

A New Approach to Atmospheric Aqueous Disperse Dyeing of Polyester

Dr. Ludwig Rebenfeld, R. D. Matkowsky and H.-D. Weigmann, Textile Research Institute Princeton, New Jersey

The effectiveness of dyeing assistants is dependent on the extent of their ability to penetrate and thoroughly saturate textile substrates. Certain organic liquids diffuse rapidly through the polyester structure at low temperatures and can serve as effective transport media for more slowly diffusing species that enhance dyeability. Model room temperature pretreatment procedures for the rapid and more efficient incorporation of dyeing assistants throughout the fiber structure are discussed in terms of diffusion kinetics, dyestuff exhaustion, practical dye cycles, and environmental considerations.

Die Wirksamkeit der Färbehilfsmittel hängt vom Ausmaß ihrer Fähigkeit ab, in textile Substrate einzudringen und sie gründlich zu durchdringen. Bestimmte organische Flüssigkeiten diffundieren rasch durch die Polyesterstruktur bei niedrigen Temperaturen und können als wirksames Transportmittel für langsamer diffundierende Substanzen verwendet werden, welche die Anfärbbarkeit erhöhen. Modellvorbehandlungsverfahren bei Raumtemperatur für die rasche und wirksamere Inkorporation von Färbehilfsmitteln durch die Faserstruktur werden unter Diffusionskinetik, Farbstofferschöpfung, praktischen Färbekreisläufen und Umweltschutzüberlegungen besprochen.

Introduction

Energy conservation and pollution control are among the major current concerns of the worldwide textile industry. Since 1972 the costs of energy have increased greatly, and there is every indication that these costs will continue to increase in the future. Of the total energy consumed by the textile industry, it is estimated that approximately one third is represented by dyeing and finishing processes. It is for this reason that these processes are under special scrutiny with regard to energy requirements, production efficiency, and product quality. Efforts to reduce energy consumption in dyeing and finishing processes are currently focused on equipment maintenance, on decreasing liquor volume, and on increasing load capacity. The amount of energy that can be saved through these means is substantial, but there are practical limitations to which such modifications can be carried without affecting product quality. Although there have been several new developments in solvent and vapor phase dyeing, which would allow major reductions in energy consumption, many of these processes still require significant refinements in order to become practical. It is therefore not unreasonable to assume that aqueous dyeing processes of textile materials will continue to predominate.

The dyeing of polyester presents a particularly acute problem with regard to energy consumption as well as a unique opportunity to achieve important reductions. Aqueous dyeing of polyester usually involves high temperature pressure dyeing conditions, frequently using carriers as dyeing assistants. These dyeing technologies require a great deal of thermal

energy in view of the high temperatures and the necessary long dye cycles.

Many approaches have been taken to reduce energy consumption in the aqueous dyeing of polyester. One concept that has not received much attention is that of using chemical energy prior to dyeing to replace a portion of the thermal energy normally required in polyester dyeing. This paper explores the concept of pretreatment of polyester in selected chemical systems in order to improve subsequent dyeability.

The mechanism of disperse dye diffusion in polyester is one of polymer segmental motion and free volume generation. The onset of segmental motion is determined by the effective glass transition temperature of the polymer. For many years it has been known that there are a number of organic compounds that possess the ability to reduce the effective glass transition temperature of polyester. This phenomenon has led to the development and extensive use of the wide range of commercial dye carriers. As these dyeing assistants or carriers are currently used in commercial practice, they diffuse into the fiber structure during dyeing and act as plasticizing agents within the fiber¹⁻⁵. By increasing segmental mobility in the noncrystalline domains, there is a lowering of the effective glass transition temperature (T_g), and a corresponding decrease in the effective dyeing transition temperature (T_p). In normal carrier dyeing procedures, it can be assumed that carrier diffusion precedes dye diffusion but is far from complete when dyeing begins. This is because carriers experience similar diffusion barriers, although not to the same degree, as are faced by disperse dyes. Usually, only a portion of the carrier that is added to the dyebath finds its way into the fiber structure. Also, since carriers are usually added in emulsion form, a substantial portion of the carrier remains in the dye liquor and does not penetrate the fiber. Consequently, in many instances the full potential of the carrier to increase segmental mobility and decrease T_g of the polymer is not attained.

In recent studies conducted at TRI, it has been shown that certain low molecular weight organic liquids diffuse rapidly through polyester at low temperatures⁶. Although these compounds do not themselves improve dyeability to a useful extent, they can function as transport media for the introduction of the plasticizing agents^{7,8}. A thorough and uniform deposition of these agents within the polymer structure should yield a maximum reduction in the effective glass transition temperature and produce uniform dyeings at lower dyeing temperatures.

Accordingly, studies have been undertaken of the influence of brief low-temperature pretreatments of polyester in biphenyl/methylene chloride systems on their subsequent dyeing behavior.

Biphenyl was chosen as a suitable model dye carrier, and methylene chloride as an effective transport medium because of its known capacity to penetrate polyester rapidly even at room temperature.

