CHEMICAL PRINCIPLES OF SYNTHETIC FIBRE DYEING

S. M. Burkinshaw

SPRINGER-SCIENCE+BUSINESS MEDIA, B.V.

Chemical Principles of Synthetic Fibre Dyeing

Chemical Principles of Synthetic Fibre Dyeing

S. M. BURKINSHAW
The University of Leeds

SPRINGER-SCIENCE+BUSINESS MEDIA, B.V.

First edition 1995

© 1995 Springer Science+Business Media Dordrecht

Originally published by Chapman & Hall in 1995
Softcover reprint of the hardcover 1st edition 1995
Typeset in 10/12pt Times by Acorn Bookwork, Salisbury, Wilts

ISBN 978-94-010-4263-5 ISBN 978-94-011-0593-4 (eBook)
DOI 10.1007/978-94-011-0593-4

Apart from any fair dealing for the purposes of research or private study, or criticism or review, as permitted under the UK Copyright Designs and Patents Act, 1988, this publication may not be reproduced, stored, or transmitted, in any form or by any means, without the prior permission in writing of the publishers, or in the case of reprographic reproduction only in accordance with the terms of the licences issued by the Copyright Licensing Agency in the UK, or in accordance with the terms of licences issued by the appropriate Reproduction Rights Organization outside the UK. Enquiries concerning reproduction outside the terms stated here should be sent to the publishers at the Glasgow address printed on this page.

The publisher makes no representation, express or implied, with regard to the accuracy of the information contained in this book and cannot accept any legal responsibility or liability for any errors or omissions that may be made. Whilst every effort has been made to ensure the accuracy of the contents of this book, the publishers and the author do not accept any liability or responsibility for any action taken or arising from any untested idea or information contained in or referred to in this work.

A catalogue record for this book is available from the British Library
Library of Congress Catalog Card Number: 95-76880

♾ Printed on acid-free text paper, manufactured in accordance with ANSI/NISO Z39.48-1992 (Permanence of Paper)

Preface

This book is based on a series of lectures given to final year undergraduates and MSc students of the Department of Colour Chemistry and Dyeing at The University of Leeds. As such, the main intention, in writing the first three chapters of the book, was to provide these students, and others who have a fundamental understanding of dyeing, with an overview of the theories of dyeing the three major synthetic fibres, namely polyester, nylon and acrylic. In the case of a reader who has less knowledge of dyeing or one who may be newly entering the field, each of the first three chapters includes an introduction to the various dye classes that have been used to dye the three fibre types.

The subject of the theory of dyeing polyester, nylon and acrylic fibres has attracted enormous interest over several decades and, whilst none of the first three chapters represents an exhaustive account of the vast amount of published literature, it was intended that the references presented should provide the reader with a broad, general background of knowledge.

Accounts are provided of the dyeing of the three types of fibre with several dye classes; whilst, nowadays, some of the classes of dye included either enjoy little usage or are not commercially employed owing to various reasons, it was decided to include such dye classes so as to provide a balanced view of the dyeing of these fibres. In a similar manner, although carrier dyeing is currently little used owing, primarily, to environmental reasons, this subject, which has attracted a great deal of attention in published literature, has been included. Furthermore, as the subject of carrier dyeing spans each of the Chapters 1–3 and as carrier dyeing was of greatest importance with regard to the dyeing of polyester, an account of the carrier dyeing of this fibre in Chapter 1 comprises a detailed description of this subject that included references to work carried out using other fibres, this having been done in an attempt to provide an account of the evolution of the theory of carrier dyeing.

The final chapter of the book concerns the dyeing of microfibre, which, although a relatively recent textile substrate, continues to grow in importance. The intention in writing Chapter 4 was to demonstrate why the dyeing of microfibre differs to that of conventional decitex fibre by the use of explanatory accounts of the effects that decreasing linear filament density have upon the colour yield and fastness properties of dyeings.

SM Burkinshaw
Leeds, April 1995

Contents

1. Polyester

1.1. Introduction

The undeniable outstanding success of polyester fibres, which were commercially introduced by ICI in 1948 under the trade name 'Terylene', can be attributed to their excellent textile properties and generally very high chemical resistance under typical dyeing and finishing conditions. The poly(ethylene terephthalate) (PET) fibres, which, typically, are prepared from terephthalic acid and ethylene glycol [1–3], now enjoy world-wide production and are marketed under a variety of trade names. Although other polyester fibres, such as the 'Kodel II' (Eastman) range prepared from 1,4-dimethylolcyclohexane and terephthalic acid [2, 4] are also available, this account concerns only the dyeing of PET fibres.

Owing to the compact and highly crystalline structure of the hydrophobic fibres the rate of dye diffusion within the fibres is very low. Copolymerisation of ethylene glycol and terephthalic acid with a third comonomer such as ethylene oxide, isophthalic acid or 4-hydroxybenzoic acid, reduces the structural regularity of the homopolymer thereby improving the dyeability of the fibre with disperse dyes. The use of non-ionic comonomers results in 'non-carrier dyeing' or 'deep-dyeing' PET fibres [5] and the use of anionic comonomers, such as 5-sulphoisophthalic acid imparts basic-dyeability to the fibres while the use of certain nitrogen-containing comonomers confers substantivity towards anionic dyes [3]; high-shrink PET fibres are also obtained by copolymerisation [6]. Additionally, the pilling performance of the fibre is enhanced by means of copolymerisation. Physical modifications employed in fibre production, such as modifications of the spinning conditions or the use of shorter molecular chains [6] also alters the fibre structure thereby modifying the dyeability and pilling performance of the fibre [2]. The 'Kodel II' (Eastman) range of poly(1,4-dimethylolcyclohexane) fibres [2, 4] also are modified in a similar manner as PET fibres [4].

PET fibres possess high resistance to oxidising and reducing agents and also to many organic solvents at room temperature although some solvents, at or near their boiling points, and in some cases at room temperature, induce shrinkage of unset fibres [7]. The fibres are prone to hydrolysis in the presence of dilute acids or alkalis as well as water [1]; however, this is of relatively little significance even under high-temperature dyeing conditions (130°C) provided that the pH is maintained within the range 4.5 to 6 [5]. Although possessing reasonable resistance to dilute aqueous acids, they are slowly degraded by concentrated acids; whilst the fibre will withstand typical alkaline conditions encountered in vat dyeing of PET/cotton blends, hot, concentrated alkali solutions hydrolyse the polymer although this is limited to surface saponification of the fibre at temperatures up to the boil [5]. Controlled saponification by means of treatment with hot aqueous sodium hydroxide is used to enhance the aesthetics of PET fabrics. Although it was observed in 1950 [8] that treatment of PET filaments with potassium hydroxide increased the fineness of the filaments, the use of sodium hydroxide to reduce fabric mass and thus enhance fabric aesthetics was first disclosed in 1952 [9] and later developed to impart high lustre [10]. Caustic treatment is now mainly used to improve the suppleness [11] of the fibre, the change in aesthetics, which is a direct function of fabric mass reduction [11], being dependent upon the temperature, duration and concentration of sodium hydroxide employed [11–13]. It has been demonstrated [14] that such alkali treatment enhances the dyeability of the fibre and it is considered [5] that alkali-treated PET is dyed more rapidly and to deeper shades than untreated fibre. A more detailed discussion of the mass reduction of PET fabric and its effects on dyeability is given in Chapter 4.

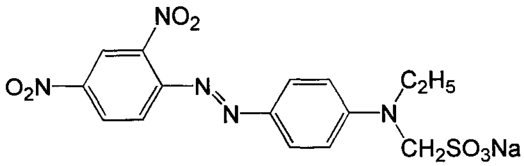
Barriness in PET fibres arises mainly from variations in crystallinity introduced during primary spinning, drawing, texturising and heat setting prior to dyeing; generally, barré effects introduced during texturising and heat setting are more prevalent than those imparted during drawing. Although an increase in crystallinity reduces the accessibility of the dye to those regions in which dye adsorption occurs, and thus rate of dyeing, the availability of such regions is also reduced, thereby reducing the saturation value of the fibre.

Although acid- and basic-dyeable variants have been developed for use in blends with conventional PET fibres, these variants enjoy considerably less usage than their disperse-dyeable counterpart. Nowadays, virtually all PET fibres are dyed using disperse dyes, although the fibres are dyeable with vat dyes, azoic colorants and, in the case of anionic-modified PET, cationic dyes.

1.2. Disperse dyes

A disperse dye is defined [15] as *a substantially water-insoluble dye having substantivity for one or more hydrophobic fibres, e.g. cellulose acetate, and usually applied from fine aqueous dispersion*; thus, in addition to polyester, this dye class is used to dye polyacrylonitrile fibres (see Chapter 3) and also polyamide and acetate fibres [16–18]. Disperse dyes were devised in the 1920s for the coloration of the relatively hydrophobic secondary cellulose acetate fibres. The 'temporarily solubilised' Ionamine (BDC) range of dyes [19–21], as exemplified by Ionamine Red KA (I), introduced in the early 1920s, were the immediate precursors of disperse dyes; water-solubility was conferred upon these dyes by means of an *N*-methylsulphonic acid group, which, during dyeing, hydrolysed to yield the parent, low-solubility dye. This dye range was superseded in the early 1920s by ranges of disperse dyes, such as SRA (Br.C) [22–25] and Duranol (ICI), that were devoid of ionic solubilising groups. These sparingly water-soluble 'Acetate' dyes were applied to cellulose acetate in the form a fine aqueous dispersion; several methods [26–29] were devised to disperse these early disperse dyes, which resulted in the dispersion method currently used for this dye class. The subsequent introduction of the more hydrophobic cellulose triacetate and, more importantly, polyester fibres, brought about considerable development of the dyes, which, in essence, was directed towards increasing the sublimation fastness of the dyes by means of increased polarity and molecular size [16–18, 30–37].

The chemistry of disperse dyes has been discussed by several authors [18, 30, 32–35, 37]; several chemical types are exemplified such as azo (CI Disperse Blue 79 (II)), anthraquinone (CI Disperse Blue 26 (III)) and methine (CI Disperse Yellow 99 (IV)). Although the dyes do not contain ionic groups they possess polar groups which impart to the relatively small molecular size dyes a small, but highly important, aqueous solubility (Table 1.1). Owing to their relative lack of cohesive energy in the

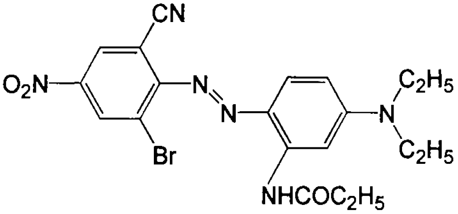


I

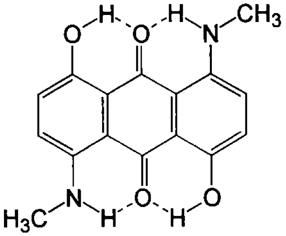
Table 1.1 Solubility of pure (dispersant-free) disperse dyes [171]

Dye	Solubility in water (mg dm^{-3})	
	25°C	80°C
V	0.3	7
VI	0.4	18
VII	7.1	240
VIII	4.4	43
IX	0.4	11
X	1.2	35

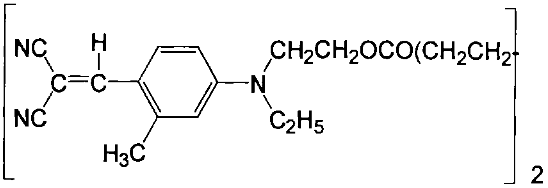
(Reproduced with permission from C.L. Bird and the Society of Dyers and Colourists)


CN
O_2N
N
N
Br
C_2H_5
N
C_2H_5
$NHCOC_2H_5$

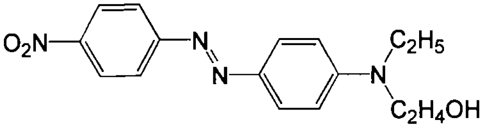
II


O
H
O
H
N
CH_3
H_3C
N
H
O
H
O

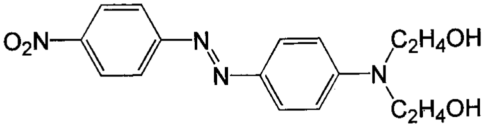
III


NC
H
C=C
NC
H_3C
N
$CH_2CH_2OCO(CH_2CH_2$
C_2H_5
2

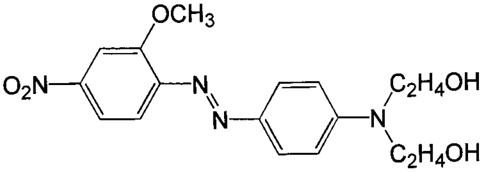
IV


O_2N
N
N
C_2H_5
N
C_2H_4OH

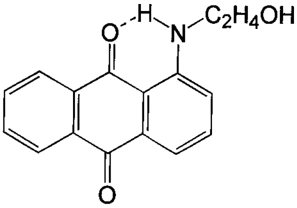
V



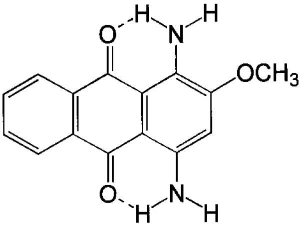
VI



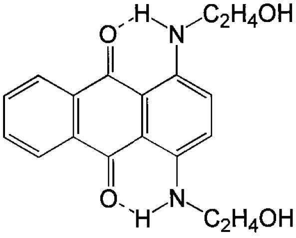
VII



VIII



IX



X

solid state the non-ionic dyes are volatile, enabling them to be applied in the vapour phase.

CLASSIFICATION. Although disperse dyes are widely used on all hydrophobic fibres, no universal system of classifying the dyeing behaviour of the dyes has been adopted by the dye makers [38]. Owing to their often varied dyeing behaviour on different fibres, the SDC has proposed a series of tests by which the dyeing behaviour of disperse dyes on secondary cellulose acetate [39], triacetate [40] and PET [41] under practical exhaustion (immersion) conditions can be determined. Some dye makers ascribe different trade names to ranges of dyes according to the fibre for which the dyes are intended; most disperse dyes marketed for use on PET fibres are classified by the respective maker, for instance, in accordance with the sublimation character of the dyes or the ability of the dyes to cover variations in texturised PET material.

GENERAL PROPERTIES. Generally, the dyes, as represented by the Dispersol (ICI), Samaron (Hoechst), Serilene (YCL), Foron (Sandoz), Palanil (BASF) and Terasil (Ciba-Geigy) ranges, furnish a wide variety of hues and possess good build-up and very good fastness to light and wet treatments on polyester fibres, although some dye combinations can exhibit anomalous light fading. The heat fastness of disperse dyes on PET is of great importance in view of the high temperatures involved during subsequent pleating, heat setting or ironing processes to which the dyed materials may be subjected.

Owing to the low rate of diffusion of disperse dyes within PET fibres at temperatures up to the commercial boil (98°C), the dyeing rate is raised to a commercially acceptable level by the use of high temperatures (commonly 130°C) and carriers; thermofixation, employing temperatures in the region of 210°C, is also used. Generally, thermofixation gives better coverage of barré effects than does exhaustion dyeing methods; in the latter case, superior coverage is achieved using elevated temperatures (up to 135°C) and prolonged dyeing times and by the use of suitable carriers at 110–125°C. However, although good coverage of barré in texturised PET can be achieved using high temperatures and long dyeing times, such conditions can degrade the bulk, handle and elasticity of the fibres. Consequently, efforts have been directed towards maximising dye migration, and thus coverage of barré, through optimisation of the rate of dyebath exhaustion achieved by control of the temperature and dye concentration as well as consideration of the diffusion behaviour of the dyes [42–44].

