THE EFFECT OF PHYSICO-CHEMICAL METHODS OF ACTIVATION
ON THE STRUCTURE AND DYEABILITY OF TEXTILE MATERIALS
MADE FROM MAN-MADE FIBRES

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A necessary condition for carrying out sorption-diffusion processes and setting of dyes by a fibre in dyeing and printing textile materials is activation of the fibre-forming polymers by temporarily weakening intermolecular interactions and correspondingly increasing the internal accessible of the bulk of the fibre. In his time, A. B. Pakshver repeatedly indicated the fruitfulness of using the principle of reversible regulation of the structure of chemical fibres; in a number of researches [1-3] he convincingly demonstrated the possibility of thus increasing the rates of diffusion and chemisorptive processes.

Thermoplastic man-made fibres go over into an activated state upon heating the material to a temperature which exceeds its glass point, \( T_g \), which, for example, for stabilized polyester fibre is 95-100°C. A more universal possibility for activation which is also suitable for nonthermoplastic natural fibres and also for synthetic materials is plasticization of the fibre as a result of hydration or solvation of active centers of the polymer under conditions of liquid or vapor treatment with water or organic solvents. For additional intensification of the activating action of plasticizing reagents on the fibre, one may also use various physical methods of treatment, such as microwave radiation, ultrasound or the like. After completion of the treatment (in particular, the dyeing process) a transition of the fibre takes place into the glassy state, which together with the presence of physical and chemical sorption bonds of the dye with the polymer, ensures obtaining colors which are stable under service conditions.

In the present article, we have shown the general laws governing the purposeful action of a medium on the state of fibre-forming polymers which have been found in the work of the Institute of the Chemistry of Nonaqueous Solutions of the Academy of Sciences of the SSSR (at Ivanovo) and of the Ivanovsk Chemical Engineering Institute, and also rational ways based on them which have been developed for intensifying processes of coloring fabrics and giving them improved customer properties.
Fig. 1. Shrinkage polytherms of polyester fibre in air (1) and in solvent medium (2-7): 2) benzyl acetate; 3) anisole; 4) acetophenone; 5) benzyl alcohol; 6) nitrobenzene; 7) aniline.

As a result of studies, it has been found that the internal volume of a fibre which is accessible for a dye is connected with the level of plasticization of the fibre-forming polymer. From the point of view of ensuring the maximum possible temporary increase in sorptive capacity of fibres, it is most desirable to bring them into the region of the highly elastic state, $t_{h}$, which is limited on the one hand by the yield temperature of the polymer, $t_{y}$, and on the other by the characteristic temperature $t'$, at which according to the data of [4] loss of cooperation in segmental thermal motion of the macromolecules takes place: $t' > t_{h} > t_{y}$. Thus, while the available internal volume of polyester fibre, $V_{d}$, at 100-120°C is 0.002-0.007 cm$^3$/cm$^3$ and the sorption of dyes is close to zero, at 180-200°C, $V_{d}$ increases to 0.030-0.190 cm$^3$/cm$^3$ and the maximum dye absorption is 60-350 g/kg of fibre [5].

The activation energy of forming $V_{d}$ at temperatures above $t'$ (171-175°C) is reduced approximately 1.5-fold.

We have demonstrated the possibility of ensuring a high sorptive power of fibres at significantly lower temperatures due to solvation activation of the fibre-forming polymers both by melts of specially selected organic compounds and also by organic solvents. From the data in Fig. 1, it follows that temporary plasticization of polyethylene terephthalate in a solvent medium leads to a displacement of all temperature transitions, thereupon $t'$ is reduced by 30-80°. Analysis of the reasons for the different plasticizing power of a broad group of organic solvents which present interest as intensifiers for the dyeing process has made it possible to obtain a generalized correlation equation

$$ \Delta t = 12.4 \left(4R/V\right)^{0.23} + 0.048 B + 0.43 E, $$

where $\Delta t$ is the reduction in $t_{g}$ or $t'$ of the polyester fibre; $R$ is molecular refraction; $B$ and $E$ are general basicity and general acidity parameters; and $V$ is the volume of the solvent molecule.

This equation reflects the quantitative dependence between the efficiency of action of a medium on polyester fibre ($\Delta t_{g}$ or $\Delta t'$) and such solvent parameters which are available in the handbook literature as ability to undergo dispersion interaction $(R)$, volume of the molecule $(V)$, or ability to undergo specific interaction $(B$ or $E)$. Using this equation one can rather accurately predict the plasticizing power of solvents and can purposefully select them for temporary plasticization of polyester materials during the dyeing and finishing processes.

Analysis of Eq. (1) has shown that the contribution of universal solvation to the total efficiency of the plasticizing action of a solvent is basic (more than 70%). This indicates the advisability of using hydroxy- or amino-derivatives of benzene as effective plasticizers for polyester fibre; these have a high energy of dispersion interaction at a comparatively small volume of the molecules (0.10-0.12 nm$^3$).

Along with this, one should note that for these solvents the presence of a rather strong intermolecular action in the liquid medium is characteristic; this hinders the display of potential plasticizing possibilities of the solvent in full measure. As is evident from Fig. 2a, the quantity $\Delta E_{as}$ characterizes the deviation of the experimentally determined activation energy of polyester fibre shrinkage in a solvent medium (points 2-8) from the ideal figures (dotted line). However, the data in Fig. 2b indicate that for all the investigated systems, the values of $\Delta E_{as}$ correlate with the energy of intermolecular interaction in the solvent, a quantitative measure of which is the heat of vaporization, $\Delta H$ [6].

To increase the efficiency of plasticizing of man-made fibres by associated solvents, it has been proposed to raise the temperature of treatment (Fig. 3, curves 2, 2') or to use additions of "structure-destroying" cosolvents. For example, when one adds such a weak plasticizer as perchloroethylene or toluene to benzyl alcohol, the plasticizing action of the mixture rises considerably (Fig. 3, curves 1, 2 and 3, 4).