Experimental Procedures

Several types of polyester in both filament and fabric form were investigated. Samples were treated in biphenyl/methylene chloride solutions of different con-

centrations for various treatment times. Typically, filament and yarn samples were treated in a 5% solution of biphenyl in methylene chloride for 45 seconds at 21°C (room temperature). After treatment the samples were air dried for an arbitrarily chosen time of 16 hours to remove the methylene chloride.

With the exception of the dyestuffs used for diffusion studies, standard commercial preparations were used. The dyestuffs were chosen so as to represent the wide range of energy levels that may be encountered in commercial practice. Exhaustion profiles were studied for dyestuff concentrations as high as 4.0% (owf). The dyebaths also contained 0.1% Avalon® I. S. Dispersing agent, and 1.0% (owf) glacial acetic acid. Dyeings were conducted in open beaker systems at a carefully maintained liquor ratio of 35:1. Samples were introduced into the dyebath at a starting temperature of 65°C, and the temperature was increased to 100°C at a rate of 1.1°C/min. After dyeing and rinsing, the fabric samples were air dried and heat set on a pin frame at their approximate original dimensions. Heat setting was conducted at approximately 170°C for 2 minutes.

Dye diffusion studies were performed on Dacron® 55 filament yarn utilizing purified press cake dyestuffs at an „infinite“ dyebath concentration and a liquor ratio of 400 to 1. Dye uptake was determined by extracting the dyed samples with methylene chloride and determining dye content spectrophotometrically. As an additional means of establishing fabric dyeability, experiments were carried out in accordance with procedures suggested by Mobay Chemical Corporation⁹. These procedures involve dyeing weighed pieces of fabric in a 1.0% (owf) Resolin® Blue FBL dyebath for 1/2 hour at 96°C. The fabric is then replaced in the partially exhausted dyebath with a fresh piece of equal weight and the remaining dyestuff is exhausted onto the fabric at 130°C. Visual comparison of the shades of the dried dyed fabrics against a standard scale is made and a relative fabric dyeability (V-rating) is estimated.

The carrier content of treated polyester samples was determined either by direct weighing or by thermogravimetric analysis using a DuPont 951 Thermogravimetric (TGA) accessory attached to a DuPont 990 Thermal Analyzer. Samples (approximately 5-10 mg) are heated at a heating rate of 10°C/min in either nitrogen or air atmospheres at flow rates of 50 cc/min.

Thermomechanical analysis (TMA), involving measurements of dimensional changes as a function of temperature, was used as a means of estimating the polymer glass transition temperature. Length changes of polyester yarns after various treatments were determined under a constant load of 5 g using a DuPont 924 Thermomechanical accessory attached to a DuPont 990 Thermal Analyzer. A heating rate of 10°C/min in air or in water was used.

Results and Discussion

Glass Transition Temperatures of Carrier/Solvent Treated Polyesters

As previously discussed, the incorporation of plasticizing molecules into the polyester structure increases segmental mobility within the polymer chains. The onset of segmental mobility is measured by the glass transition temperature (T_g), which in turn is closely

related to the dyeing transition temperature (T_D) at which rapid dye diffusion occurs²⁻⁴. The polymer T_g can be estimated by TMA involving measurements of changes in the rate of deformation under constant load as a function of temperature.

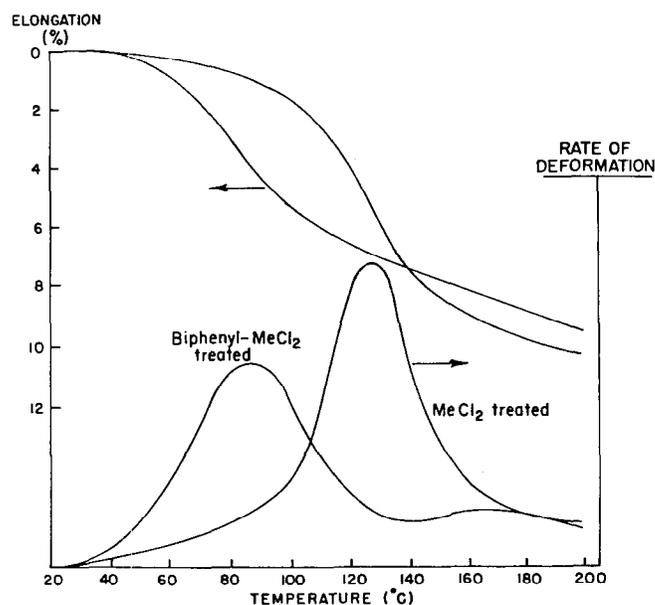


Fig. 1 TMA and derivative curves for Dacron® 55 filament yarns treated with MeCl₂ and biphenyl/MeCl₂ (add-on of ~ 5%)

The TMA curve in air of a polyester yarn that had been treated with a biphenyl/methylene chloride solution is compared in Figure 1 with the TMA curve after a blank treatment, i. e., a treatment with methylene chloride only. The derivative curve which represents the rate of deformation (elongation in this case) shows a maximum at a temperature which is linearly dependent on the concentration of the plasticizer inside the fiber structure (Fig. 2). It is assumed that this maximum in the rate of deformation corresponds to the maximum in segment mobility in the noncrystalline