DEGRADATION. Many disperse dyes degrade if the pH is uncontrolled during aqueous dyeing; some dyes are hydrolysed by acids or alkalis, the hydrolysed form of the dye being of different shade and in some cases of different affinity for PET to the unhydrolysed dye. In some cases, such pH induced changes are reversible although, commonly, alkaline conditions are considered to cause a permanent deterioration of the dye [45]. Schmitt [46] concluded that the colour yield obtained with disperse dyes decreases with increasing pH; in some cases, application at pH values of 8–10 destroy the dye. From measurements of redox potentials [47] it was considered that reduction and hydrolysis of disperse dyes were the main sources of problems encountered in the dyeing of PET blends and the use of a buffer system to alleviate such problems was proposed. In a study of the dyeing of wool/PET blends, Shnider [48] showed that under neutral to alkaline conditions, certain disperse dyes are hydrolysed and that saponification of certain functional groups in the dyes occurs leading to the formation of by-products that exhibit low affinity for PET. This author [48] also demonstrated that the wool component of PET/wool blends reduced disperse dyes and that at negative redox potentials, certain azo and AQ dyes are reduced, the extent of which increases with increasing pH; Shnider [48] further proposed the use of oxidising agents as well as a buffer system to reduce the extent of dye reduction during the dyeing of wool/PET blends. Richter and Wergerle [49] showed that azo disperse dyes that are susceptible to reduction are reduced, primarily by the thiol groups in wool, during the aqueous dyeing of wool/PET blends; hydrazo and amine degradation products were isolated, the extent of dyestuff reduction increasing with increase in pH, as found earlier by Shnider [48]. It has been observed [48] that under acidic conditions, the semi-acetal formed by degradation of the cellulosic chain can reduce certain disperse dyes during the dyeing of cotton/PET blends and also that dye saponification occurs during the HT dyeing of cellulose triacetate fibre; the use of acidic buffers to counteract these effects has been proposed. As discussed in section 1.2.6, some dispersing agents reduce azo disperse dyes.

EFFECT OF METALS. Dulling of shade of AQ disperse dyes can occur owing to the presence of metals in the dyebath, the extent of dulling varying from dye to dye [50]. Although sequestering agents can be employed to counter this problem [50, 51], whilst sequesterants are beneficial in the case of AQ disperse dyes, their presence can cause loss of colour yield of some azo dyes, especially during dyeing at pH values greater than 5. This has been attributed to the sequestering agent displacing metals from ligninsulphonate-dispersing agents which accentuates the reductive potential of this particular type of dispersant [51]. In order to minimise reductive dye decomposition, the pH of dyeing preferably should be in the range 4 to 5; reduction inhibitors may also be employed [45].

DISPERSING AGENTS. A detailed account of the effects of dispersing agents on dye adsorption is given in section 1.2.6. As mentioned above, disperse dyes are sparingly soluble in water; furthermore, the dyes, as

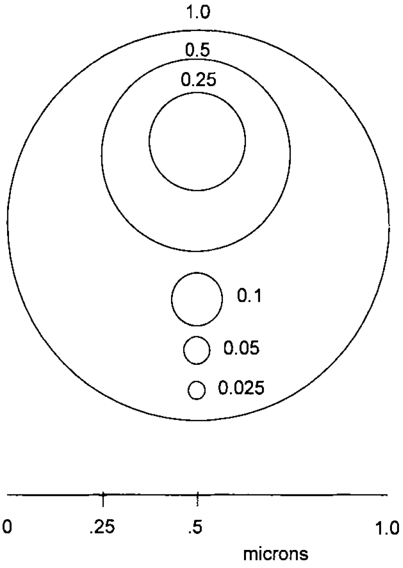


Figure 1.1 Range of size of particles present in a good dye dispersion [52]
(Reproduced with permission from the Society of Dyers and Colourists)

synthesised, are often crystalline and of varying particle size. These characteristics are inadequate for practical purposes as difficulties will arise in dispersing the dyes in water and the resultant dyeings will be unlevel and weak. In order to achieve the required particle size and particle size distribution (commonly a maximum of less than 1 μm [45, 52–54]) the disperse dye is milled, usually in the presence of a dispersing agent [17, 36, 53, 55–58]. Figure 1.1 shows the range of particle sizes present in a dye dispersion.

The dispersing agent, commonly anionic, ligninsulphonates or polycondensates of aryl sulphonic acids [53, 55, 56, 59, 60], facilitates milling by preventing agglomeration of the dye particles and enables the dye to be prepared in powder or liquid forms [17, 36, 56, 58]. Commonly, less dispersing agent is incorporated into disperse dyes prepared in liquid form than in powder form since the preparation of liquid brands entails less mechanical and thermal processing; also, liquid forms of the dyes are predispersed and therefore do not require to be redispersed in the dyebath. Although the dispersing agent also facilitates dispersion of the dye in water (Table 1.5), its main function, other than facilitating comminution of coarse dye particles, is to maintain a stable dispersion during dyeing [17, 36, 55–59]. Additional dispersing agent is often added to the dyebath to maintain dispersion stability, especially in the case of liquid forms of the dye and when dyeing is carried out at high temperature. A discussion of the effects of dispersing agent, particle size as well as the crystal form of the dye on dye adsorption is given in sections 1.2.4 to 1.2.6.

1.2.1. Aqueous phase transfer

Since their introduction in the 1920s, a considerable volume of work has attended the nature of the interaction of disperse dyes with hydrophobic fibres. Although much of this work has concerned fibres other than polyester, it is generally accepted that the mechanism of the aqueous phase transfer of disperse dyes is identical for all hydrophobic fibres.

Shortly after their introduction, Clavel [61] proposed that disperse dyes were adsorbed by secondary cellulose acetate fibres from a saturated aqueous solution of the dye which, during dyeing, was replenished by dissolution of dye particles present in a bulk dispersion. Burns and Wood [62] also proposed that the disperse dye was adsorbed on to secondary cellulose acetate from aqueous solution and suggested that adsorption occurred at sites present within the fibre. In contrast, Kartaschoff [63] proposed that the positively charged, solid dye particles were attracted to, and formed a surface layer on, the negatively charged secondary cellulose acetate fibre; the solid dye then dissolved or diffused within the substrate by means of a solid-state mechanism forming a solid solution.

Clavel's proposal is now generally accepted as describing the aqueous phase transfer of disperse dyes to hydrophobic fibres. As illustrated in Figure 1.2, a small amount of the disperse dye forms an aqueous solution with, initially at first, the greater proportion of the dye in dispersion in

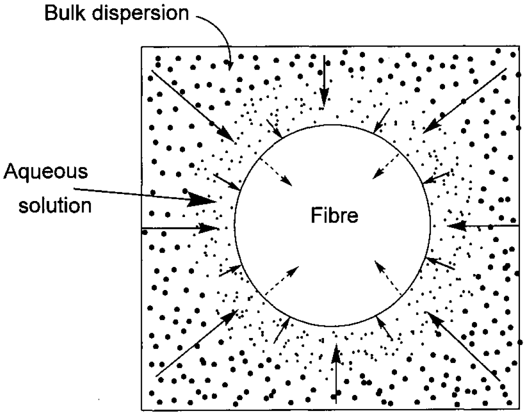


Figure 1.2 Mechanism of the aqueous phase transfer of disperse dyes to hydrophobic fibres

the dyebath. Monomolecular dye is adsorbed on to the surface of the fibre from the aqueous dye solution situated at the fibre surface; as dye molecules diffuse, monomolecularly, from the surface to the interior of the substrate, dye particles from the bulk dispersion dissolve in the depleted aqueous dye solution which is thus replenished with monomolecular dye that can be further adsorbed on to the fibre surface. This process continues until either the dyebath is exhausted of dye or the fibre is saturated with dye.

The mechanism by which the disperse dye interacts with the fibre has attended much debate; in the context of the solid solution mechanism proposed by Kartaschoff [63], several workers [64–67] demonstrated that when dyeing was carried out in the presence of dispersing agent, disperse dyes did not adhere to secondary cellulose acetate, thereby contradicting the suggestion made by Kartaschoff that the positively charged dye molecules were attracted to the fibre. However, Bird *et al.* [66, 67] showed that in the absence of dispersing agent, as was the case in Kartaschoff's work [63], disperse dye particles were attracted to cellulose diacetate and it has been suggested [16, 17] that in the presence of dispersing agent, the dye particles are negatively charged and therefore not attracted to the fibre. Although some workers have adopted Kartaschoff's solid solution theory to explain all disperse dye–hydrophobic fibre interaction, the adsorption-at-sites mechanism proposed by Burns and Wood has also gained support [16]; however, as discussed below, there is little difference between these two, seemingly diverse, theories.

1.2.2. Thermodynamics of dyeing

Although practical aspects of the dyeing of PET fibre with disperse dyes appeared shortly after its commercial introduction [8, 68–79] the first detailed discussion of the mechanism of dye–fibre interaction did not appear until 1953. Schuler and Remington [80] demonstrated that the uptake of three pure disperse dyes (1-amino-4-hydroxyanthraquinone (Figure 1.3), 1,4-dihydroxyanthraquinone and N,N′-diphenyl-3-nitrosulphanilamide), in the absence of dispersing agent, on PET fibres followed a Nernst or Partition mechanism obeying equation (1.1) wherein K is the partition coefficient, D_f and D_s represent the concentration of dye in the fibre and solution and S_f and S_s the saturation values of the dye in the fibre and solution, respectively.

$$\mathrm{K} = \frac{D_f}{D_s} = \frac{S_f}{S_s} \qquad (1.1)$$

These workers [80] showed that the isotherm obtained for each dye was linear up to saturation of the fibre; linear isotherms have also been obtained for the adsorption of disperse dyes on other hydrophobic [17,

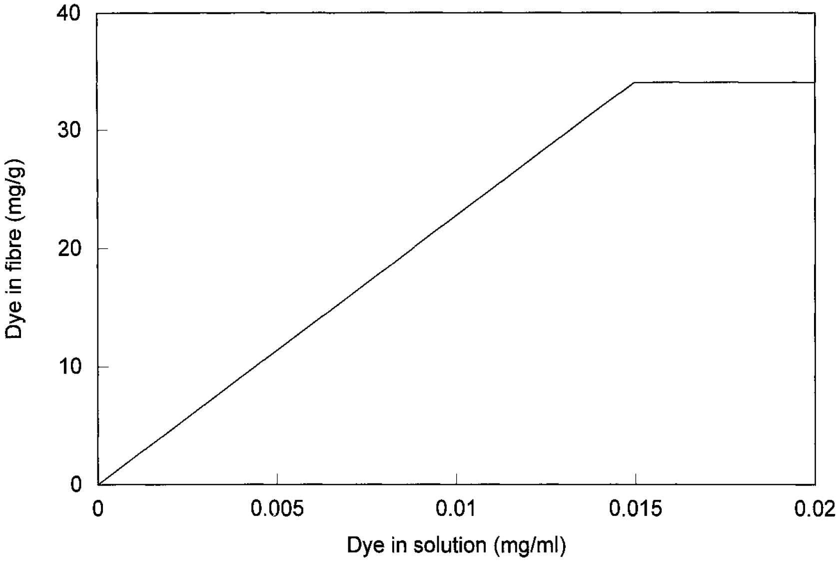


Figure 1.3 Adsorption isotherm of 1-amino-4-hydroxyanthraquinone on polyester at 98°C [80]
(Reprinted with permission from the Royal Society of Chemistry)

66, 81] as well as hydrophilic [17, 82, 83] fibres. From the linearity of the adsorption isotherm, Schuler and Remington [80] considered that the mechanism of adsorption of disperse dyes on PET was one of dye solution in the fibre, although solution was not ideal. The findings that linear partition isotherms have been obtained for the adsorption of disperse dyes on a variety of hydrophobic fibres have been considered to support the view that the disperse dye interacts with the fibre by means of a solid solution mechanism, according to which the dye dissolves and diffuses in the fibre as it would in an organic solvent. However, as Rattee and Breuer [31] point out, the view that the hydrophobic fibre acts as a solvent for the dye in a manner analogous to that of a solvent such as ethyl acetate, is highly tenuous, since linear partition isotherms are also obtained for the adsorption of disperse dyes on hydrophilic fibres such as wool. Indeed, as discussed by Vickerstaff [84], there is little difference between these two seemingly diverse theories. According to the solid solution theory, the dye will dissolve in the fibre by means of various forces of interaction, such as hydrogen bonding and dispersion forces. The adsorption-at-sites theory requires that the disperse dye interacts with sites in the fibre; since these sites can be considered as being identical to those with which the dye would interact if it dissolved in the fibre, then it can be proffered that there is little, if any, difference between the two mechanisms. Since, at present, no direct experimental evidence is available in support of either of these two mechanisms and that there may, in fact, be no difference between the two mechanisms, it seems reasonable to propose that the distinction between the mechanisms is nebulous. In the context of disperse dye adsorption on to polyester fibres, Patterson [85] and Patterson and Sheldon [86] obtained results which suggested that dye–polymer interaction could not be described as solid solution. In a discussion of the results obtained by several workers [86–90], Rattee and Breuer [31] consider that disperse dyes are adsorbed on to sites in the fibre, the energies of interaction being such that isothermal behaviour is obtained which is comparable to that of ideal mixing processes.

1.2.2.1. Molecular dispersion. Schuler and Remington [80] concluded from the linearity of the isotherms obtained for the adsorption of disperse dyes on PET that the dye was monomolecularly dispersed in both the fibre and dyebath phases; Hoffmann *et al.* [91] also proposed that the dyes were monomolecularly dispersed in both the dyebath and PET fibre phases. Merian [92] concluded that disperse dyes were monomolecularly distributed in PET fibres whilst Wegmann [93] considered that although a monomolecular distribution of CI Disperse Violet 1 (1,4-diaminoanthraquinone) in PET was probably achieved when dyeing had been carried out from a monomolecular solution of the dye, multilayer adsorption occurred when the dye was applied from over-saturated solution. Lipp-Symonowicz and Urbancyk [94] proposed that the dyes stimulate crystallisation of the component polymer macromolecules and participate in the formation of mixed, polymer–dye crystalline aggregates within the fibre whilst Kuehni [95], in a study of the normalised ratios of absorptivity of disperse dyes in solution and in polyester fibre, concluded that the dyes were partially aggregated in the fibre. In a study of the anomalous light fastness of disperse dyes on various fibres including PET [96], and in a later study of the fading of various dyes [97], Giles *et al.* proposed that although a proportion of the adsorbed dye was monodisperse the remainder was present in the fibre as very small aggregates, a view which this author, from surveys [98, 99] of relevant literature, concluded was applicable to all hydrophobic fibres. McDowell and Weingarten [100] concluded that with some disperse dyes, association of the dye in aqueous solution may occur. The relative lack of conclusive evidence in this context can, as discussed by Jones [101] be attributed to the experimental difficulties involved in such examinations. Nevertheless, it can be argued that the various forces of interaction that contribute to the substantivity of the hydrophobic dyes for hydrophobic fibres (discussed below) may well also contribute to dye–dye interaction (aggregation) in both the fibre and dyebath; however, the dis-aggregating effect of dispersing agents may reduce the propensity to aggregation in the dyebath. The foregoing clearly reveals that the precise molecular state of the dye in both the dyebath and PET fibre remains a matter of debate.

