# NOTES

## Dyeing of Textile Fibers through Redox Polymerization. I. Dyeing Nylon-6 Fiber Using Potassium Peroxydiphosphate–Thiourea Redox System

### INTRODUCTION

Dyeing of textile fibers using different categories of dyes is an intriguing problem in the textile industry. Generally dyeing takes place by absorption of the dye molecules in voids present in the fiber matrix. Hence the process of dyeing depends on the introduction of the dye molecule into these voids. Sometimes if the structure of the dye molecule is very large and the void is very narrow, the dye molecule cannot easily enter into the fiber matrix. Redox systems<sup>1-3</sup> have been extensively used by us for the graft copolymerization of vinyl monomers onto a multitude of natural and synthetic fibers. This method of grafting involves the creation of transient free radicals on the backbone of the fiber that initiate copolymer growth on the fiber matrix. The redox system can be used for attachment of the dye molecule to various conventional fibers. This process of dyeing by utilizing the redox method involves covalent bonding between the dye and the fiber. Hence this method is extremely useful for enhancing dyeing of fibers with much higher color strength and dye fixation at relatively low temperature and low cost.

The present research program represents the use of a peroxydiphosphate-thiourea redox system for dyeing nylon-6 fiber.

#### EXPERIMENTAL

A sample of nylon-6 fiber was supplied by J. K. Synthetics, Kota, Rajsthan (India). The purification of nylon-6 and monomer was done according to our previous procedure.<sup>5</sup>

Potassium peroxydiphosphate  $(K_4P_2O_8)$  (PP) was obtained as a sample from F. M. C. Corporation (U.S.A.). Thiourea used was of AR grade. All other reagents used were of AR sample. The scored nylon sample was added to a dye bath containing dye and the redox system using a material-liquor ratio of 1 : 100. The dyeing was performed at temperatures ranging from 30 to 55°C for varying lengths of time with occasional stirring. At the end of dyeing, the dyed sample was thoroughly rinsed with cold water, soaped at 60°C for 30 min, then rinsed and finally vacuum dried.

The concentration of the dye before and after the dye treatment was calculated by using a Systronics Spectrophotometer.

## **RESULTS AND DISCUSSION**

Peroxydiphosphate has been extensively used for the polymerization of vinyl monomers.<sup>5-8</sup> We have reported the vinyl polymerization and graft copolymerization<sup>4,9,10</sup> using peroxydiphosphate alone and coupled with an organic substrate. This has been proven to be a potential initiator for vinyl polymerization.

In the present investigation, nylon fiber was dyed by using acryflavin either in the presence or absence of this redox system. The color strength was expressed as gram per kilogram. The result indicates that the intensity of dyeing is higher in the presence of the redox system than it is without. The dye uptake was recorded at different temperatures and at different time intervals. With increasing temperature from 30 to 40°C, the dye uptake increases, and with further increase of temperature, the dye uptake decreases (Fig. 1). The dye uptake increases with increasing peroxydiphosphate concentration at the initial stages, but at higher concentration of peroxydiphosphate, the dye uptake decreases (Fig. 2). The increase of thiourea concentration has a profound influence on the dye uptake of the fiber. Increasing the concentration of thiourea from  $1.25 \times 10^{-6}$  to  $3.75 \times 10^{-6} M$ , the dye uptake increases significantly and thereafter it decreases (Fig. 3).

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Fig. 1. Effect of temperature on dyeing: [Acryflavin] =  $1.5 \times 10^{-3} \text{ mol/L}$ ; [PP] =  $1 \times 10^{-3} \text{ mol/L}$ ; [TU] =  $5 \times 10^{-4} \text{ mol/L}$ ; pH = 6;  $M : L = 1 : 100; 1 h: (\bigcirc); 2 h: (\spadesuit); 3 h: (\triangle)$ .

The decomposition of peroxydiphosphate in the presence of thiourea to produce a number of free radicals is represented here.

 $P_{2}O_{8}^{4-} + H^{+} \xrightarrow{k_{1}} HPO_{4}^{-} + PO_{4}^{2-}$   $PO_{4}^{2-} + H_{2}O \rightarrow HPO_{4}^{2-} + OH$   $HPO_{4}^{-} + H_{2}O \rightarrow H_{2}PO_{4}^{-} + OH$ 



Fig. 2. Effect of [peroxydiphosphate] on dyeing: [Acryflavin] =  $7.5 \times 10^{-5}$  mol/L; [TU] =  $5 \times 10^{-4}$  mol/L; pH = 6; time = 1 h; M : L = 1 : 100.

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Fig. 3. Effect of [thiourea] on dyeing: [Acryflavin] =  $1.5 \times 10^{-3} \text{ mol/L}$ ; [PP] =  $0.2 \times 10^{-3} \text{ mol/L}$ ; pH = 6; time = 1 h; M : L = 1 : 100.

The preceding free radicals (R<sup>•</sup>) react with thiourea forming isothiourea radicals as represented here.



The preceding radicals ( $\mathbf{R}^*$  and  $\mathbf{R}^*$ ) interact with the nylon and the dye producing the nylon macroradicals and the dye radicals.

$$N - H + R^{\bullet} \rightarrow N^{\bullet} + RH$$
  
 $DN + R^{\bullet} \rightarrow D^{\bullet} + RH$ 

where N' and D' are nylon and dye radicals, respectively.

The combination of the preceding radicals results in a covalent bond formation between the dye and the fiber as shown here.

$$D' + N' \rightarrow N' - D$$

In the absence of the redox system, the dye molecule is either absorbed in the voids present in the fiber matrix or attached to the fiber matrix through salt linkages. But in the presence of the redox system, the dye molecule is covalently bonded to the fiber matrix along with the formation of salt linkages. Hence there is a significant increase in dye uptake in presence of the redox system. Further work, utilizing other redox systems in this line of investigation is in progress.

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