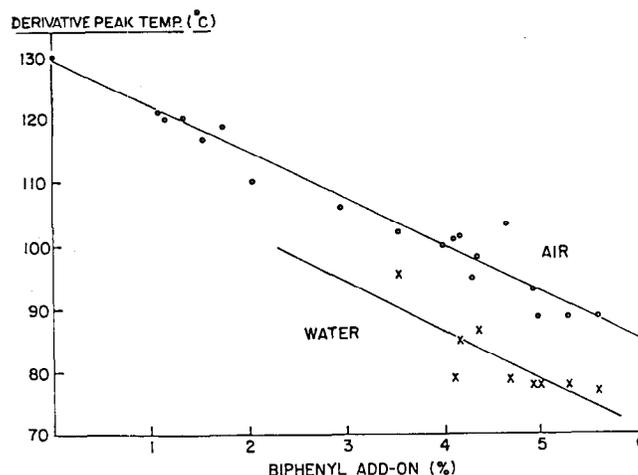


Fig. 2 Derivative peak temperature (TMA in water and air) for Dacron® 55 yarns as a function of biphenyl add-on

domains of the fiber. Introduction of 5% biphenyl into the fiber structure through a biphenyl/methylene chloride treatment produces a downward shift of about 20°C in the derivative peak temperature. If the experiment is carried out in water, the TMA derivative peak temperature is further lowered by approximately another 15°C.

Since only the biphenyl that is inside the fiber can contribute to the lowering of T_g , it was of interest to determine the extent of surface deposition at any given level of biphenyl add-on. Accordingly, biphenyl desorption measurements were undertaken using thermogravimetric analysis. As a control, biphenyl was deposited on the surface of a glass fabric from a methylene chloride solution in an identical manner as described for polyester fabric treatments. Figure 3 compares the desorption of biphenyl at 25°C from a polyester fabric with that from the glass fabric. As can be observed PE Dacron® 56 yarn loses biphenyl at a much slower rate than the glass fabric, this behavior is attributed to the fact that most of the biphenyl must diffuse out of the internal fiber structure in the case of polyester, whereas sublimation from the surface is the only possible mode of desorption from the glass fabric.

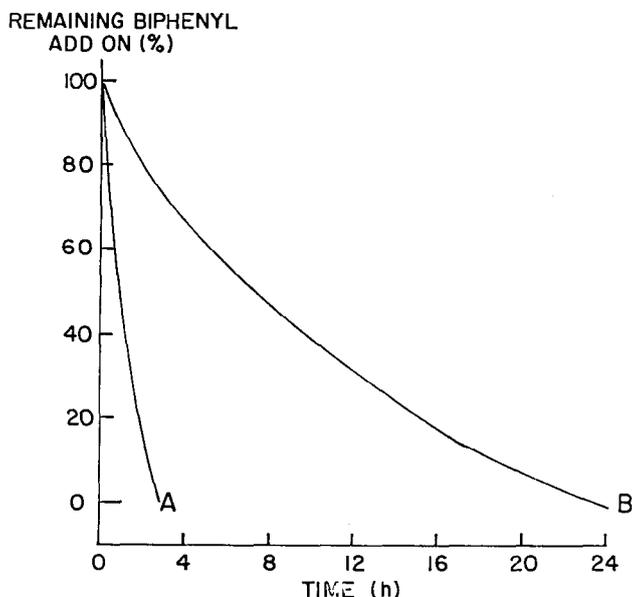


Fig. 3 Isothermal weight loss at 25°C of biphenyl from A) glass fabric; B) 2.5% biphenyl/MeCl₂ treated Dacron® 56 fabric

Further confirmation of the lowering of T_g , as a result of the biphenyl/methylene chloride treatments can be obtained from a comparison of dye diffusion coefficients in untreated and biphenyl/methylene chloride treated polyester yarns. As shown in Table 1, a 5% biphenyl content increases the dye diffusion coefficient by about 2 orders of magnitude, while the corresponding amount of biphenyl in the dye bath results only in a minor increase in the dye diffusion coefficient.

The temperature dependence of the apparent dye diffusion coefficients (Fig. 4) clearly shows the substan-

Table 1: Dye Diffusion Coefficients at 100°C and Estimated Dyeing Transition Temperatures

Conditions	Diff. Coef. $\times 10^{10}$ (m ² /s)	Est. T_D
Untreated control	24.8	110°C
5.0% (owf) Biphenyl in Dye bath	72.1	—
2.5% (owf) Biphenyl — MeCl ₂	368.9	85°
5.0% (owf) Biphenyl — MeCl ₂	2750.0	65°