1.2.2.2. Dye–fibre substantivity. Schuler and Remington [80] proposed that the mechanism of adsorption of disperse dyes on PET was one of dye solution in the fibre; however, owing to the relatively large heat of dyeing obtained (61.7 kJ mol^{-1}) for the adsorption of 1-amino-4-hydroxyanthraquinone, these authors proposed that solution was not ideal and that the dye interacted with the fibre, possibly by hydrogen bonding. Although Allingham *et al.* [102], using dimethyl terephthalate as a homomorph of PET, also suggested that hydrogen bonding may be responsible for adsorption of dyes to the PET fibre, subsequent authors [58, 98, 99, 103–105] have proposed that the adsorption of disperse dyes on all hydrophobic fibres can be accounted for by the combination of strong hydrogen bonding and weak dispersion forces. Although Glenz *et al.* [106] concluded that hydrogen bonding was a more important contributor towards dye–fibre interaction than were dispersion forces, these authors proposed that dipole–dipole and dipole induced dipole forces of interaction also may operate between the fibre and the dye; Majury [87] also considered that dipole–dipole and dipole induced dipole forces as well as hydrogen bonding may be operative. It can thus be concluded that, as with all dyes on all fibres, the substantivity of disperse dyes towards PET fibre can be attributed to a variety of forces of interaction. In the case of disperse dyes and PET fibre, although it is considered that hydrogen bonding predominates, the relative contribution that dispersion forces, and possibly dipole–dipole and dipole–induced dipole forces, make towards substantivity will depend to a greater or lesser degree on the structure of the dye.

1.2.2.3. Solubility parameter concept. It is well known that marked differences in substantivity of disperse dyes for PET and other hydrophobic fibres can accompany subtle differences in the structure of the dyes; the solubility parameter concept has been employed in an attempt to explain such structure–substantivity relationships. The following account of solubility parameter concept serves only as a brief introduction; more detailed accounts are available [107–109]. In 1916 Hildebrand and Scott [108] published the first of many papers concerning the compatibility of nonpolar compounds to which Scatchard [110] later introduced the concept of cohesive energy density (CED). In a liquid, the molecules possess a potential energy, E, that arises from the forces of attraction operating between the molecules and which is equal in magnitude to the energy required to separate the molecules by an infinite distance. The cohesive energy is numerically equal to the potential energy per unit volume of the material and, since E for the individual molecules in a liquid is reduced to zero during evaporation, *CED* is defined [108] as the energy of vaporisation per cm^3 and its square root as the solubility parameter, δ (equation (1.2)), where H_v and E_v are, respectively, the heat and energy of vaporisation of the liquid, V the molar volume of the liquid, R the gas constant and T the temperature (K).

$$\delta = (CED)^{0.5} = \left(\frac{\Delta E_v}{V}\right)^{0.5} = \left(\Delta H_v - \frac{RT}{V}\right)^{0.5} \qquad (1.2)$$

CED and thus δ can be measured for all vaporisable compounds using equation (1.2) from a knowledge of the molar heat of vaporisation; δ for liquids can also be determined using methods based on the physical properties of the liquids [107–109, 112]. The solubility parameter concept was developed to predict the ease of mixing of non-polar liquids in terms of the enthalpy of mixing, ΔH_m (equation (1.3)), wherein V_m is the total volume of the mixture and V_1 and V_2 are the volume fractions of the two liquids in the mixture) but has been extended to embrace polar solvents and polymers as well as the mixing of fibres (semicrystalline polymers) with dyes and also carriers.

$$\Delta H_m = V_m[(\delta_1 - \delta_2)V_1 V_2 \qquad (1.3)$$

In the context of a polymer/solvent system, for a polymer to dissolve spontaneously in a solvent, then the free energy change (ΔG_m) of the process must be negative (equation (1.4)), where ΔG_m, ΔH_m and ΔS_m are, respectively, the free energy, enthalpy and entropy changes on mixing.

$$\Delta G_m = \Delta H_m - \mathrm{T}\,\Delta S_m \qquad (1.4)$$

Since the dissolution of a polymer in a solvent is always accompanied by an increase in entropy, then, according to equation (1.4), the magnitude and sign of the enthalpy change involved (ΔH_m) determines the sign of ΔG_m. Thus, in order for ΔG_m to be negative and therefore for mixing to occur, ΔH_m must be negative or zero, or, if positive, must be numerically less than the term ($\mathrm{T}\,\Delta S_m$); usually, ΔH_m is positive and thus mixing will occur optimally when ΔH_m is at a minimum. Equation (1.3) shows that ΔH_m is at a minimum when the solubility parameter of both components (in this case polymer and solvent) are equal. Therefore, in essence, the solubility parameter concept predicts that two components will be miscible if the solubility parameters of the components coincide; the application of this theory in the context of fibres has been discussed by Ingamells [112] and Moore [113].

As mentioned, there are several methods available for determining the solubility parameter of a compound. Commonly, the group molar attraction constant method of Small [114] or Hoy [115] has been used to determine δ of disperse dyes [116–124], although Siddiqui [119, 125] used a solubility method. Different values of δ have been obtained for the same disperse dye by different workers [116, 119, 120, 125], which can be attributed to the difference in the methods employed in their determination. From a consideration of the various groups present in both PET fibre and typical disperse dyes, three contributions to the cohesive energy density can be expected for each component – namely, dispersion forces, hydrogen bonding and polar forces. Although the solubility parameter concept originally concerned only dispersion forces, various modifications [107, 109, 111] have been made to the concept so as to permit the partition of the total solubility parameter (δ_t) into contributions from the various forces involved, as given by equation (1.5) in which δ_d, δ_p and δ_h are the contributions from dispersion forces, polar forces and hydrogen bonding respectively:

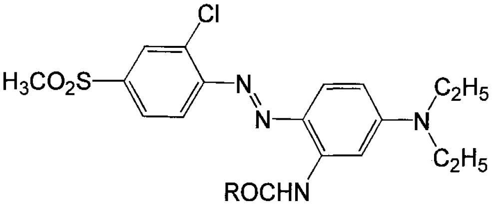
$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (1.5)$$

More simply, equation (1.5) takes the form of equation (1.6), where δ_a, the association solubility parameter, represents all polar forces that contribute to cohesive energy density.

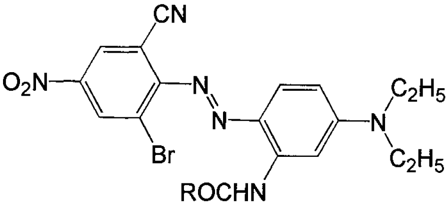
$$\delta_t^2 = \delta_d^2 + \delta_a^2 \qquad (1.6)$$

Owing to the non-volatility of polymers, methods other than from heats of vaporisation must be employed to determine their solubility parameters [107, 109, 111]. Several values, for example, 10.7 [113, 114, 116], 10.8 [117], 11.2 and 11.3 [116] (cal cm^{-3})$^{0.5}$ have been ascribed to the total solubility parameter (δ_t) of PET, the variation in these values being attributable to the different methods employed in their determination. Generally, values of solubility parameter are quoted at 25°C and will decrease with increasing temperature; in this context, Urbanik [116] cited that the value of δ_t for PET will change from 11.2 (cal cm^{-3})$^{0.5}$ at 25°C to 10.4 (cal cm^{-3})$^{0.5}$ at 129.4°C and the values of δ_d and δ_a will reduce from 9.6 to 8.9 and from 5.8 to 5.4. (cal cm^{-3})$^{0.5,}$ respectively, over the same temperature difference. Koenhen and Smolders [126], using several methods of determination, gave values of 9.54, 1.7 and 4.2 (cal cm^{-3})$^{0.5}$ for δ_d, δ_p and δ_h contributions respectively to the δ_t of PET and values of 4.8 [118], 4.53 [123] and 5.8 [116] (cal cm^{-3})$^{0.5}$ have been quoted for the δ_a contribution at 25°C. Although, owing to differences between the methods of determination, the values quoted in the literature for the total solubility parameter, δ_t, and the δ_d, δ_a and δ_p contributions for both PET and disperse dyes are not absolute, they nevertheless are reasonably consistent.

In the context of the application of the solubility parameter concept to the substantivity of disperse dyes towards PET fibres, Ibe [118] determined δ_t for several disperse dyes and attempted to relate the solubility of the dye in both cellulose di- and triacetate to the δ_t of the dye; a very low correlation was obtained. Kaushik and Deshpande [127] also obtained no



XI: R = $-CH_3$; XII: R = $-C_2H_5$

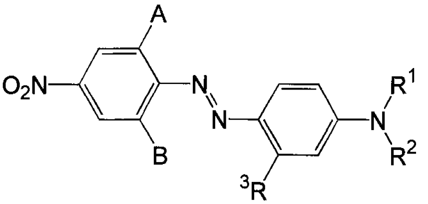


XIII: R = $-C_2H_5$; XIV: R = $-CH_3$

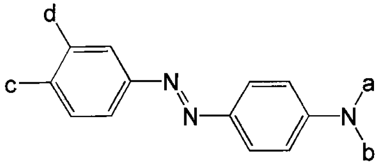
correlation between saturation uptake and δ_t of six monoazo disperse dyes on Indacrylon fibre.

Gerber [117], in a study of the relationship between the structure of monoazo disperse dyes and their dyeing behaviour on polyester, found that of two pairs of dyes, XI/XII and XIII/XIV of δ_t 11.3/13.0 and 10.9/11.7 (cal cm^3 mol^{-1})$^{0.5}$, respectively, high substantivity was exhibited only by dyes XI and XIII whose δ_t deviated from that of PET (δ_t = 10.8 (cal cm^3 mol^{-1})$^{0.5}$) by less than one unit.

This worker also found that of 60 monoazo dyes of general structure XV, for those dyes which displayed very high substantivity towards PET,



XV



XVI

(Reprinted with permission from AATCC)

Table 1.2 Disperse dyes used by Ingamells and Thomas [123]

Dye	Substituent in XVI			
	a	b	c	d
A	CH_3	CH_3	OCH_3	–
B	C_2H_5	C_2H_5	CH_3	–
C	H	C_2H_5	CH_3	–
D	CH_3	CH_3	–	–
E	C_2H_5	C_2H_5	–	–
F	CH_3	CH_3	Cl	–
G	C_2H_5	C_2H_5	Cl	–
H	C_2H_5	C_2H_5	NO_2	–
I	C_2H_5	C_2H_5	NO_2	CH_3
J	C_2H_5	C_2H_5	NO_2	Cl
K	C_2H_5	C_2H_5	NO_2	NO_2
L	H	CH_3	NO_2	–

a linear relationship existed between the molar attraction constant (ΣF_i) and molar volume (V_M) of the dyes. As $\delta_t = \Sigma F_i/V_M$ (the slope of the straight line obtained for the ΣF_i versus V_M plot was 10.8 (cal cm^{-3} mol^{-1})$^{0.5}$, this corresponding to the δ_t of the fibre used, this author [117] therefore concluded that suitable dyes for the fibre must have a value of δ_t close to that of the fibre. However, as only few dyes whose total solubility parameter lay in the region 10.3 to 11.3, this being within one (cal cm^{-3})$^{0.5}$ unit of that of polyester (δ_t of 10.8), showed good substantivity towards the substrate, this worker commented that coincidence of δ_t for dye and polymer does not necessarily imply miscibility of the two components since the nature of the cohesive forces present in dye and PET may differ [117]. This latter point was investigated by Ingamells and Thomas [123] who measured the equilibrium uptake of twelve closely related monoazo disperse dyes of general structure XVI (Table 1.2) on PET at 100°C.

The series of monoazo dyes used had a restricted range of total (δ_t) and dispersion (δ_d) solubility parameter values that were close to the respective values for PET (δ_t of 10.56 and δ_d of 9.54 [126]) but displayed

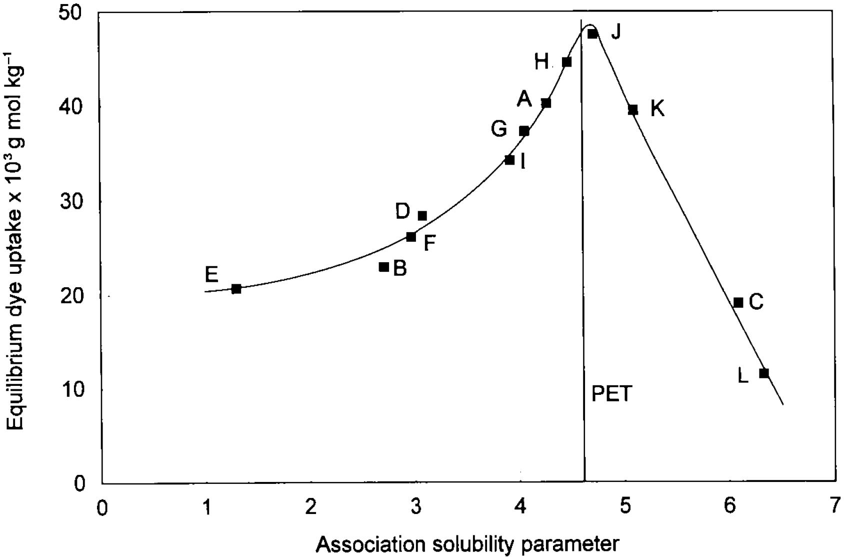


Figure 1.4 Equilibrium uptake of twelve disperse dyes on PET as a function of δ_a (the dotted line represents the δ_a of PET) [123]
(Reprinted with permission from AATCC)

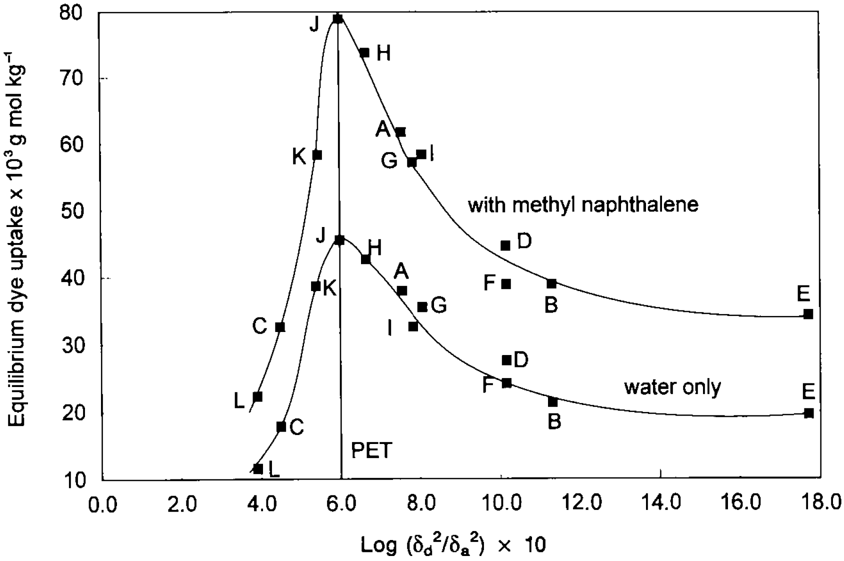


Figure 1.5 Equilibrium uptake of twelve disperse dyes on PET as a function of (δ_d^2/δ_a^2) (the dotted line represents the (δ_d^2/δ_a^2) of PET) [123]
(Reprinted with permission from AATCC)

a wide range of association solubility parameter (δ_a) values that were within some ± 2 (cal cm^{-3})$^{0.5}$ units of the δ_a value of PET (δ_a of 4.53 [126]). These authors [123] demonstrated that equilibrium uptake of the dyes increased with increasing δ_a value of the dye, reaching a maximum value for the dye whose association solubility parameter was closest to that of the fibre, and thereafter decreased with further increase in δ_a of the dye (Figure 1.4). Furthermore, these workers [123] also claimed that the relative magnitude of the dispersion (δ_d) and polar (δ_a) cohesive forces involved in dye–fibre interaction, as given by (δ_d^2/δ_a^2), influence the affinity of disperse dyes for PET insofar as, for the twelve dyes examined, maximum equilibrium dye uptake occurred when the δ_d^2/δ_a^2 of the dye was closest to the value of δ_d^2/δ_a^2 for PET (Figure 1.5), a finding subsequently observed by Kaushik and Deshpande [127] for the saturation uptake of six monoazo dyes on PAN fibre.

