THE PROBLEM OF CYCLIC Oligomers in Dyeing AND PROCESSING POLYESTER AND WAYS OF SOLVING IT


Approaches to reducing the content of oligomers on the surface of PET fibres are substantiated. The first one is based on reducing surface sorption of oligomers on the fibre by rational selection of textile auxiliaries for dyeing polyester fabric and creating new preparations based on them; the second consists of chemical decyclization of the oligomers by use of catalysts of ammonolysis and hydrolysis in low concentrations. A method of eliminating cyclic oligomers and unfixd dye from the surface of the dyed textile material was developed based on use of aqueous solutions of ammonia in 0.04-0.06% concentration. Technology is created for giving polyester fibres stable antistatic properties, and this significantly reduces its resistivity from $2.8 \times 10^{14}$ to $2.68 \times 10^7 \text{\Omega}$.

Polyester [poly(ethylene terephthalate)] fibres contain up to 4% cyclic oligomers [1] which make it difficult to dye, finish, and process them. The cyclic oligomers distributed in the bulk of the polymer have almost no effect on its properties, while the oligomers on the surface of the fibres negatively affect the quality of dyeing and processing of dyed polyester fibre materials. In textile factories, up to 0.2-0.3 kg of oligomer debris is collected per ton of processed fibre [2].

In the course of hydrothermal treatments of polyester materials characteristic of periodic dyeing technologies, the oligomers migrate to the surface of the fibre and into the solution, affecting physicochemical processes in both the fibre and in the solution. The use of carriers that reduce the glass transition temperature of a fibre-forming polymer and electrolytes in dyeing increases the oligomer content on the surface of the fibres [3, 4].

There are two ways of eliminating the negative effect of oligomers on the quality of textile materials. The first consists of preventing accumulation of oligomers on the fibre and the second consists of chemically decomposing them. However, both methods require using frequently very toxic organic substances or additional power. In addition, these methods are not always effective and can worsen the quality of dyeing. The use of an oligomer disperser makes the dyeing process technology more complicated and expensive and causes additional contamination of wastewaters.

Studies are being conducted at the Institute of Chemistry of Solutions on theoretical substantiation and process application of some methods of “oligomer control” — both to prevent accumulation of cyclic oligomers on the surface of the fibre and to decompose them. Selection of preparations for dyeing that prevent accumulation of oligomers on the fibre surface is the most economical way to solve the problem. However, this can only be done after studying the effect of different surfactants (SF) on both sorption and diffusion of disperse dyes and on the oligomer content on the fibre surface.

We investigated the effect of a number of cation-active (CSF), anion-active (ASF), and nonionogenic (NSF) surfactants on dyeing of polyester materials with disperse dyes. All products selected are nonylphenol ethoxylate derivatives with an index of 9/6 or 9/10 (in the numerator: number of carbon atoms in the hydrophobic part of the molecule; in the denominator: degree of hydroxyethylation). They are manufactured by Ivkhimprom Open Joint Stock Co. (Ivanovo) and are used as the base for many composite textile auxiliaries.

The effect of the SF on the emergence of oligomers on the surface of fibres in traditional conditions of periodic dyeing at 130°C for 30 min is compared in Fig. 1. The oligomer content on the dyed fibre is very weakly dependent on the type of dye
Fig. 1. Effect of surfactants on the oligomer content on the surface of dyed polyester fibres in knitted fabric: 1) with no SF; 2) CSF 9/6; 3) CSF 9/10; 4) ASF 9/6; 5) ASF 9/10; 6) NSF 9/6; 7) NSF 9/10.

![Graph](image1)

Fig. 2. Effect of temperature and time of treating polyester fibres with 0.03 M aqueous ammonia solution on the oligomer content on the surface of the fibre: 1) $\tau = 30$ min; 2) $\tau = 5$ min.

![Graph](image2)

Fig. 3. Effect of the concentration of aqueous solutions of ammonia on surface resistance $\rho$ of polyester fibre. $\tau = 10$ min, $t = 130^\circ$C.

![Graph](image3)

and is determined by the type of SF. Use of CSF increases the oligomer content on the surface of the fibre, while ASF decreases it significantly. NSF causes the most complete dispersion of oligomers and their passage into solution. Note that the efficiency of the dispersing effect of SF of all types on the oligomers increases with an increase in the degree of hydroxyethylation. The results of the study can be used for purposeful selection of SF in creating preparations for dyeing polyester materials so that not only is high-quality dyeing obtained, but sloughing of oligomers during processing is also prevented.

Research has also been conducted for many years on the effect of weak aqueous solutions of ammonia on poly(ethylene terephthalate). These studies led to the creation of a series of original, highly efficient technologies for dyeing and surface treatment of fibre materials.

The study of the processes generated by aqueous solutions of ammonia with a 0.01-0.1 M concentration at 25-130$^\circ$C on the polyester fibre—solution phase interface [5] showed that in these conditions, the ammonia reacts with poly(ethylene terephthalate) cyclic oligomers so that the oligomers partially or totally decompose with formation of water-soluble linear oligomers and terephthalic acid derivatives.

Varying the temperature-time parameters of water—ammonia treatment of polyester materials led to a four-fold decrease in the concentration of oligomers in the fibre — from 3.8 to 0.92%.

Studies to estimate the amount of oligomers on the surface of polyester fibre after treatment with aqueous solutions of ammonia were important for solving this problem. As Fig. 2 shows, the oligomer content on the fibre surface decreased...