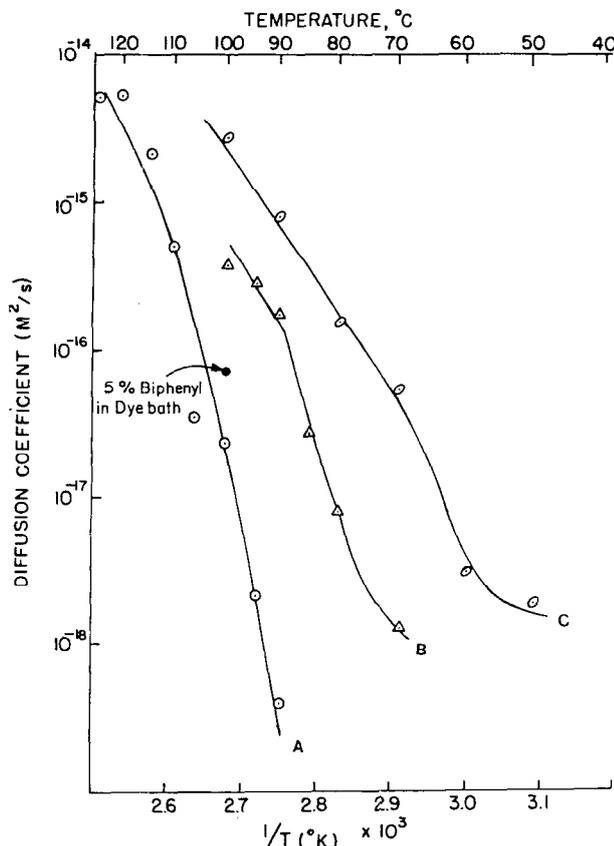


Fig. 4 Temperature dependence of diffusion coefficients of Resolin® Red BBL in untreated Dacron® 55 yarns and in yarns containing, 2.5 and 5.0% biphenyl

tial shift to lower temperatures for the 5% biphenyl-containing polyester yarns. A slightly smaller shift is observed for the lower uptake level.

The temperature dependence of dye diffusion permits an estimate of a dyeing transition temperature T_D which is related to the glass transition temperature of the fibers. At dyeing temperatures above T_D an approximately linear dependence of the dye diffusion coefficient as a function of $1/T$ is observed. A non-linear decrease in $\log D$ occurs as the temperature falls below the dyeing transition temperature. Values for the inflection points defining T_D were determined through linear regression analyses and are also shown in Table 1. The dependence of T_D on biphenyl content is shown in Figure 5, which includes a comparison with the corresponding derivative peak temperatures obtained from TMA. A linear relationship appears to exist between both transition temperatures and biphenyl add-on.

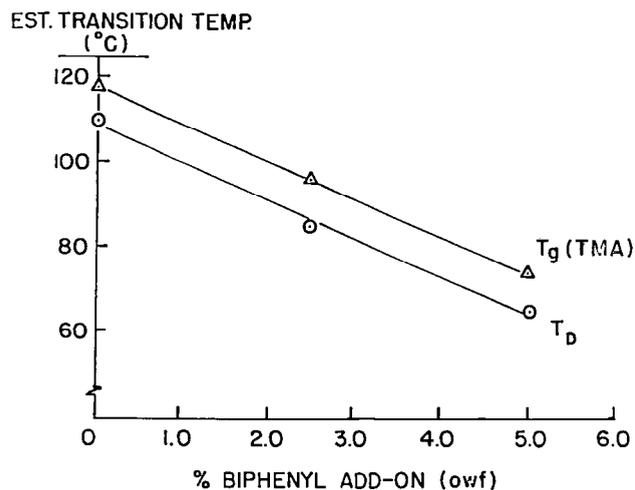


Fig. 5 Estimated glass and dyeing transition temperatures for pretreated Dacron® 55 yarns as a function of biphenyl add-on

Dyeability of Carrier/Solvent Pretreated Polyester Fabrics

As discussed above, the introduction of plasticizing molecules into polyester yarns using a fast diffusing transport medium results in a lowering of the glass transition temperature and a corresponding increase in dye diffusion rate. These changes are reflected in the exhaustion profiles of various polyester fabrics that have been treated with biphenyl/methylene chloride solutions under what would appear to be acceptable production conditions, i. e., 45 seconds at 21° C.

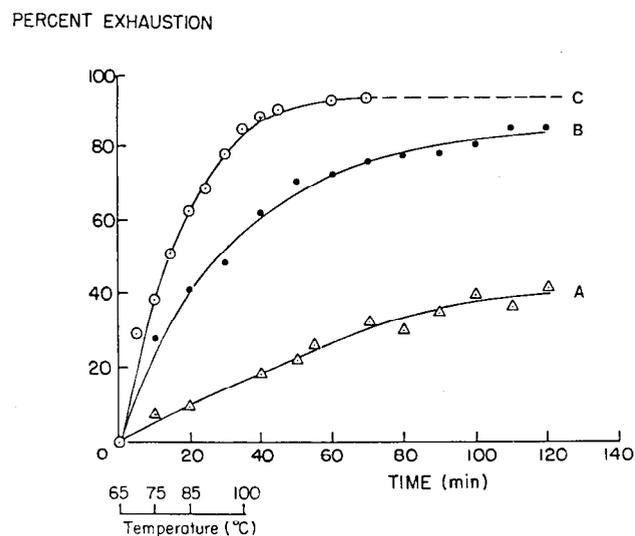


Fig. 6 Dyebath exhaustion profiles for Dacron® 56 fabric. Dyestuff 2.0% (owf) Resolin® Blue FBL: A) Untreated; B) Commercial carrier in dyebath; C) Biphenyl/MeCl₂ treated

