# *Conditions for Stability of Crosslinks in Cellulose*

## INTRODUCTION

Meaningful studies involving sorption and desorption of permeants (dyes, water, urea, etc.) by crosslinked collulose require that the network structure remain stable during the experiments. Previous experiments by Ibe[1] have shown that unless the pH of the dyebath is adjusted for their maximum stability, the crosslinks are partially lost during the long exposure to the hot dyebath required to ensure the approach to absorption equilibrium. The experiments reported here were part of a study on the absorption of direct dyes by crosslinked cellulose previously reported.[2]

## EXPERIMENTAL

### Materials

The cellophane used was made by the du Pont Company and had the trade name Dupont PD-215. DMEU (dimethylolethyleneurea) was obtained from Rohm and Haas Co. as a 50% solution RHONITE-1. BHES bis(hydroxyethyl)sulfone was obtained from J. P. Stevens and Co., Garfield, New Jersey. Crosslinking was achieved by the pad–dry–cure method using zinc nitrate as catalyst for DMEU crosslinking and potassium bicarbonate as catalyst for BHES treatment. The full experimental details have been previously reported.[2,3] White cotton cloth was first thoroughly washed by boiling in hot water to remove any sizing materials.

### Procedure

Samples of crosslinked cellulose film and cotton cloth were exposed for varying times to the blank dye bath containing 5 g/l. sodium chloride and the appropriate buffer. In some experiments 1.0 g/l. Chrysophenine G was added to the dyebath to evaluate the effect of its presence on the stability of crosslinks. Nitrogen and sulfur contents before and after the exposure were considered as measure of the presence of the DMEU and BHES crosslinks, respectively, in the cellulose samples. Nitrogen content was measured by the Kjeldahl method, and sulfur content was estimated from ash content.

## RESULTS AND DISCUSSION

The results are shown in Tables I–IV. They lead to the following conclusions:

(a) BHES crosslinks on cellulose are stable in the absence of dye at all pH values investigated and lose only 20% of their original density after 16½ hr of dyeing at pH 10.5. This is rather surprising since the ether linkage of the sulfone crosslinks is known to be destroyed at alkaline pH values.

(b) At pH 6.0, 60% of the DMEU crosslinks are lost in 2 hr in the absence of dye and 91% are lost in the presence of dye. The crosslinks are, however, stable at pH greater than 8.9.

(c) The presence of dye leads to a lowered stability of crosslinks. Since the dye anions are

TABLE I
Stability of BHES Crosslinks in Cotton[a]

| | Case 1 (blank baths, no dye) | | | | | Case 2 (dyebath containing 1.0 g/l. Chrysophenine G) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| pH of bath | 5.13 | 5.2 | 7.00 | 8.9 | 10.5 | 5.13 | 5.2 | 7.00 | 8.9 | 10.5 |
| Residence time, hr | 17 | 26 | 17 | 17 | 16½ | 17 | 27 | 17 | 17 | 16½ |
| Sulfur content, % | 0.81 | 0.80 | 0.84 | 0.84 | 0.83 | 0.81[b] | 0.82[b] | 0.82[b] | 0.73[b] | 0.63[b] |
| Decrease in sulphur content, % | 2 | 3 | (−1) | (−1) | 0 | 2 | 1 | 1 | 11 | 22 |

[a] Initial sulfur content of sample, 0.83%; temperature, 100°C; all solutions buffered.

[b] Corrected for the sulfur content of the dye.

Journal of Applied Polymer Science, Vol. 22, 3345–3346 (1978)

0021-8995/78/0022-3345$01.00

TABLE II
Stability of DMEU Crosslinks on Cotton[a]

| | Case 1 (blank baths, no dye) | | | | | | | Case 2 (dyebath containing 1.0 g/l. Chrysophenine G) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pH of bath | 5.13 | 6.00 | 6.00 | 7.00 | 8.9 | 9.2 | 10.5 | 5.13 | 6.00 | 6.00 | 7.00 | 8.9 | 9.2 | 10.5 |
| Residence time, hr | 17 | 16 | 2 | 17 | 18 | 28 | 18 | 17 | 16 | 2 | 17 | 18 | 28 | 18 |
| Nitrogen content, % | 0.25 | 0.30 | 0.48 | 0.95 | 1.15 | 1.18 | 1.20 | 0.0[b] | 0.0[b] | 0.13[b] | 0.88[b] | 1.09[b] | 1.17[b] | 1.18[b] |
| Decrease in nitrogen content, % | 81 | 75 | 60 | 20 | 2.0 | 0 | 0 | 100 | 100 | 91 | 25 | 14 | 2 | 1 |

[a] Initial nitrogen content of sample; 1.19%.
[b] Corrected for the nitrogen content of the dye.

TABLE III
Stability of BHES Crosslinks on Cellophane[a]

| Time in bath, hr | 9 | 3 | 24 | 72 |
|---|---|---|---|---|
| Corrected % S | 1.01 | 1.00 | 0.99 | 0.98 |
| Change in % S | 0 | −1 | −2 | −3 |

[a] Original sample; 1.01% sulfur; dyebath containing 1.0 g/l. Chrysophenine G.

TABLE IV
Stability of DMEU Crosslinks on Cellophane[a]

| Time in bath, hr | 0 | 4 | 25½ | 48 |
|---|---|---|---|---|
| Corrected % N | 0.88 | 0.89 | 0.87 | 0.86 |
| Change in % N | 0% | +1% | −1% | −2% |

[a] Dyebath containing 1.0 g/l. Chrysophenine G; pH 9.2; original sample; 0.88% nitrogen.

negatively charged on the cellulose surface, they will attract $H^+$ ions so that the internal pH in the fiber will decrease. The decreased internal pH may be responsible for higher loss of DMEU in the presence of the dye.

(d) The accelerated decomposition of crosslinks in the presence of dye is not limited to Chrysophenine G. A DMEU-treated cotton behaved similarly with Chlorazol Sky Blue FF.

The authors are indebted to Dr. E. I. Valko of the Massachusetts Institute of Technology, who supervised this work, and regret his untimely death on June 20, 1975.

## References

1. E. C. Ibe, S. M. Thesis, M.I.T., June 1967.
2. E. C. Ibe and E. I. Valko, *J. Appl. Polym. Sci.*, **21** 371 (1977).
3. E. C. Ibe, Sc.D. Thesis, M.I.T., June 1970.

E. C. IBE

Nigerian National Oil Corporation
P.M.B. 12650
Lagos, Nigeria

STELLA N. IBE

Faculty of Science
University of Lagos
Lagos, Nigeria

Received May 16, 1977