However, this latter result may not provide conclusive evidence of the relative contributions that dispersion and polar forces make towards dye affinity since, although the series of dyes used by Ingamells and Thomas [123] displayed a wide range of association solubility parameter (δ_a) values that were within some ± 2 (cal cm^{-3})$^{0.5}$ units of the δ_a value of PET, the dyes had a restricted range of dispersion (δ_d) solubility parameter values that were close to the respective value for PET. Thus, this work [123] showed that maximum dye–fibre affinity occurred when the association solubility parameter of the dye was close to that of the fibre.

It is therefore possible to conclude that the solubility parameter concept has provided some information concerning the nature of the interaction between the dyes and PET and, as Gerber [117] commented, the concept deserves further consideration in this context.

1.2.3. Kinetics of dyeing

Glenz *et al.* [106] determined the rate of dyeing curves for several disperse dyes on PET from infinite dyebaths and observed that values of apparent diffusion coefficient, calculated using Hill's equation for different dyeing times, were reasonably constant over a range of M_t/M_∞ values. Patterson and Sheldon [128] showed that the rate of dyeing of three disperse dyes on PET at 100°C was independent of dye concentration insofar as, in a plot of dye uptake/dyebath concentration versus dyeing time for several dyebath concentrations, all points lay on a single curve (Figure 1.6). These workers [128] also demonstrated that the diffusion coefficients of CI Disperse Red 1 and CI Disperse Red 15 within both continuous filament and staple PET fibre, calculated using Vickerstaff's [84] approximation of Crank's equation for diffusion from semi-infinite media employing desorption studies carried out over the temperature range 70 to 95°C, were independent of concentration. Confirmation of the concentration-

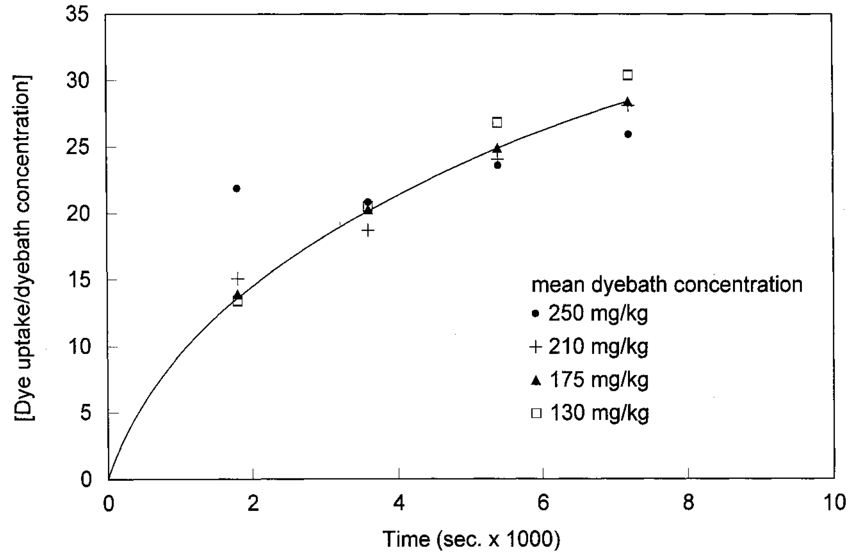


Figure 1.6 Concentration-independence of dyeing rate of CI Disperse Yellow 1 on PET fibre for different mean dyebath concentrations at 100°C [128]
(Reprinted with permission from D. Patterson and the Royal Society of Chemistry)

independence of dye diffusion within PET at 100°C has subsequently been obtained by other workers using infinite dyebaths [129–132]. Datye and Rajendran [131] demonstrated the concentration independence of diffusion coefficient of 4-anilino-1,5-dihydroxy-8-nitroanthraquinone within dyed PET at 210°C and also that in the case of two initial dye concentrations, values of diffusion coefficient calculated using several equations were reasonably consistent. In later work, Datye *et al.* [132] showed that the diffusion coefficients of ten disperse dyes within PET at different temperatures up to 210°C were concentration independent. As similar results have been obtained by other workers for disperse dyes on several hydrophobic fibres, it is considered [16, 133, 134] that the diffusion of disperse dyes within all hydrophobic fibres is governed by a constant diffusion coefficient. It is considered [16, 134] that owing to the concentration-independent diffusion coefficient of disperse dyes within hydrophobic fibres, concentration–distance profiles for dye diffusion within such fibres typically show that experimental results fall on the curve calculated from Fick's law assuming a constant diffusion coefficient, thereby indicating that a constant surface concentration of dye is achieved. However, Blacker and Patterson [135] obtained evidence of time-dependent surface concentration.

Glenz *et al.* [106], employing a size factor, S, that was considered to reflect the geometrical properties of disperse dyes, found that for several disperse dyes on PET, the reciprocal of diffusion coefficient increased linearly with increase in S. In a similar manner, Sekido and Kojima [129] found that the diffusion coefficient of several disperse dyes within PET decreased with increasing molecular size of the dye. Datye *et al.* [136] found that for a series of dyes of similar constitution, the diffusion coefficient of the dyes in PET at 170, 190 and 210°C decreased with increasing molecular area of the dye and Cegarra and Puente [137] devised an equation relating the diffusion coefficient, time of half-dyeing ($t^{1/2}$) and the specific surface of several disperse dyes on PET. These findings support those of other workers using secondary cellulose acetate [92, 138, 139] and nylon [84], thereby indicating that the diffusion of disperse dyes within hydrophobic fibres is related to steric factors of the dye.

Glenz *et al.* [106] obtained a value of approximately 34 kcal mol^{-1} for the activation energy of diffusion (E^*) of CI Disperse Yellow 1 on PET over the temperature range 100 to 138.5°C and Datye *et al.* [132] obtained E^* values in the range 24 to 39 kcal mol^{-1} for the diffusion of several disperse dyes in PET at temperatures over the range 170 to 210°C. Patterson and Sheldon [128] obtained greater values for E^* (between 46 and 80 kcal mol^{-1}) for the diffusion of CI Disperse Red 1 and CI Disperse Red 15 in PET over the range 70 to 95°C and also found that values of E^* varied for the diffusion of the same dye within different types of PET fibre, increasing with increase in draw ratio of continuous filament and being greatest for heat-set staple fibre. In a similar manner, Cegarra and Puente [140] obtained values for E^* of between 67 and 75 kcal mol^{-1} for the diffusion of CI Disperse Red 15 within PET over the temperature range 70 to 95°C and found that the values of E^* varied between fibres of different denier. Patterson and Sheldon [128] considered that the high E^* values obtained for dye diffusion coupled with the low diffusion coefficients confirmed that dye diffusion within the polymer was the rate-determining step in the dyeing process. These authors [128] also found that the diffusion coefficients of both CI Disperse Red 1 and CI Disperse Red 15 at 70°C were considerably lower than those at 80°C and higher temperatures, the values obtained at this lower temperature falling well below the Arrhenius plots from which the E^* values had been derived. It was proposed [128] that the activation energy of diffusion below 80°C was very high owing to the T_g of PET being in the region of 80°C and the corresponding virtual absence of segmental mobility of the polymer chains below the T_g. Furthermore, Patterson and Sheldon [128] considered that the E^* values obtained in their work were close to the value of 40 kcal mol^{-1} obtained [141] for the activation energy of viscous flow, thereby indicating that the size of the polymer segments involved in both dye diffusion and viscous flow were similar. Blacker and Patterson [135] found that the apparent diffusion coefficients of three disperse dyes within PET at 100°C decreased with increasing time of dyeing. From the finding that dye molecules adsorbed in later stages of dyeing were more highly orientated than those adsorbed earlier, these workers [135] proposed that the observed reduction in diffusion coefficient that accompanied an increase in dyeing time was attributable to an increase in the entropy of activation of diffusion arising from the observed increase in orientation of the system.

Several workers have proposed empirical rate of dyeing equations by which the rate of dyeing of disperse dyes can be described in terms of a rate constant. Patterson and Sheldon [128] concluded that in the initial stages of dyeing, the rate of dye uptake could be described by equation (1.7), in which Q_t is dye uptake at time t and c_b the dyebath concentration.

$$Q_t = \text{const. } c_b t^{1/2} \tag{1.7}$$

Cegarra and Puente [130] concluded that equation (1.8) fully represented the kinetics of dyeing PET where M_t and M_∞ represent the masses of dye adsorbed at time t and equilibrium, respectively, and k' is the velocity constant.

$$\frac{M_t}{M_\infty} = \left[1 - \exp\left(\frac{-2k'}{M_\infty^{\,2}}\right)t\right]^{1/2} \tag{1.8}$$

Militky [142] developed equation (1.9) whereby the integral diffusion coefficient, D', of Hill's equation could be obtained from the velocity constant, k', of the Cegarra–Puente equation (equation (1.8)) and the radius, r, of the fibre.

$$D' = 0.204k'r^2 \tag{1.9}$$

Etters and Urbanik [143] developed equation (1.10) to describe the experimentally determined rate of disperse dyeing curves and also an equation for calculating time/temperature relationships necessary to maintain a linear dye exhaustion rate during the package dyeing of PET with disperse dyes.

$$\frac{M_t}{M_\infty} = [1 - \exp(-k''t^{1/2})] \tag{1.10}$$

Shibusawa [144] used statistical curve-fitting to compare the rate of dyeing curves calculated from the equations of Wilson and Newman, which describe the rate of diffusion of a non-ionic dye in a cylindrical fibre from a finite and infinite dyebath, respectively, with those obtained from several empirical rate of dyeing equations in the range M_t/M_∞ of zero to about 0.8. Shibusawa [144] demonstrated that many of the empirical equations, including equation (1.8), described the rate of disperse dyeing when dye adsorption was characterised by a delay in the early stages of dyeing (i.e. for sigmoidal plots of M_t/M_∞ versus $t^{1/2}$) as have been obtained for the sorption of disperse dyes on PET [145, 146] and also cellulose diacetate [89, 147] fibres. Shibusawa [144, 148] considered that the sorption delay can be attributed to resistance towards dye transport provided by the diffusional boundary layer that surrounds the fibre. This author [144] also found that equation (1.10) described the rate of disperse dyeing which was devoid of an initial sorption delay.

Bird [149] suggested that in aqueous dyeing with disperse dyes, the dyebath initially behaves as a saturated solution of dye but at some later stage becomes unsaturated. Etters and McGregor [150] considered that disperse dyeing systems may follow one of three main types of kinetic behaviour – namely, finite, infinite and transitional. If the dyebath is initially unsaturated, then solutions of Fick's equation for finite dyebaths are appropriate whereas for an initially saturated dyebath, then either infinite or transitional dyebath kinetics operate. These workers [150] proposed that when dyeing at high depths of shade with dyes of low aqueous solubility, the dyebath may remain saturated throughout the course of dyeing and thus infinite dyebath kinetics can be employed, whilst in the case of dyes of high water solubility when applied at low concentrations or at high liquor ratios, finite kinetics are appropriate.

1.2.4. Effect of crystal form of the dye on dye adsorption

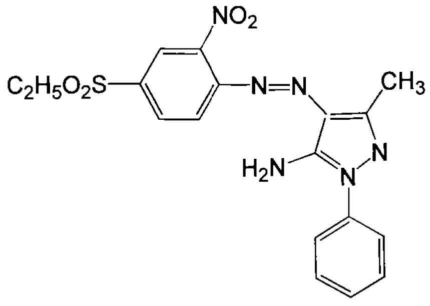
Biedermann [151] demonstrated that the saturation uptake of five different crystal forms (α, β, γ, δ and ε (amorphous)) of an aminopyrazole yellow dye (XVII) on cellulose diacetate, at 80°C in the presence of an anionic dispersing agent, increased with decreasing thermodynamic stability of the crystal form of the dye (Table 1.3) and proposed that these results were applicable to polyester fibres. The findings (Table 1.4) of Shenai and Sadhu [152] that three crystal forms of CI Disperse Yellow 42 and CI Disperse Red 54 possessed different saturation values on polyester at 100°C in the presence of an anionic dispersing agent support the findings of Biedermann.

It is considered [52, 151] that the differing saturation values obtained for different crystallographic forms of a chemically identical dye are attributable to a difference in the vapour pressure, and, thus, solubility of the

Table 1.3 Saturation values of different crystal forms of XVII on cellulose diacetate at 80°C [151]

Crystal form	Saturation value (g dye 100 g^{-1} fibre)
α	0.77
β	1.0
γ	2.13
δ	3.07
ε	5.5

(Reproduced with permission from the Society of Dyers and Colourists)



XVII

various forms of the dye in both the water and fibre. Since the solubility of a particular form of a dye will depend on the difference between the chemical potential of that crystal modification in the solid state compared with that in either the fibre or water phases, then the difference in chemical potential, and hence solubility, will be lowest for the most stable crystallographic form of the dye since this is of lowest energy content. Jones [153] proposed that modification of a particular crystallographic form of a disperse dye can occur during dyeing under aqueous conditions or in thermal treatments and demonstrated that such modifications occurred when an aqueous suspension of crystals of CI Disperse Yellow 3 was heated at 80°C. Biedermann [151] showed that although metastable forms of an aminopyrazole yellow dye gave higher saturation values on cellulose diacetate, they transform to more stable, lower solubility forms upon heating during dyeing. Subsequently, Jones and Patterson [154] used hot-stage microscopy to demonstrate the transformation of the γ form of an aminopyrazole yellow dye to the β form that occurred during heating of an aqueous dispersion of the dye in a non-ionic dispersing agent as well as the conversion of the β form of the dye to the α form brought about by heating in the presence of an anionic dispersing agent and also employed differential scanning calorimetry (DSC) to detect transformations in disperse dye solids during thermal treatments [155, 156]. It is con-

Table 1.4 Saturation values of crystal forms I, II and III of two disperse dyes on PET at 100°C [152]

Dye	Saturation value (g dye 100 g^{-1} fibre)		
	I	II	III
CI Disperse Yellow 42	0.97	1.10	1.53
CI Disperse Red 54	1.30	1.09	1.08

(Copyright © 1976 John Wiley & Sons, Inc. Reprinted by permission) sidered [45] that transformation proceeds more rapidly under aqueous conditions than in dry dyestuff. Such transformations, which can give rise to dyeings of low rub fastness [151] as well as reduced colour yield and dyeing rates [153], can be influenced by the presence of either non-ionic [155] or anionic [151, 154, 157, 158] surfactants as well as carriers [45]. In an excellent review of this particular topic, Braun [52] discusses the difficulties involved in determining the dissolution and thus dyeing properties of enantiotropic modifications of a disperse dye. This author [52] concludes that although, during dyeing, it is probable that a metastable form of a disperse dye is transformed into a more stable, less soluble form, with some exceptions, the effect of the various modifications on the dyeing properties of the dye is small in comparison to the characteristics imparted to the dye dispersion by milling and formulation. Nevertheless, many disperse dyes are sold in a metastable form; often [45] the dye maker submits the dye to a thermal treatment in order to secure a form that has adequate dispersion stability and dyeing behaviour.