The dyebath exhaustion profiles under atmospheric dyeing conditions of three pretreated polyester fabrics are compared in Figures 6, 7 and 8 with the exhaustion profiles of the corresponding untreated materials. Figure 6 also includes the exhaustion profile of a Dacron® 56 fabric from a dyebath containing 5.0%

(owf) of a commercial biphenyl-based carrier. The treated fabrics begin to exhaust the dyebath almost immediately after temperatures are increased above 65° C and reach an acceptable equilibrium exhaustion level within 15 to 20 min after attaining 100° C. A comparison of dyed samples against pattern card standards indicates identical color yields. As would be expected,

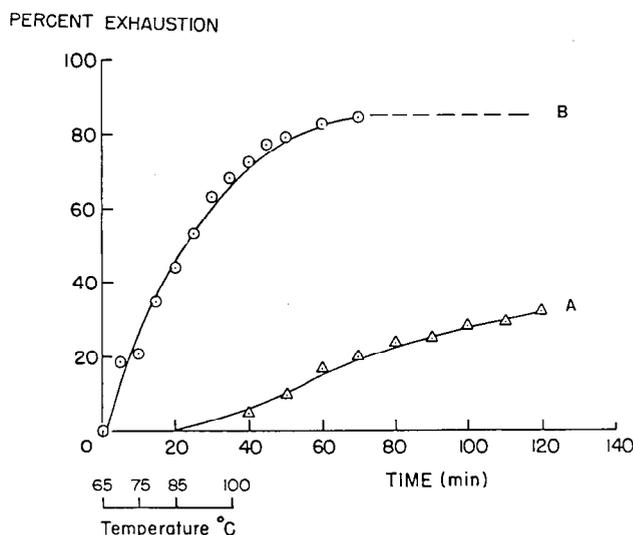


Fig. 7 Dyebath exhaustion profiles for Fortrel® 760 fabric. Dyestuff: 2.0% Resolin® Blue FBL A) Untreated; B) Biphenyl/MeCl₂ treated.

the untreated fabrics never achieve equilibrium exhaustion levels under these conditions even after a dyeing time of 120 min. Dyebath exhaustion of the pretreated Dacron® 56 fabric is also significantly faster than untreated samples dyed in the presence of the commercial carrier. It should be noted that the effects of pretreatments in methylene chloride alone give only a marginal improvement in dyeability. Cross-sections of yarns from pretreated and dyed fabrics usually show complete fiber penetration by

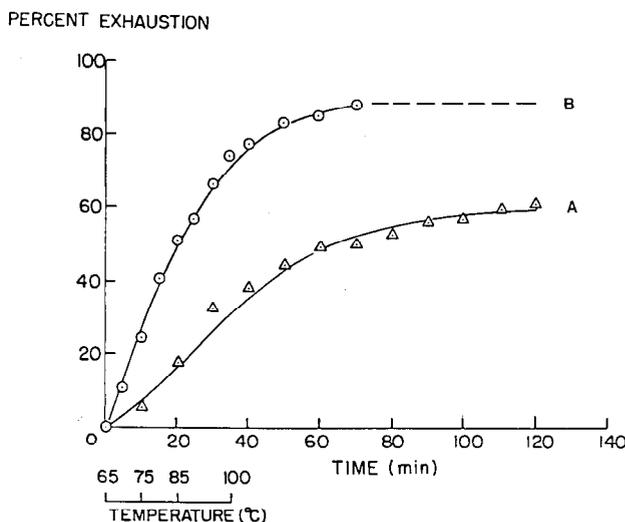


Fig. 8 Dyebath exhaustion profiles for Dacron® 54 fabric. Dyestuff 2.0% Resolin® Blue FBL A) Untreated; B) Biphenyl/MeCl₂ treated.

the dyestuff, suggesting a uniform distribution of the carrier throughout the fiber.

An alternative demonstration of the effect of the carrier content inside the polyester structure on fabric dyeability is shown in Figure 9 where V-ratings (reflecting dyeing rate) of biphenyl/methylene chloride treated Fortrel® 760 fabric samples are shown as a function of carrier content. A linear relationship between the dye speed rating and carrier add-on is observed, and the maximum value of 8 is reached with a carrier content slightly greater than 5.0 % (owf).

