in cellulose to their absorption equilibrium and diffusion coefficients in aqueous solution, based on this model. They found satisfactory agreement between theory and experiment. Later, Weiss[10] proposed the extension of the pore model to explain the diffusivity of dyes in hydrophobic fibers such as nylon and polyester.

In order to explain the observed dependence of the diffusivity on the degree of crosslinking in terms of the pore model, we have to consider the three variables; namely, the total volume, the tortuosity, and the width of the pores. The diffusivity in the polymer is assumed to be proportional to the porosity, that is, the relative volume of the pores. The swelling data reported in the first paper show that in the uncrosslinked film, 65% of the volume is occupied by water, that is, by the pores. At the highest degree of crosslinking (in film S_7), 50% of the volume consists of pores. This alone would account for the reduction of the diffusivity by 23%. However, the observed decrease of diffusivity is more than 90%. Experimental observations indicate an average pore diameter in cellophane of 3–4 microns, not much larger than the long axis of the dye molecules. If the di-

mension of the diffusing molecule approaches the width of the pore, a drag factor reduces the rate of diffusion.

This reduction could be considerable already in the uncrosslinked cellulose, although it was generally neglected in the quantitative application of the pore theory. During crosslinking in the dry state, a "spot welding" of the opposite walls of collapsed pores most probably leads to significant narrowing of the pores formed upon renewed swelling. The resulting drag factor could easily explain the observed reduction in diffusivity, especially if we consider that some of the pores could remain accessible to water and become inaccessible to the large dye molecules. An increase in tortuosity could be another contributory factor.

The gel model or free-volume model visualizes the accessible (amorphous) portion of the film or fiber as a quasihomogeneous mixture of the polymer molecule and those of the swelling agent and the dye. This mixture differs from a polymer solution only in the constraint on the mobility of the polymer chain caused by its merger into the crystalline regions. The diffusion of dissolved molecules, according to Eyring, is thought to proceed by jumps into adjacent holes of accommodating size. In a gel, the segmental motion of the polymer is assumed to have an important role in determining the frequency of the jumps and, therefore, the diffusion coefficient. This model has been applied with some success by Rosenbaum et al.[11] to the diffusion of dyes in hydrophobic fibers formed from thermoplastic polymers, but it was hardly ever applied to cellulosic substrates. The difficulty is caused here by the lack of knowledge of the flexibility of the "dissolved" cellulose chain. Nevertheless, it is obvious that crosslinking increases the stiffness of the chains and that the increased density of the network reduces the probability of the formation of holes large enough to accommodate the large dye molecules. At the present state of knowledge, it would be futile to attempt a quantitative assessment of these effects, but it is evident that they could amply account for the observed dependency of the diffusivity on the degree of crosslinking. The high activation energy and its increase with increasing degree of crosslinking can be directly related to the probability of hole formation.

In summary, satisfactory explanation for the observed effect of crosslinking on the rate of dyeing can be supplied by both models, and a choice between them has to be based on different considerations.

SUMMARY AND CONCLUSIONS

1. Crosslinking in the dry state reduces the rate of dyeing and the diffusivities of direct dyes in cellulose.

2. When the crosslink density reaches values similar to those in commercially crosslinked cotton fibers, the diffusivity is reduced by as much as 99%. At the same time, the equilibrium absorption of the dyes is reduced by less than 50%. The crosslinked fibers are considered in industrial practice undyeable, but the reason for this is the reduced diffusivity of the dyes rather than the reduced equilibrium absorption.

3. The pore and gel models of swollen cellulose can equally well account for the reduced diffusivity. According to the pore model, crosslinking reduces the pore diameter and therefore increases the drag and the tortuosity. According to the gel model, crosslinking reduces the free volume by increasing the concentration and rigidity of the cellulose chains.

References

1. E. C. Ibe and E. I. Valko, *J. Appl. Polym. Sci.*, **21,** 371 (1977).

1a. W. M. Garvie, L. R. Griffiths, and S. M. Neale, *Trans. Faraday Soc.,* **30,** 271 (1934).

1b. J. McBain, *Z. Phys. Chem.,* **68,** 471 (1909).

2. J. Crank, *Trans. Faraday Soc.,* **51,** 1632 (1955).

3. W. M. Garvie and S. M. Neale, *Trans. Faraday Soc.,* **34,** 335 (1938).

4. R. McGregor, *J. Soc. Dyers Colour.,* **81,** 429 (1965).

5. R. McGregor and R. H. Peters, *J. Soc. Dyers Colour.,* **60,** 2062 (1964).

6. M. Kärrholm, *J. Text. Inst.,* **47,** T453 (1956).

7. T. H. Morton, *Trans. Faraday Soc.,* **31,** 262 (1935).

8. E. I. Valko, *Trans. Faraday Soc.,* **31,** 278 (1935).

9. H. A. Standing, J. O. Warwicker, and H. F. Willis, *J. Text. Inst.,* **38,** T335 (1947).

9b. J. O. Warwicker, *J. Appl. Polym. Sci.,* **7,** 2062 (1963).

10. P. B. Weiss, Ph.D. thesis, Swiss Federal Institute of Technology (ETH), 1966.

11. S. Rosenbaum, H. I. Mahon, and O. J. Cotton, *J. Appl. Polym. Sci.,* **11,** 2041 (1967).