1.2.5. Effect of particle size and distribution on dye adsorption

Vickerstaff and Waters [64] observed that the uptake of 1-methylamino-4-anilinoanthraquinone on to cellulose diacetate at 85°C after 24 hours increased with increasing severity of milling of the crystalline dye. Daruwalla and Limaye [159], in a study of the steam printing of disperse dyes on cellulose diacetate, found that the rate of transfer of CI Disperse Red 1 from starch increased with increasing time of milling of the dye. These results are attributable to the fact that, in a manner analogous to that of the vapour pressure of a liquid in spherical drops, the aqueous solubility of disperse dye particles in a dispersion increases with decreasing particle size. Thus, an increase in milling reduces the size of the dye particles, thereby enhancing the solubility and hence dye uptake.

In a typical dispersion comprising a distribution of particle sizes, the greater solubility of the small particles may cause the solution to become supersaturated with respect to the large particles with the result that dye crystallisation occurs on the surface of the large particles. Such crystal growth will increase the mean particle size and thus reduce the mean solubility of the dispersion with the result that dye uptake falls. This crystal growth or Ostwald maturation has been demonstrated by several workers [45, 160] including Vickerstaff and Waters [64] who observed that the saturation uptake of 1-isobutylamino-4-anilinoanthraquinone decreased during prolonged dyeing of cellulose diacetate. Crystal growth is intensified and accelerated by periodical heating and cooling, as often is encountered during shading operations. Heimann [53] considers that the phenomenon is unimportant in HT dyeing; however, crystal growth will occur during cooling of the dyebath owing to crystallisation of dye which had previously been in solution at the higher temperature. In a study of the high-temperature dyeing of texturised PET, Skelly [161] showed that several Terasil (Ciba-Geigy) disperse dyes could be classified into three groups according to their propensity to recrystallisation during cooling from 130 to 95°C in both the absence and presence of dispersing and levelling agents. Beckmann and Hamacher-Brieden [162] observed that non-ionic levelling agents can promote crystal growth, thereby reducing saturation uptake of disperse dyes on PET, a view subsequently confirmed by Skelly [161], who showed that only anionic products were suitable additional dispersing agents for the HT package dyeing of PET; anionic dispersants are considered to stabilise a disperse dye dispersion against crystal growth [45]. In a review of the use of dispersing agents in the dyeing of PET using disperse dyes, Heimann [53] concludes that in addition to crystal growth and crystal transformation contributing to particle size increase during dyeing, agglomeration of dye particles resulting from deterioration of the efficiency of dispersing agents above a certain temperature may also contribute. This worker [53] also suggests that such agglomerates may be redispersed at lower temperatures owing to the corresponding increase in efficiency of the dispersing agent at lower temperatures.

1.2.6. Effect of dispersing agents on dye adsorption

As discussed previously, dispersing agents are used to facilitate milling of the dyes and to maintain dispersion stability (i.e. prevent agglomeration of dye particles) during dyeing. Dispersion stability is of prime importance in exhaust dyeing since failure of the dispersion will result in agglomeration and possibly precipitation of the dye which, in turn, will result in unlevel dyeing. The propensity to dispersion failure is greatest in the case of HT dyeing [56, 163] and additional dispersing agent can be added to the dyebath to maintain dispersion stability under these conditions [55]. Skelly [161] showed that only selected anionic dispersing agents are suitable as added dispersing agents for the HT package dyeing of texturised PET. Some dispersing agents, such as ligninsulphonates, promote reduction of azo disperse dyes under HT dyeing; Murray and Mortimer [59] first reported the reductive tendency of ligninsulphonates, which was subsequently confirmed by several authors [164–167] and has been attributed to the presence of catechols and other easily oxidisable species in lignin [164]. Although azo disperse dyes are more susceptible to reduction than are anthraquinone dyes, the latter undergo partial reduction to leuco derivatives which can be re-oxidised using mild oxidants [166]. Murray and Mortimer [59] showed that the presence of air during dyeing counteracts the reductive effect of ligninsulphonates, a finding that was subsequently confirmed by Dilling [164]. Ions of metals of high oxidation potential, such as Fe^{2+} and Cu^{+}, were shown to accentuate the reductive tendency of the ligninsulphonates [164] whereas other metal ions, such as Mn^{2+}, Zn^{2+}, Mg^{2+}, and Ni^{2+} inhibited azo dye reduction. Dilling [164] also demonstrated that the addition of sodium nitrite to ligninsulphonate eliminated the reduction of several disperse dyes in both an oxygen-enriched and oxygen deficient environment in both the presence and absence of iron salts. In a later study [168] this worker compared the dispersing properties of sodium and ammonium ligninsulphonate salts with those of ligninsulphonate salts incorporating other inorganic ions, alkylamines and alkanolamines. It was demonstrated [168] that amine and alkanolamine salts of ligninsulphonates exhibited a considerably lower reductive propensity than sodium ligninsulphonate salts. Yin [169] demonstrated that increasing the relative molecular mass (M_r) and phenolic hydroxyl content of a ligninsulphonate dispersing agent decreased the reductive tendency of the dispersing agents towards azo disperse dyes. Synthetic thickeners used in textile printing are sensitive to both electrolytes and anionic dispersing agents [170], as a result of which several dye makers [53] have marketed disperse dyes, dispersed using non-ionic dispersants in place of anionic products. In addition to being compatible with many thickeners, these dyes yield brighter shades, higher colour yield and are less susceptible to reduction than conventionally dispersed dyes [170].

Dispersing agents increase the aqueous solubility of disperse dyes, as demonstrated by Bird [171] who found that the aqueous solubility of several pure disperse dyes, at 25°C, was increased in the presence of pure sodium 1-oleyl-4-anisidine-2-sulphonate to an extent that depended on the solubility of the dye. Furthermore, this worker demonstrated [171] that the aqueous solubility of several dyes at 80°C was increased in the presence of other dispersing agents to an extent which depended on the dispersing agent used (Table 1.5).

Dispersing agents also affect both the rate and extent of uptake of disperse dyes on hydrophobic fibres; Bird [171] showed that the addition of

Table 1.5 Solubility at 80°C of pure (dispersant-free) disperse dyes in water and 0.5% dispersing agents (Lissapol C (ICI) [sodium oleyl sulphate]; Dispersol VL (ICI) [fatty alcohol-ethylene oxide condensate]) [171]

CI Disperse	Solubility ($mg\ dm^{-3}$) at 80°C			
	water	Sodium oleate	Lissapol C	Dispersol VS
Red 1	7	240	104	41
Orange 3	9.5	60	31	29
Orange 1	0.5	46	18	21.5
Violet 1	17	57	36	27.5
Red 11	11	49	36	20
Blue 24	5.5	40	17	8

(Reproduced with permission from C. L. Bird and the Society of Dyers and Colourists) dispersing agent lowered the exhaustion of the dyes on cellulose diacetate to an extent that was proportional to the degree of solubilisation affected. In later work, this author [173] demonstrated that the exhaustion of several commercial disperse dyes on cellulose diacetate at 80°C decreased with increasing concentration of sodium 1-oleyl-4-anisidine-2-sulphonate and that the equilibrium partition coefficient of CI Disperse Red 1 on secondary cellulose acetate at 80°C decreased with increasing concentration of the pure dispersing agent [173]. Furthermore, it was found [173] that whilst at concentrations of 2 and 4×10^{3}M sodium 1-oleyl-4-anisidine-2-sulphonate, identical saturation values for the dye were obtained, a concentration of 2×10^{-2}M markedly lowered the saturation value. These findings can be attributed to the dispersing agent having increased the aqueous solubility of the dye, as previously demonstrated by Bird [171] or, as Peters [17] comments, having increased the affinity of the dye for the aqueous phase. Bird *et al.* [172] observed that the rate of uptake of CI Disperse Blue 24 on to cellulose diacetate at 80°C increased with increasing concentration of anionic dispersing agent, which was attributed to the surfactant having increased the rate of solubilisation of the particles of this low aqueous solubility dye. In contrast, the rate of uptake of two, more soluble, commercial disperse dyes decreased with increasing concentration of dispersing agent, this being attributed to a lowering of the effective concentration of dye in the dyebath [172]. In the context of the effects of dispersing agents on the dyeing of PET fibres, Carbonell [163] showed that a typical anionic dispersing agent (disodium dinaphthylmethane disulphonic acid) lowered both the rate and saturation uptake of two disperse dyes on Dacron at 130°C, the extent of this decrease increasing with increasing concentration of dispersing agent in the dyebath; this author [163] attributed this effect, the extent of which differed for the two dyes used, to the dispersing agent having increased the aqueous solubility of the dye. Similarly, Thakore *et al.* [60] also demonstrated that the uptake of seven commercial disperse dyes on PET fibre at 130°C decreased with increasing concentration of Dispersol F (Sandoz) in the dyebath, this effect being more marked for azo rather than anthraquinone dyes and also for dyes of higher aqueous solubility.

1.2.7. Effect of levelling agents on dye adsorption

Although dispersing agents are known to improve the migration [56] and levelling [163] of disperse dyes on polyester fibres under HT dyeing conditions, levelling during exhaust dyeing is most usually expedited by the addition, to the dyebath, of specific levelling agents, which can be non-ionic or anionic surfactants or an anionic/non-ionic surfactant blend. Non-ionic compounds increase the solubility of the dye thereby lowering the initial strike [60] and overall rate of dye uptake [56,174-176] which can also cause a restraining effect that results in a loss of colour yield [56, 60, 162, 174]. However, such compounds, whose effects are highly dye specific, can have a deleterious effect on the stability of dyebath dispersions [56, 59, 162, 174]. The solubility of the agents decreases with increasing temperature [59] and, if the temperature of the dyebath is raised above the agent's cloud point (the temperature at which the surfactant becomes insoluble), then the dye dispersion breaks down resulting in dye aggregation and attendant unlevel dyeing. Although some non-ionic levelling agents of high cloud point do not cause dye aggregation, they can, nevertheless, impair dispersion stability [56]. Herlinger *et al* [176–178] propose that at concentrations greater than the CMC (critical micelle concentration) non-ionic agents lower dye uptake owing to a corresponding increase in solubility of the dye, this reduction increasing with increasing concentration of surfactant [177]. Anionic agents increase the cloud point of non-ionic levelling agents [59] and the use of non-ionic/anionic surfactant blends has been described [59, 175]. Careful consideration must be given to the amount of non-ionic levelling agent used owing to the often marked restraining effect exerted by these compounds on dye uptake. Anionic levelling agents, typically polycondensate dispersing agents, exhibit little if any restraining effect on dye uptake but can induce dye migration [56], are considered not to penetrate the fibre [162] and function by increasing the solubility of the dye and thus retarding dye uptake.

1.2.8. Effect of temperature on dye adsorption

In their study of the adsorption of disperse dyes on PET fibre, Remington and Schuler [80] found that the gradient of the linear equilibrium isotherm (the partition coefficient, K) decreased with increasing temperature of application whilst the saturation value of the dye in the fibre (S_F) increased with increasing temperature (Figure 1.7). Identical findings were subsequently obtained by Bird *et al.* [67] for the adsorption of 1-β-hydroxyethylaminoanthraquinone on cellulose diacetate and by White [179] for the adsorption of CI Disperse Red 1 on the same substrate. In order to explain the effects of temperature on the distribution of disperse dyes between water and hydrophobic fibres it is firstly necessary to consider that, since for the adsorption of disperse dyes on to PET (and other hydrophobic) fibres, the partition coefficient (K) is constant, then the standard affinity ($\Delta\mu^0$) of the dye at temperature T K is given by equation (1.11) wherein K is the partition coefficient and R the gas constant:

$$-\Delta\mu^0 = \mathrm{R}T \ln K \qquad (1.11)$$

Thus, from the finding [80] that K decreased with increasing temperature, equation (1.11) shows that the affinity of the disperse dye also decreases

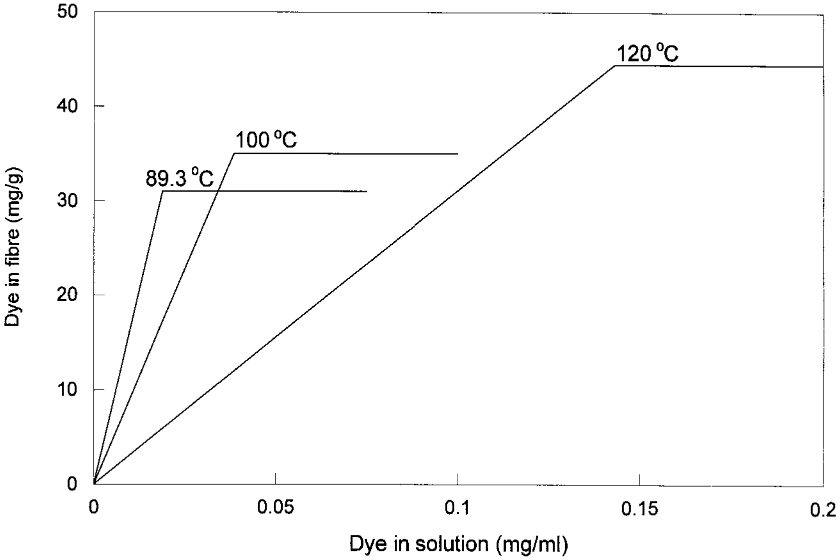


Figure 1.7 Effect of temperature on the adsorption of 1-amino-4-hydroxy-anthraquinone on PET [80]
(Reproduced with permission from the Royal Society of Chemistry)

with increase in application temperature. Generally, for all dye–fibre systems, the standard affinity of a dye decreases with increasing temperature for two reasons. Firstly, since dye adsorption is generally an exothermic process, then an increase in temperature will reduce standard affinity; indeed, Schuler and Remington [80] found that the heat of dyeing of CI Disperse Red 15 on PET was -61.7 kJ mol^{-1} and several workers have also demonstrated the exothermic nature of the adsorption of disperse dyes on various hydrophobic [87, 90, 180] and hydrophilic fibres [83]. Secondly, the standard affinity comprises both the heat (ΔH°) and the entropy (ΔS°) of dyeing as shown in equation (1.12).

$$\Delta\mu^0 = \Delta H^\circ - T\Delta S^\circ \tag{1.12}$$

Combining equations (1.11) and (1.12) gives equation (1.13).

$$-\Delta\mu^0 = \mathrm{R}T \ln K = \Delta H^\circ - T\,\Delta S^\circ \tag{1.13}$$

Hence

$$\ln \mathrm{K} = -\left(\frac{\Delta H^\circ}{R}\right)\cdot\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R} \tag{1.14}$$

and thus

$$\ln K = -\left(\frac{\Delta H^\circ}{RT}\right) + \frac{\Delta S^\circ}{R} \tag{1.15}$$

Thus, as equation (1.15) shows, if ΔH° is a constant (independent of temperature), then as temperature increases, $\Delta H^\circ/RT$ approaches zero and the partition coefficient (K) approximates to $\Delta S^\circ/R$. Thus, with increase in temperature, the partition coefficient (i.e. the partition of dye between dyebath and fibre) becomes increasingly governed by the entropy change (ΔS°) that accompanies dye adsorption. Since the adsorption of a dye molecule from the dyebath on to a fibre generally represents a loss in entropy (disorder) for the dye molecule, then with increase in temperature, adsorption of the dye on to the fibre becomes less probable than desorption of the dye into the dyebath so that the partition coefficient and thus standard affinity both decrease. Several workers have shown that the adsorption of disperse dyes by various several fibres is accompanied by a negative entropy change [17, 83, 87, 90, 180].