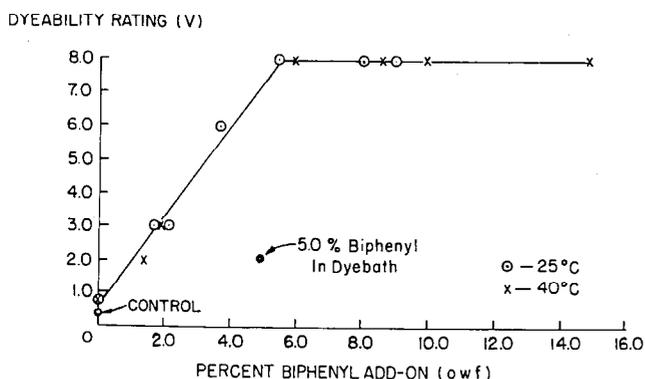


Fig. 9 Dye speed ratings (V) for biphenyl/MeCl₂ treated Fortrel® 760 fabric as a function of biphenyl add-on

Higher dyeing speeds cannot be determined due to the limitation of the comparison standards. The V-rating dependence on the biphenyl content of the fabric does not appear to be influenced by the temperature of the pretreatment. The addition of 5.0 % (owf) biphenyl to the dyebath increases the fabric dyeability to the same degree as approximately 1.5 % (owf) of biphenyl introduced into the polyester through the transport medium.

Dyeability as a Function of Prior Thermo-mechanical History

Various dyeing uniformity problems including that of barré are due to differences in the prior thermome-

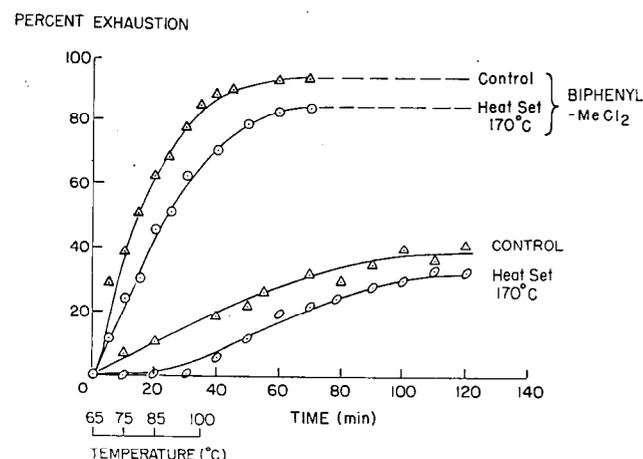


Fig. 10 Dye bath exhaustion profiles for Resolin® Blue FBL on heat set Dacron® 56 fabric untreated and treated with biphenyl/MeCl₂

chanical history of the yarns. Although yarn producers take every precaution to assure that identical merge numbers possess physical properties that are as closely matched as possible, observed variations can be significant. Further variations in dyeing characteristics may be caused by texturing or by proprietary finishing procedures.

Since variations in the prior thermal and mechanical history of a yarn or fabric can pose real problems in terms of product quality, efforts were made to establish the effects of prior heat treatments on the effectiveness of the biphenyl/methylene chloride system. In Figure 10 are shown exhaustion profiles with and without treatment in a 5 % biphenyl/methylene chloride solution of fabrics that have been heat set on a tenter frame (with slight extension) at 170°C for 2 minutes. Comparison with corresponding control (not heat set) samples is also shown. The effectiveness of the carrier inside the polyester structure is only slightly lowered by the prior heat treatment and accompanying structural changes. These results suggest that the biphenyl/methylene chloride pretreatment is capable of overcoming structural differences which could result in dyeing nonuniformity.

Dyestuff „Energy Levels“

Disperse dyes are conveniently assigned to groups of dyestuffs of various energy levels. Diffusion coefficients and affinity of the dye generally govern the

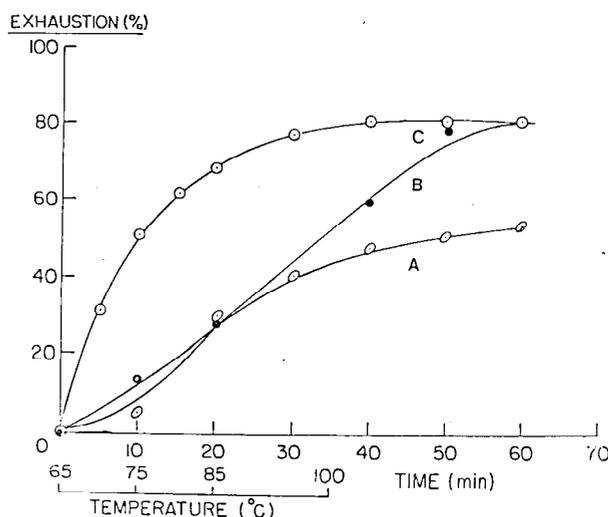


Fig. 11 Dyebath exhaustion profiles for 1.56 % (owf) Resolin® Blue GRL on Dacron® 56 fabric: A) Untreated; B) Carrier-assisted dyeing; C) Biphenyl/MeCl₂ treated

group assignments, the energy required to achieve dyeing being the guiding principle. Fast diffusing dyes are therefore low energy dyes, while high energy dyes have low diffusion coefficients. The effects of biphenyl/methylene chloride pretreatments on the dyebath exhaustion behaviour of dyes belonging to various energy groups have been studied. Figure 11 shows exhaustion profiles associated with Resolin® Blue GRL (1.56 % owf), a low energy dye. The untreated control reaches only about 50 % exhaustion in 60 min and exhaustion does not begin until a tem-

perature of about 75°C is exceeded. In contrast, biphenyl/methylene chloride pretreated samples reached equilibrium exhaustion levels within approximately 35 min, with high exhaustion rates observed even at low temperatures. A commercial carrier in the dyebath does produce equilibrium exhaustion levels within 60 min, but the exhaustion rates are much lower than those for the pretreated samples, and further dyeing time is required for leveling. Figure 12 shows the exhaustion profiles obtained with a dyebath containing 2% (owf) Latyl® Yellow 5R, a medium energy dyestuff. As would be expected, the untreated control

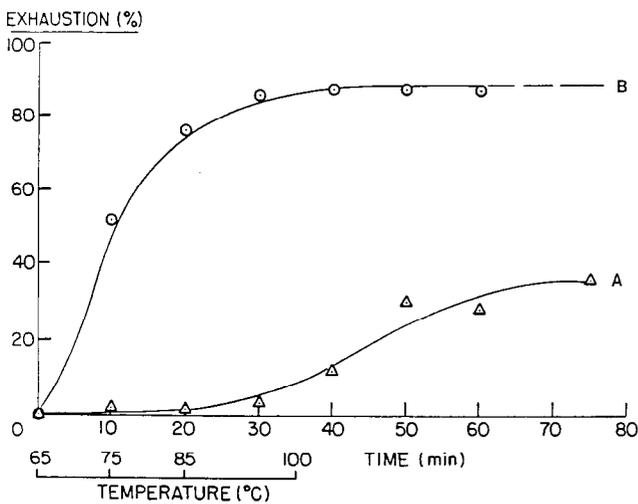


Fig 12 Dye bath exhaustion profiles for 2.0% (owf) Latyl® Yellow 5R on Dacron® 56 fabric:
A) Untreated; B) Biphenyl/MeCl₂ treated

exhausts this dyestuff at a significantly lower rate and requires even higher dyeing temperatures than those for the low energy dyestuff shown in Figure 11. Pretreatment with biphenyl/methylene chloride again results in rapid exhaustion even at lower temperatures reaching an exhaustion level of 88% in about 35 to 40 min. Figure 13 shows exhaustion profiles for Bucron® Rubine 2BNS, a high energy dyestuff, at a 1.5% (owf)

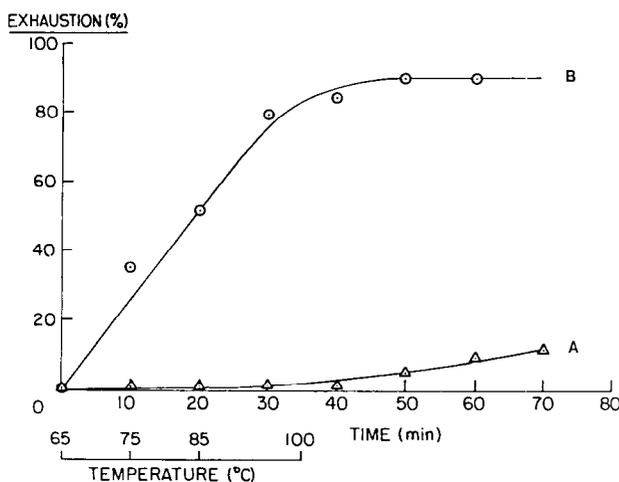


Fig 13 Dye bath exhaustion profiles for 1.5% (owf) Bucron® Rubine 2BNS on Dacron® 56 fabric:
A) Untreated; B) Biphenyl/MeCl₂ treated

dyebath concentration. The control sample shows extremely slow exhaustion even at 100°C, resulting in less than 10% exhaustion in 60 min. In comparison there is a rapid exhaustion rate and an equilibrium exhaustion level of 90%, which is reached within 45 min, for the biphenyl/methylene chloride pretreated fabric.

The effect of biphenyl/methylene chloride pretreatments with respect to dyestuff energy levels is most clearly demonstrated in Figure 14, which compares the exhaustion rates from a constant dye concentration of 2.0% (owf) of three dyes of different energy level prior to and after carrier incorporation. While overall exhaustion rates of 0.53% per min, 0.33% per min, and 0.15% per min were observed for the three dyestuffs, pretreatment with biphenyl/methylene chloride essentially eliminated the differences.