The effects of temperature on dyeing can be further explained (Figure 1.8) in the context of the various enthalpy terms relevant to dyeing as first described by Majury [87] in a study of the nature of the interaction between disperse dyes and cellulose acetate. Majury's initial study, involving the adsorption of five model disperse compounds on cellulose diacetate, which, as discussed by Peters [17], was subsequently enlarged [90, 181], concerned the determination of three enthalpy terms namely, the standard heats of dissolution of the solid dye in water (ΔH°_{SW}), dyeing (ΔH°_{WF}) and dissolution of the solid dye in the fibre (ΔH°_{SF}). It was observed for the adsorption of a series of disperse dyes on cellulose diacetate [90] that dissolution of the dye in water entailed the absorption of heat in order to create an interface between the water and the dye [17], and thus ΔH°_{SW} was positive. This energy (heat) was then regained during the transfer of the dye from solution to the fibre so that ΔH°_{WF} was negative and, finally, that the transfer of the solid dye to the fibre

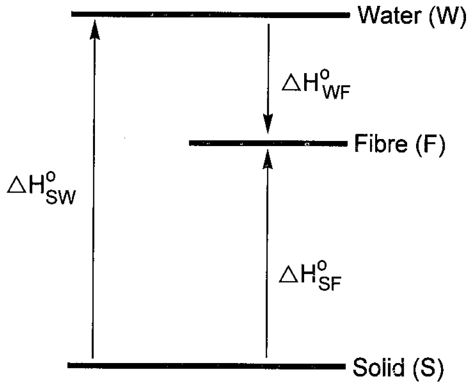


Figure 1.8 Enthalpy diagram (after Majury [87])

required the absorption of a small quantity of heat so that ΔH°_{SF} was positive. Thus, since dissolution of the dye in water is an endothermic process, the aqueous solubility of the disperse dye will increase with increasing temperature, as has been observed by several workers [86, 171], and, similarly, since dissolution of the solid dye in the fibre is an endothermic process, then this too will increases with increasing temperature. Bird and Harris [90] showed that for the adsorption of several disperse dyes on cellulose diacetate, and also from the results obtained for the adsorption of 1-amino-4-hydroxyanthraquinone on PET fibre [80], that the absolute heat changes involved increased in the order $\Delta H^{\circ}_{SF} < \Delta H^{\circ}_{WF} < \Delta H^{\circ}_{SW}$ from which it can be concluded that since ΔH°_{SW} was greater than ΔH°_{SF} then the rate of dissolution of the dye in water was greater than the rate of dissolution in the fibre with the effect that the partition coefficient (K) decreases with increasing temperature. Since transfer of the dye from the water to the fibre phase was an exothermic process then this will decrease with increasing temperature thereby further supporting the observations that K decreases with increasing temperature. Bird and Harris [90] demonstrated the significance of aqueous solubility in dye adsorption by showing that the partition coefficient of several disperse dyes on cellulose diacetate decreased with increasing aqueous solubility of the dyes.

However, although the partition coefficient and thus affinity of disperse dyes on hydrophobic fibres decreases with increasing temperature, the saturation value of dye uptake increases with increasing temperature [67, 80, 179]. This may be attributed to the dissolution of the dye in both the aqueous and fibre phases (ΔH°_{SW} and ΔH°_{SF}, respectively) being endothermic processes as a consequence of which, both D_S and D_F will increase with increasing temperature and thus saturation uptake will increase with increasing temperature. The findings of Giles [182], that the saturation uptake of several disperse dyes on cellulose diacetate increased with increasing aqueous solubility of the dyes, can be considered as providing support in favour of this view. One further possible explanation for the observed increase in saturation value of dye uptake that accompanies an increase in temperature is that the fibre undergoes some structural change whereby the accessibility of the fibre towards the dye is increased; however, as Peters [17] points out, no evidence is available in this particular context.

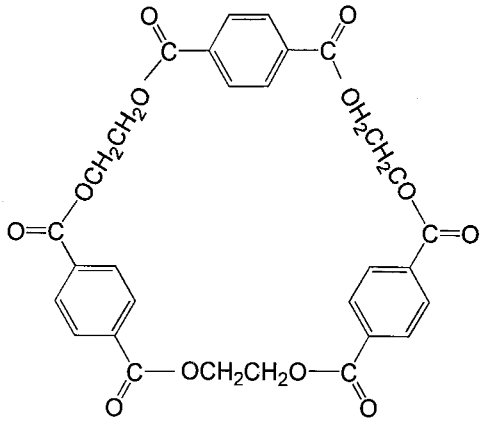
1.2.9. Isomorphism

On the basis of the mechanism of adsorption of disperse dyes on hydrophobic fibres proposed earlier – namely, that of 'ideal mixing' – when several disperse dyes are applied in admixture, the adsorption of an individual disperse should occur independently of the other dyes in the mixture. In support of this, Schuler and Remington [80] showed that when 1-amino-4-hydroxyanthraquinone and N^1,N^4-diphenyl-3-nitrosulphanilamide were applied to PET fibres in admixture, the saturation values and partition coefficients obtained were virtually identical to those obtained for application of the dyes alone. In a study of the rates of uptake of several commercial disperse dyes on to nylon 6.6, Vickerstaff [183] concluded that adsorption of the individual components in admixture proceeded in the same manner as when applied alone and Daruwalla and Limaye [159] demonstrated that in the application of binary mixtures of CI Disperse Red 1 and CI Disperse Red 11 to cellulose diacetate, both the rate and saturation uptake of each dye were unaffected by the presence of the other component in any proportion. Furthermore, Johnson *et al.* [184], in a study using four disperse dyes of dissimilar structure on cellulose diacetate and triacetate as well as nylon fibres, demonstrated that the isotherms obtained for the dyes when applied in binary mixture were identical to those given when each dye had been applied separately.

However, Vickerstaff and Waters [64] found that in the dyeing of cellulose diacetate with binary mixtures of closely related anthraquinone disperse dyes, certain mixtures gave greater saturation values than any of the individual components, the value being almost that of the sum of the two components. Similar results were obtained [185] for the adsorption of closely related anthraquinone disperse dyes in admixture on cellulose diacetate. Such additivity of saturation values, which has been employed as a means of improving the build-up characteristics of disperse dyes [64, 186–189], involves only dyes of similar structure.

In contrast, several workers [63, 185] have obtained evidence of interaction between dye molecules insofar as less dye was adsorbed in admixture than when the dyes had been applied separately. Schuler and Remington [80] observed that the saturation values of 1-amino-4-hydroxyanthraquinone and 1,4-dihydroxyanthraquinone on PET were lowered by some 20% when one component was applied in the presence of a large concentration of the other and both Vickerstaff and Waters [64] and Bird and Rhyner [185] found that interaction occurred with some mixtures of closely related anthraquinone dyes on cellulose diacetate fibres. These latter workers [185] observed that the decrease in the saturation values of dyes in admixture was paralleled by a reduction in the aqueous solubility of the dyes whereas Johnson *et al.* [184], in their study of the solid-state properties of dye mixtures, observed that non-interacting dyes, which exhibited additivity of isotherms in admixture, gave conventional melting point diagrams with a eutectic point whereas interacting dyes showed no eutectic from which it was considered that interacting dyes were isomorphous insofar as such dyes, which are of very similar structure, can form mixed crystals within the fibre. However, Hoffmann *et al.* [91] considered that mixed crystal formation did not occur in the fibre but instead suggested that isomorphous pairs of dyes interact in the dyebath as a result of which the aqueous solubility of the dyes is reduced, as first proposed by Bird and Rhyner [185].

1.2.10. Oligomers



XVIII

Typically, PET fibres contain between 1.5 and 3.5% [7] by mass of low M_r esters, the principal oligomer being cyclic tris(ethylene terephthalate) (XVIII) with smaller quantities of a dimer, pentamer as well as traces of other compounds [190, 191]. These substances migrate from PET fibre during dyeing and steam setting and, to a lesser extent, during dry-heat setting. Although little migration occurs at temperatures below 110°C the amount increases with increase in temperature up to those commonly encountered in HT dyeing and steam setting namely, 125–135°C [7]. Skelly [161] showed that following treatment at 130°C for one hour in the presence of a dispersing agent, an average of 0.13% of cyclic trimer was deposited on the surface of both untexturised and texturised PET. The finding that treatment in the presence of a carrier increased the surface deposition to an average of 0.18% demonstrated that carriers can promote migration of the trimer to the surface of the fibre. It is considered [7] that a similar quantity (about 0.2%) of oligomer is present in the dyebath and, in part, on the surfaces of the dyeing vessel. Although the deposition of crystalline oligomers on the fibre surface is of little significance for several forms of dyed PET fibre, other than the appearance as a white deposit, it may, for example, impair the spinning characteristics of yarns and reduce liquor flow during package dyeing. Although the crystalline cyclic trimer is not dyed with disperse dyes, its presence may cause nucleation and growth of dye crystals or agglomeration of dye particles under certain conditions. Although the cyclic trimer may initially be dispersed in the dyebath at 125–130°C, owing to the marked reduction in solubility of the crystalline material at temperatures below this [7], deposition on the dyeing vessel or fibre surface may occur as the bath cools. Such deposition can be reduced by discharging the HT dyebath without prior cooling and Skelly [161] suggests that certain carriers may aid the solubility or dispersion of the trimer from the fibre surface thereby reducing recrystallisation on the fibre or dyeing vessel during cooling of HT dyebaths. The liberation of oligomers during dyeing can be minimised by lowering the dyeing temperature from 130 to 120°C and by using the shortest possible dyeing time; non-ionic levelling agents are considered to minimise redeposition of oligomers produced during HT dyeing. Calhoun *et al.* [192] demonstrated that an emulsified silicone lubricant present in the dyebath or in an aftertreatment bath reduced oligomer deposition in the package dyeing of PET. Oligomer deposits are effectively removed from the fibre surface by reduction clearing followed by rinsing, and, if necessary, neutralisation using dilute acetic acid; more severe treatments are often necessary to remove deposits of the cyclic trimer from dyeing vessels [5].

1.2.11. Carrier dyeing

The term ‘carrier’ describes *a type of accelerant particularly used in the dyeing or printing of hydrophobic fibres with disperse dyes* [15]. In an early study of the dyeing behaviour of PET fibres, Waters [8] demonstrated that disperse dyes characteristically exhibited a slow rate of uptake on to the substrate even at the commercial boil (98°C) and established that this was attributable to the low rate of diffusion of the dyes within the substrate. This author examined some 300 compounds, and ascribed the term ‘carriers’ to those which, when added to the dyebath, accelerated the rate of dyeing. Waters [8] divided the compounds that he used into four groups namely, phenolics, primary amines, hydrocarbons and esters, and concluded that although some compounds were effective in increasing the rate of dyeing at the boil, with phenolics being the most practicable, all compounds examined possessed inherent disadvantages or hazards such as toxicity, malodour, volatility in steam and shrinkage effects that prevented this author from recommending any one particular compound. Waters [8] proposed the use of a limited range of fast-diffusing dyes in the absence of carrier to obtain medium-depth dyeings but mentioned that carriers would probably be used for full depths or in printing.

Despite the reservations expressed by Waters [8] concerning the undesirable characteristics of carriers, their use became widespread as a means of achieving a comprehensive shade range until high-temperature (HT) dyeing machinery became widely available. However, although some carrier dyeing of PET fibre is still carried out, HT dyeing is by far the preferred immersion application method.

In this account of carrier dyeing, reference is made not only to research that has been carried out on the carrier dyeing of PET fibres with disperse dyes but also to work on the carrier dyeing of other classes of dye on other substrates, so as to provide a comprehensive account of this topic.

A vast number of compounds have been examined as potential carriers for use in the dyeing of PET and other hydrophobic fibres; typically, carriers are small molecular size, aromatic compounds which are added to the disperse dyebath in solution or emulsion form. Currently, their use is mostly restricted to PET and cellulose triacetate fibres; for PET, popular carriers include *o*-phenylphenol, diphenyl or chlorinated benzenes whilst tripropyl phosphate or butyl benzoate are commonly used for cellulose triacetate. Carriers increase the rate of uptake of disperse dyes on to hydrophobic fibres such that acceptable dyeing rates are achieved in the presence of a carrier at the commercial boil rather by recourse to high temperatures (commonly 130 and 125°C for PET and triacetate fibres respectively). Murray and Mortimer [193] reviewed the carriers used in the early 1970s and outlined the desirable characteristics of a carrier, concluding that no single carrier possessed all the desirable characteristics.

1.2.11.1. Adsorption of carriers. Fortess and Salvin [194] proposed that the adsorption of carriers on to PET fibre occurs by a mechanism identical to that of the adsorption of disperse dyes, a view subsequently affirmed by other workers [126, 195, 196]. Indeed, linear isotherms have been obtained for the adsorption of various carriers on PET [195, 197–199] (Figure 1.9) and PAN fibres [200, 201, 202].

It has been demonstrated that hydrophobic carriers are more effective on PET fibres than their hydrophilic counterparts [203] and that the more hydrophobic a carrier then the larger is its partition coefficient on PET [195] and PAN [200] fibres. Lemons *et al.* [204] proposed that PET–solvent (carrier) interactions occur primarily by means of dispersion forces; similarly, Derbyshire and Peters [205] suggested that carriers were adsorbed on to PET primarily by virtue of non-polar forces operating between the aromatic regions in both carrier and fibre although with carriers, such as phenol, that carry polar substituents, polar forces may also contribute to adsorption. Support for this view was furnished by the findings of Ingamells *et al.* [126, 206, 208] that plasticisation of PET fibres is dominated by dispersion forces with polar forces playing a small part in the process. Brown and Peters [208, 209] observed no detectable shifts in the infrared absorption spectra of PET which had been treated in various

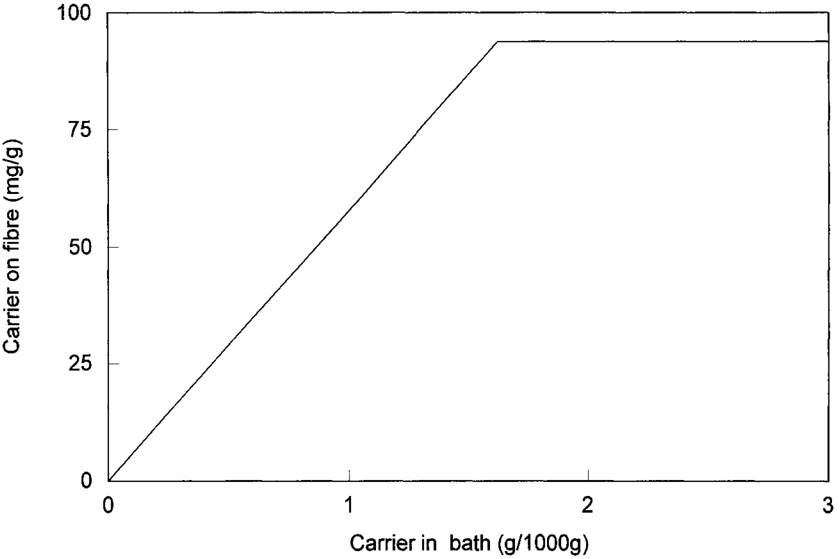


Figure 1.9 Adsorption isotherm of *o*-phenylphenol on PET fibre at 98°C [197]

chlorobenzenes and concluded that only van der Waals' forces were operative. However, although relatively little work has attended the nature of the forces of interaction that contribute towards carrier–fibre substantivity, it seems reasonable to suggest that the substantivity of carriers towards PET and other hydrophobic fibres accrues from the various forces of interaction that have been proposed to account for the substantivity of disperse dyes towards such fibres (as discussed previously).