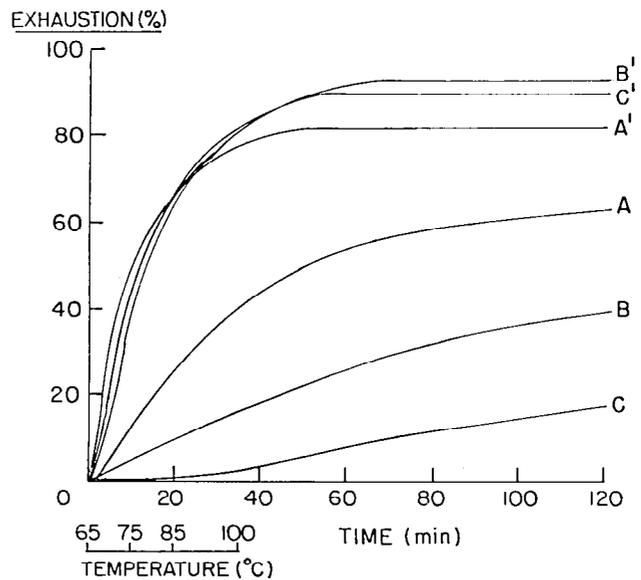


Fig 14 Dye bath exhaustion profiles for 2.0% (owf) dyeings on Dacron® 56 fabric:
A) Resolin® Blue GRL; B) Resolin® Blue FBL; and C) Bucron® Rubine 2BNS. A, B and C untreated fabric; A', B' and C' biphenyl/MeCl₂ treated fabric

Physical and Aesthetic Properties

Low temperature (21°C) treatments with biphenyl-methylene chloride solutions result in only minor levels of shrinkage. As would be expected the shrinkage is dependent on yarn properties and fabric construction. Mechanical properties are not adversely affected by the pretreatment and dyeing procedures. Subjective evaluations of fabric hand and drape reveal no changes. The stability of the dyed fabrics to dry cleaning fluids (perchloroethylene), and wet and dry crock fastness appear to be good. Lightfastness of pretreated and dyed polyester fabrics as determined in preliminary exposure tests showed no significant difference from corresponding high-temperature dyed fabrics.

Energy Conservation

The incorporation of carriers into polyester prior to dyeing results in a substantially more energy efficient

dye cycle. These savings would result not only from lower dyeing temperatures but also from greatly reduced dye cycle times. Typical commercial polyester dyeing cycles require approximately 3 hours and temperatures between 120 and 130°C. Of these 3 hours, about 1 hour is consumed in heat-up, about 45 and 60 min during the dye migration period, and about 40 min during cooling. In the case of biphenyl/methylene chloride pretreated fabrics, modifications could be programmed into the dyeing cycle which would result in substantial savings of time and energy. Figure 15 gives a comparison between a typical commercial cycle and one which might be visualized for pretreated fabrics.

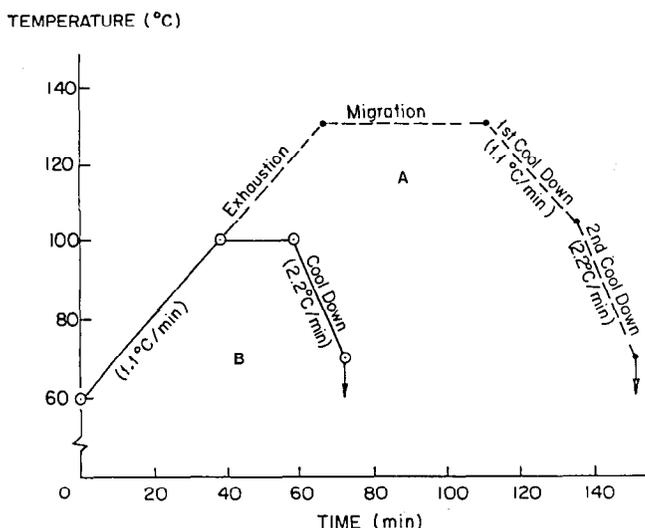


Fig. 15 Comparison of temperature and time requirement of:
 A) Conventional high temperature dye cycle;
 B) Rapid low temperature dye cycle for biphenyl/MeCl treated polyesters

Based on standard conditions and a normal thermal maintenance efficiency, a 36% reduction in energy consumption can be anticipated for this cycle. The total dye cycle time (including loading and unloading) might be reduced by approximately 40%, which should allow a significant increase in productivity. This increase in productivity should significantly offset the cost incurred by the fabric pretreatment.

Conclusions and Summary

The effectiveness of any dyeing assistant is dependent upon its ability to penetrate a textile substrate. The use of rapidly diffusing compounds as transport media for dyeing assistants permits their uniform and rapid introduction into the fiber structure at room temperature. Thermomechanical analysis of the resulting carrier-containing fibers shows a lowering of the effective polymer glass transition temperature. The enhanced dye diffusion in these pretreated structures results in rapid exhaustion rates even under atmospheric dyeing conditions. Complete and uniform penetration of the fiber cross section is achieved within relatively short periods of time, reflecting the uniform distribution of the carrier during the pretreatment. Preliminary data suggest that barré coverage would be improved by the carrier/solvent pretreatment. Differences in the exhaustion rates of low, medium, and high-energy dyes are essentially eliminated by the pretreatment so that multicomponent formulations containing dyes of different diffusivity can be used successfully without any special process modifications. Mechanical properties and fastness properties are essentially unaffected and comparable to those observed after high temperature dyeing. Energy consumption is significantly reduced, since dyeing time and dyeing temperature are decreased. The savings may more than compensate for the cost of the pretreatment step.

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