Schuler [210], using a dyeing system of 2,2,4-trimethylpentane, demonstrated that the rate of uptake of several carriers in PET fibre increased with increasing concentration of carrier and proposed that the carrier diffuses into the fibre ahead of the dye. McGregor *et al.* [211] used a microdensitometer technique to establish that when CI Disperse Red 15 was applied in the presence of trichlorobenzene to PET film, the carrier and dye diffused simultaneously into the film. However, the penetration front of the carrier was invariably found to be ahead of that of the dye and these workers concluded that the carrier penetrated the film more rapidly than the dye can penetrate the region in the fibre that the trichlorobenzene has already occupied. Herlinger *et al.* [212], using a carrier dyeing process that involved a heating-up phase from 20 to 95°C, found that the adsorption curve of several carriers on to PET fabric was sigmoidal in shape, with carrier uptake increasing only gradually with increase in temperature up to about 70–80°C, after which uptake increased dramatically with further increase in temperature up to 95°C and reached a

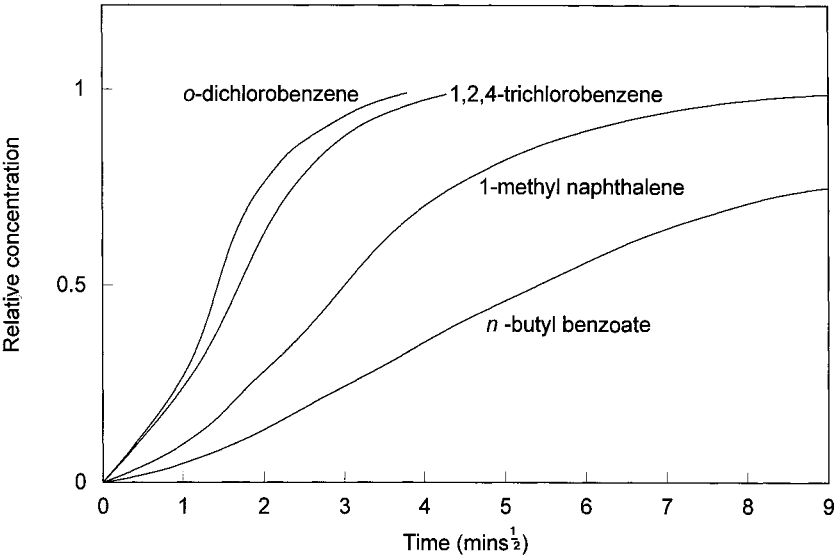


Figure 1.10 Concentration–distance profiles for 1,2,4-trichlorobenzene, *o*-dichlorobenzene, 1-methylnaphthalene and *n*-butyl benzoate on PET yarn at 97°C [213]

(Reproduced with permission from G. Roberts and the Society of Dyers and Colourists)

constant value after some 30 to 60 minutes at this temperature; the extent of carrier uptake was found to vary between the carriers used. The rate of uptake of CI Disperse Red 60 in the presence of carrier was found to follow closely that of the carrier but the adsorption of both methyl naphthalene and 1,2,4-trichlorobenzene preceded that of the dye.

Roberts and Solanki [213] found that the concentration profiles of four carriers on PET were sigmoidal in shape (Figure 1.10) and therefore differed to those of disperse dyes in the fibre. These workers considered that the initial increase in the gradients of the profile curves was due to increasing plasticisation of the fibre as the concentration of carrier in the substrate increased, causing a reduction in the glass transition temperature (T_g) of the polymer and a consequent increase in rate of carrier diffusion; the subsequent decrease in rate of uptake of the carriers may then be attributed to a reduction in the carrier concentration gradient as equilibrium uptake is approached. In explaining this finding, these workers [213] referred to the findings of McGregor *et al.* [211] that the rate of dyeing curves obtained for CI Disperse Red 15 in the presence of trichlorobenzene on to PET film were markedly sigmoidal and suggested that these sigmoidal curves arose from the plasticisation of the polymer, during dyeing, by the more rapidly diffusing carrier. Roberts and Solanki [213] also found that the apparent diffusion coefficients of four carriers

Table 1.6 Apparent diffusion coefficients, D_a, (calculated at $M_t/M_\infty = 0.5$) and apparent activation energies and entropies of diffusion of carriers within PET yarn [213]

Carrier	$D_a \times 10^{11}$ cm^2 s^{-1} 85°C	89.5°C	93°C	97°C	E^* kJ mol^{-1}	ΔS^* J mol^{-1} K^{-1}
o-dichlorobenzene	27.5	25.7	47.9	72.4	96 ± 6	95 ± 15
1,2,4-trichlorobenzene	12.9	14.8	28.8	49.0	129 ± 7	182 ± 19
1-methylnaphthalene	3.6	6.6	10.2	16.6	139 ± 7	201 ± 17
n-butyl benzoate	0.8	1.4	3.2	5.0	172 ± 6	280 ± 16

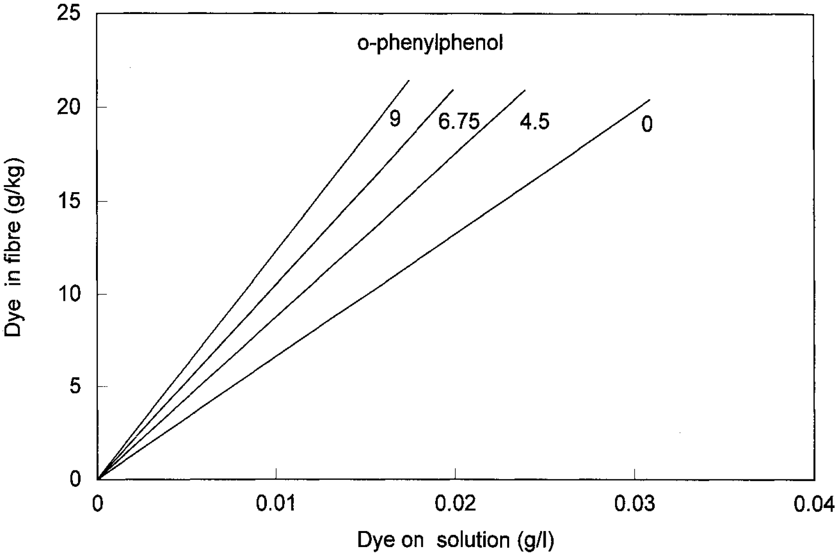
(Reproduced with permission from G. Roberts and the Society of Dyers and Colourists)

within PET fibre were several orders higher, whilst the apparent activation energies and entropies of activation of diffusion were lower than those of typical disperse dyes in PET, which was attributable to the smaller size of the carrier molecules (Table 1.6).

Furthermore, both the rates of uptake and the equilbrium uptake of the four carriers varied considerably with variation in the chemical nature of the carrier. The observation [213] that the apparent diffusion coefficient of each of the four carriers increased with increasing concentration of carrier in the fibre differs to that for disperse dyes, for which the values of diffusion coefficient decrease with increasing dye uptake owing to a reduction in concentration gradient. The authors [213] concluded that the observed increase in apparent diffusion coefficient that accompanied an increase in carrier content of the polymer was attributable to a corresponding increase in plasticisation (reduction in T_g) of the fibre. Roberts and Solanki [213] consider that the major difference between the diffusion behaviour of carriers and disperse dyes in PET fibres is the concentration-dependence of the diffusion coefficients of carriers; these workers proposed that the more rapidly diffusing the carrier, the greater the concentration-dependence of apparent diffusion coefficient.

1.2.11.2. Effect on dye adsorption. Although the linearity of the adsorption isotherm of disperse dyes is unaffected by the presence of carriers [80, 195, 196] the partition coefficient of the dye is altered [195, 196].

Balmforth *et al.* [195] found that although the three hydrophobic carriers (biphenyl, phenyl salicylate and *o*-phenylphenol) increased the partition coefficient (K) of CI Disperse Red 15 on to PET, the more hydrophilic benzoic acid decreased K of the dye (Figure 1.7), the latter finding thus confirming the result obtained by Remington and Schuler [80] that benzoic acid reduced K of several disperse dyes on PET. Balmforth *et al.* [195] also observed that the three hydrophobic carriers each had a high partition coefficient for the fibre whereas benzoic acid had a low K; also, the solubility of the dye in benzoic acid was considerably greater than that in each of the three hydrophobic carriers used (Table



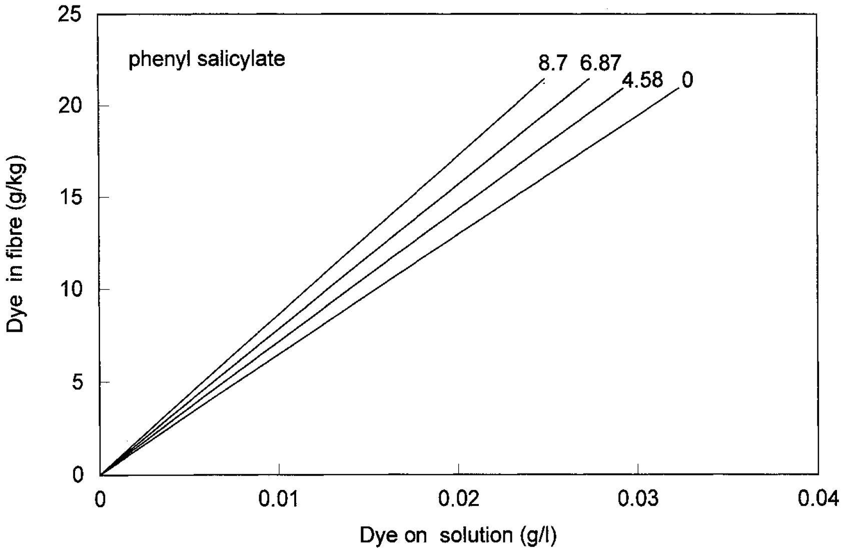
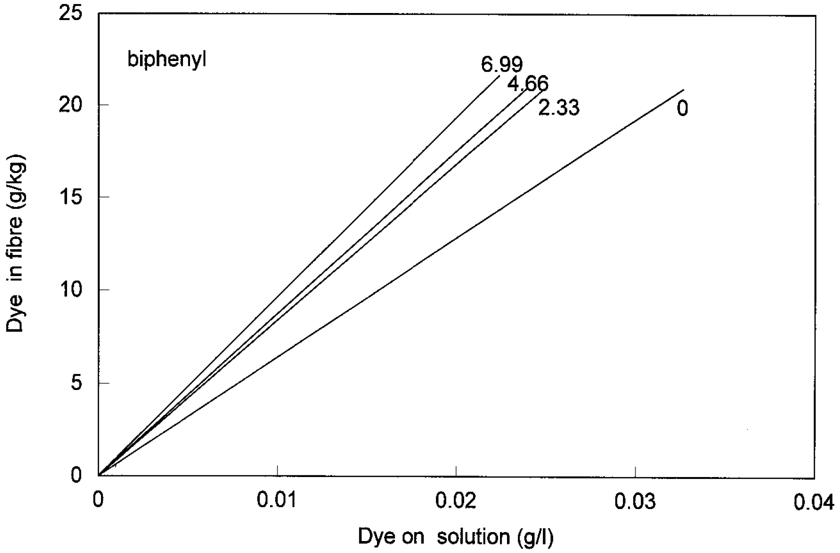


Figure 1.7 Effect of carriers on the partition of CI Disperse Red 15 between polyester fibre and water at 95°C [195]

(Reproduced with permission from D. Balmforth and the Society of Dyers and Colourists)


biphenyl
6.99
4.66
2.33
0
Dye in fibre (g/kg)
0
5
10
15
20
25
Dye on solution (g/l)
0
0.01
0.02
0.03
0.04

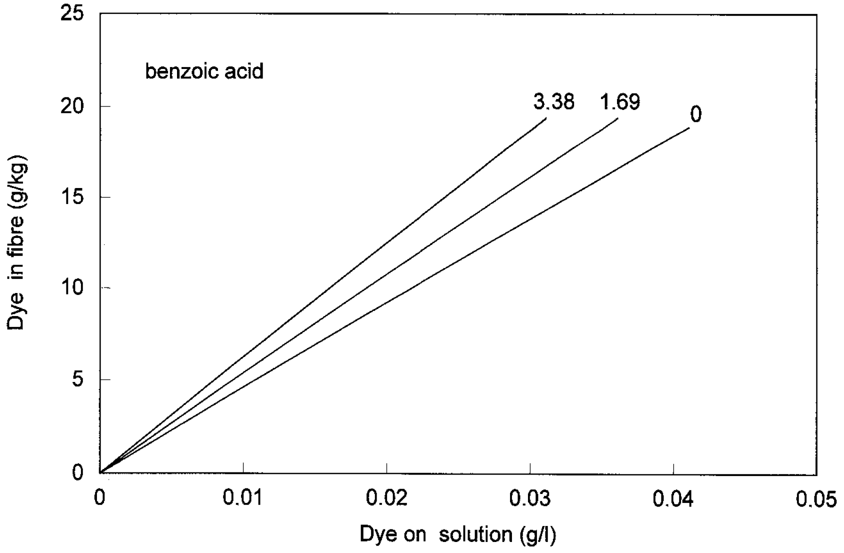

benzoic acid
3.38
1.69
0
Dye in fibre (g/kg)
0
5
10
15
20
25
Dye on solution (g/l)
0
0.01
0.02
0.03
0.04
0.05

Table 1.7 Partition coefficients of carriers between water and polyester fibre as well as solubility of CI Disperse Red 15 in saturated solutions of carriers at 95°C [195]

Carrier	Partition coefficient	Dye solubility (mg dm^{-3})
None	–	29.0
Biphenyl	574	34.1
o-phenylphenol	90	40.0
Phenyl salicylate	437	42.9
Benzoic acid	3.7	344

(Reproduced with permission from D. Balmforth and the Society of Dyers and Colourists)

1.7). These authors [195] concluded that the manner by which hydrophobic carriers assist dyeing differed to that of hydrophilic carriers.

Schuler [210] observed that the rate of uptake of disperse dyes on to PET fibre was increased in the presence of carrier and found that the effect of different carriers on dyeing rate was similar when a similar concentration of different carriers was present in the fibre. Glenz *et al.* [106] showed that the increase in rate of uptake of several disperse dyes on to PET brought about by two carriers was approximately the same for a similar concentration of each carrier in the fibre. These workers [106] also demonstrated that the diffusion coefficient of several disperse dyes in PET was increased in the presence of both carriers used and found a wide variation in the effect of the two carriers on enhancement of diffusion coefficient for dyes of similar structure. As discussed later, the observation that carriers increase the diffusion coefficient of disperse and other classes of dye within hydrophobic fibres has been employed by several workers to explain the mechanism of carrier action in terms of fibre plasticisation. Ingamells and Yabani [206] showed that the diffusion coefficient of CI Disperse Orange 3 into undrawn PET filaments at 95°C increased exponentially with increasing concentration of 2-phenoxyethanol in the dyebath and also with increasing dyebath concentration of five different carriers in the case of drawn PET filaments [214]. The diffusion coefficient of CI Disperse Red 1 at 95°C in PET fibre was also found to increase exponentially with increase in concentration of four carriers in the fibre [215]. The latter workers [215] and others [216, 217] have observed that the diffusional behaviour of various dyes was independent of the chemical nature of the carrier and thus confirmed previous suggestions [106, 206, 210] that different carriers have approximately equivalent action when present in PET in similar concentrations. However, although the influence of different carriers on the diffusional behaviour of a given disperse dye within PET is relatively independent of carrier structure, the effect of a given carrier on the diffusion of several disperse dyes varies [106, 162, 215].

1.2.11.3. Theories of carrier action. Several theories have been proposed to explain carrier action. In essence, the various mechanisms can be considered to support one of two main theories of carrier action – namely, that the carrier has an effect on the disperse dye in the dyebath or that the carrier has an effect upon the fibre; at present, it is generally considered that carrier action is attributable to the latter effect. Although in the following account of the various mechanisms that have been proposed to explain carrier action, the majority of the evidence presented concerns PET fibre, results of work carried out using other hydrophobic fibres are also included so as to present a full account of this large topic.

1.2.11.3.1. Complex formation. Fern and Hadfield [218] proposed that the disperse dye and carrier formed a complex that could diffuse more readily into the fibre than the dye alone; however Elöd [219, 220], using UV spectroscopy, was unable to verify such dye–carrier complex formation and the work of Senner *et al.* [221, 222] showed no evidence in support this theory of carrier action.

1.2.11.3.2. Increased dye solubility. On the basis of the currently accepted mechanism of the aqueous phase transfer of disperse dyes to hydrophobic fibres namely, that dyeing occurs from a dilute aqueous solution of the dye, Zimmerman *et al.* [223], in a study of the effects of various types of carrier on the uptake of several disperse dyes on to PET, proposed that the carrier increased the solubility of the dye in the aqueous phase, as a consequence of which, more dye was available for adsorption and thus diffusion within the fibre. It was shown [196] that six disperse dyes possessed high solubility in five carriers at 80°C although it was concluded that solubilisation was both dye- and carrier-specific. Balmforth *et al.* [195] demonstrated that four carriers each increased the aqueous solubility of CI Disperse Red 15 at 95°C and Murray and Mortimer [59] found that whilst the rate of uptake of CI Disperse Red 60 on PET fibre decreased with increasing concentration of methylnaphthalene in the dyebath, the rate of dyeing increased with increasing concentration of an *o*-phenylphenol-based carrier. This latter observation was attributed [59] to the dye being more soluble in methylnaphthalene than in *o*-phenylphenol with the result that a greater proportion of the dye was retained in the dyebath containing methylnaphthalene. These workers [59] concluded that although the solubilising effect of carriers influences the rate of dyeing and extent of dye exhaustion, these effects are both dye- and carrier-specific and also depend on the concentration of carrier employed. Herlinger *et al.* [212] demonstrated that three disperse dyes possessed high solubility in 1,2,4-trichlorobenzene and also that the extent of solubilisation varied for the three dyes. These workers [212] also showed that solubilisation of the three disperse dyes was time-dependent, insofar as the solubility of the dyes in the carrier increased with increasing time, reaching a maximum value after a particular period of time that was specific for each dye, and thereafter decreased with further increase in time. The reduction in dye solubility observed for prolonged times was attributed [212] to modification of the crystal form of the dyes, which, as discussed in section 1.2.4, is considered to occur during prolonged dyeing. Balmforth *et al.* [195] demonstrated that there was no correlation between the solubility of CI Disperse Red 15 in three carriers and the effectiveness of the carrier in enhancing uptake of the dye on to PET fibre; similar findings have been obtained [224] for the dyeing of Courtelle S with CI Basic Green 4 in the presence of several carriers. Murray and Mortimer [59] demonstrated that carriers which have a marked solubilising effect on disperse dyes are highly effective levelling agents for disperse dyes in the HT dyeing of PET, insofar as the solubilising power of the carriers expedites dye migration during dyeing. Similar findings to those of Murray and Mortimer [59] were obtained [196] during a study of the desorption of fifteen dyes from two types of PET fibre affected by three carriers; this earlier work [196] also demonstrated that considerable variation occurred in the levelling character of the dyes examined. Beckmann and Hamacher-Brieden [162] also demonstrated the marked levelling action exerted by carriers on the uptake of disperse dyes on PET and found that the effect was strongly dye-specific but varied for different carriers. No correlation was obtained between the solubility of CI Disperse Blue 27 in five different carriers and the extent of uptake of the dye on to cellulose triacetate fibre; also, whilst tripropyl phosphate was an excellent solvent for CI Disperse Blue 27, this carrier did not increase the rate of uptake of the dye on to PET fibre [196]. These workers [196] concluded that whilst increased solubility of the dyes as affected by the carrier may contribute to enhanced dyeing rate for dyes of very low water solubility, this theory was not the major contributor to carrier action.

1.2.11.3.3. Film formation. The ability of carriers to act as solvents for disperse dyes was also considered by Vickerstaff [225], who, in quoting the work of Peters and Sumner, proffered that water-insoluble compounds form a film, that surrounds the fibre, in which the disperse dye dissolves. Dyeing then occurs more rapidly since the concentration of dye in this dye-rich film is greater than in the aqueous solution of the dye in the dyebath. Choquette [226] also proposed that in the dyeing of PET using monochlorobenzene as carrier, the dye dissolves in the carrier forming a layer of concentrated dye solution around the fibre. In support of this 'film' theory, Millson [227] observed the presence of droplets of *p*-phenylphenol on the surface of PET fibres. Herlinger *et al.* [212], using CI Disperse Blue 139 and 1,2,4-trichlorobenzene as carrier, obtained microscopical evidence that dye-saturated carrier droplets were deposited on the surface of PET fibres at temperatures up to 50°C; at higher temperatures the droplets assumed a flatter configuration and eventually resulted in the presence of a dye-saturated film. Ravichandran *et al.* [228] obtained electron microscopical evidence of the deposition of both salicylic acid and anthranilic acid at or just below the surface of PET yarns. Furthermore, from a study of cross-sections of Courtelle S which had been dyed using CI Basic Green 4 in the presence of 2% o.w.f. *o*-phenylphenol, it was shown [224] that after 30 minutes' dyeing at 80°C, the fibre was markedly ring-dyed and also that the interstitial regions of the fibre matrix were deeply coloured. The observation that the extent of this ring-dyeing was considerably reduced by subsequent rinsing in acetone and that the interstitial coloration was completely removed by an acetone rinse, led these workers [224] to conclude that the carrier was present both at the periphery of the fibre and in the interstitial regions and that the carrier effect of *o*-phenylphenol on PAN fibres may in part be attributable to dissolution of the dye within the adsorbed carrier and the consequent establishment of a high concentration gradient of the dye within the fibre. Fortess and Salvin [194] suggested, from work carried out using cellulose triacetate fibres, that carrier present within the fibre may solvate the dye with the possible formation of a fibre-additive media for dye solubilisation. However, since other workers [196], from studies using several carriers on PET, concluded that carrier action does not occur by dissolution of the dye in a film of carrier located at the surface of the fibre, this particular aspect of the mechanism of carrier dyeing remains open to debate.

1.2.11.3.4. Increased water imbibition. Vickerstaff [225] suggested that carriers, such as *o*-phenylphenol and benzoic acid, which contain hydrophilic groups diffuse rapidly within the fibre; whilst the aromatic portion of the carrier is involved, via the operation of van der Waals' forces, with the hydrophobic fibre, the hydrophilic groups (e.g —OH) of the carrier attract water molecules. The ensuing increased water imbibition of the hydrophobic fibre was considered to result in a more hydrophilic environment within the fibre thereby creating a more acceptable medium for the sparingly soluble dyes. It was demonstrated [196] that although the presence of *o*-phenylphenol and also trichlorobenzene increased the water imbibition of PET, the increase furnished by the presence of trichlorobenzene was only very slightly lower than that secured using the more hydrophilic *o*-phenylphenol and, consequently, these workers concluded that their results did not support the theory of increased water imbibition as the basis of carrier action.

1.2.11.3.5. Fibre swelling. Waters [8] was the first of many workers [68, 72, 74, 75, 218, 229] to propose that carriers swell PET fibre, as a result of which, the rate of dye diffusion and thus dyeing rate are increased. Waters [8] showed that several carriers induced shrinkage in PET fibre but was unable to demonstrate a correlation between the extent of fibre swelling (as measured by fibre contraction) imparted by a carrier and the effectiveness of the carrier in enhancing the rate of disperse dye uptake. Although methyl salicylate and trichlorobenzene were found not to swell PET fibres, as determined using specific gravity measurements [196], both these compounds and also *o*-phenylphenol caused considerable shrinkage of PET yarn. However, it was considered [196] that no correlation existed between the extent of yarn shrinkage induced by the three carriers and the effectiveness of the carriers in enhancing the rate of uptake of the disperse dyes used in this work. Although Hendrix [230] observed that PET fibres were swollen by phenolic compounds, this author found no correlation between fibre swelling and carrier action, as was also found by other workers [204]. Asquith *et al.* [231], from a study of the effect of *p*-nitrophenol on the dyeing of Acrilan with CI Basic Blue 22, concluded that the compound exerted carrier action, as demonstrated by a reduction in T_g of the fibre, but did not swell the substrate and proposed that *p*-nitrophenol decreased aggregation of the dye. Gur-Arieh and Ingamells [232] found no correlation between fibre swelling and T_g reduction of wet Acrilan filaments for a series of organic compounds; indeed, some compounds were shown to cause swelling but to slightly increase the T_g of the fibre. In a later study of the effects of nine carriers on undrawn PET filament, Ingamells and Yabani [206] demonstrated that although none of the compounds examined caused significant swelling of the undrawn filaments, the diffusion coefficient of CI Disperse Orange 3 in undrawn PET filaments increased markedly with increasing concentration of 2-phenoxyethanol in the dyebath, thus showing that increased dyeability was not related to increased swelling. In later work [214], these workers demonstrated that several carriers caused significant swelling of drawn PET filaments and that the diffusion coefficient of CI Disperse Orange 3 in drawn PET filaments was little affected in the presence of varying concentrations of 2-phenoxyethanol in the dyebath, which supported their earlier findings that increased swelling and increased dyeability are not related. Hence, as Waters [8] argued, the effectiveness of a carrier is not solely a function of its ability to swell the fibre.

1.2.11.3.6. Fibre modification. Salvin [233] established that a characteristic aspect of carrier action is that the carrier must be adsorbed by the fibre; in support of this, Salvin *et al.* [196] demonstrated that tripropyl phosphate is adsorbed by cellulose triacetate fibre and acts as a carrier for the fibre whereas this compound is not a carrier for PET fibre on which it is not adsorbed. Rochas [234, 235] and coworkers [236] determined the extent of carrier uptake on to PET gravimetrically and observed that treatment of the carrier-treated fibre with acetone failed to remove all carrier. This small quantity of carrier was considered by Rochas to be responsible for carrier action and, since enhanced disperse dye uptake was obtained even after the complete removal of this carrier, it was proposed that it had caused some permanent physical modification of the fibre. Rawicz *et al.* [203] obtained similar results to Rochas in that the effectiveness of several carriers on dye uptake on to PET yarn persisted after the carrier had been removed from the fibre and concluded from results of X-ray diffraction that the carrier produced changes in the mechanical properties of the substrate that were consistent with those expected in partial disorientation. Brown and Peters [208, 209], in a study of the effects of mono- and polyhalogenated benzenes on the uptake of 2-nitro-4′-ethoxydiphenylamine-4-sulphonamide on PET, found that dye uptake on to fibre which had been treated with *o*-dichlorobenzene and from which all carrier had been subsequently removed by extraction with acetone was greater than that obtained when dyeing had been carried out in the absence of carrier. These workers [209] also employed X-ray diffraction to establish that permanent disorientation of the fibre occurred as a result of treatment with the carriers. However, although Brown and Peters confirmed Rochas' findings that structural alterations to the fibre contribute to carrier action, their observation that 1,2,3-trichlorobenzene exhibited high carrier action at concentrations lower than those required to affect permanent fibre modification casts some doubt as to the contribution that permanent fibre modification makes towards carrier activity.

1.2.11.3.7. Fibre plasticisation. On the basis of results obtained using PET, Schuler [210] proposed that carriers reduced the interchain forces within the fibre, as a result of which, the diffusion rate of the dye (and also carrier) was increased. Rawicz *et al.* [203] obtained some correlation between disperse dye uptake and the mechanical properties of PET in that the uptake of an anthraquinone disperse dye was related to the extent of contraction of the fibre caused by the presence of several carriers. These workers [203] considered that the contraction of PET filaments brought about by immersion in several carriers was indicative of swelling and that the carrier reduced the attractive forces operating between the polymer chains in PET thereby increasing their mobility and leading to increased dye diffusion within the fibre. In a similar vein, as a result of studies of the dyeing of cellulose triacetate, Fortess and Salvin [194] proposed that the carrier, once adsorbed on to the fibre, solvates the fibre molecules, reducing intermolecular forces and thereby increasing the segmental mobility of the macromolecular chains. These workers [194, 203, 210] thus considered that carrier action entails disruption of the fibre structure; this particular theory of carrier action – namely, that carriers plasticise hydrophobic fibres – subsequently has received considerable support from the results of many workers.

As is also discussed in Chapter 3, Rosenbaum [237] correlated the temperature-dependence of the diffusion of CI Basic Green 4 with the T_g of PAN fibres using the WLF equation expressed in the form of equation (1.16) wherein A and B are constants, D_T and D_{T_g} are diffusion coefficients at ambient temperature T and at T_g and $\log a_T$ is the shift factor.

$$\log \frac{D_T}{D_{T_g}} = -\log a_T = \frac{A(T-T_g)}{B+(T-T_g)} \tag{1.16}$$

The finding that the variation of diffusion coefficient of the dye with temperature was related to T_g of the fibre by the variable $(T - T_g)$ confirmed that the segmental mobility of the polymer chains, which controls the viscoelastic properties of the substrate, also governs dye diffusion within the polymer. Bell and Murayama [238] confirmed the findings of Rosenbaum using CI Basic Blue 22 and also showed that the diffusion of non-metallised acid dyes in nylon [239] and that of disperse dyes in PET [240] was controlled by the segmental mobility of the polymer chains.

Fujino *et al.* [241] suggested that carriers adsorbed on to PET increased the segmental mobility of the molecular chains and reduced the T_g of the fibre by an extent that was proportional to the concentration of the compounds adsorbed. Ingamells *et al* [242, 243], by measuring the elongation in length of Acrilan filaments immersed in aqueous solutions of phenol and other carriers, established that the carriers reduced the T_g of the filaments and that the decrease in T_g was proportional to the concentration

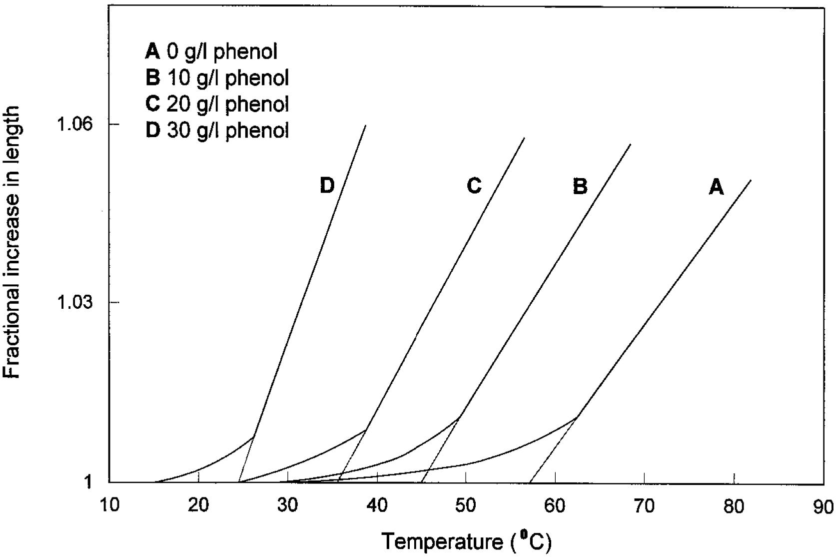


Figure 1.12 Effect of phenol concentration on the T_g of Acrilan fibres [243]
(Reproduced with permission from R.H. Peters and the Society of Dyers and Colourists)

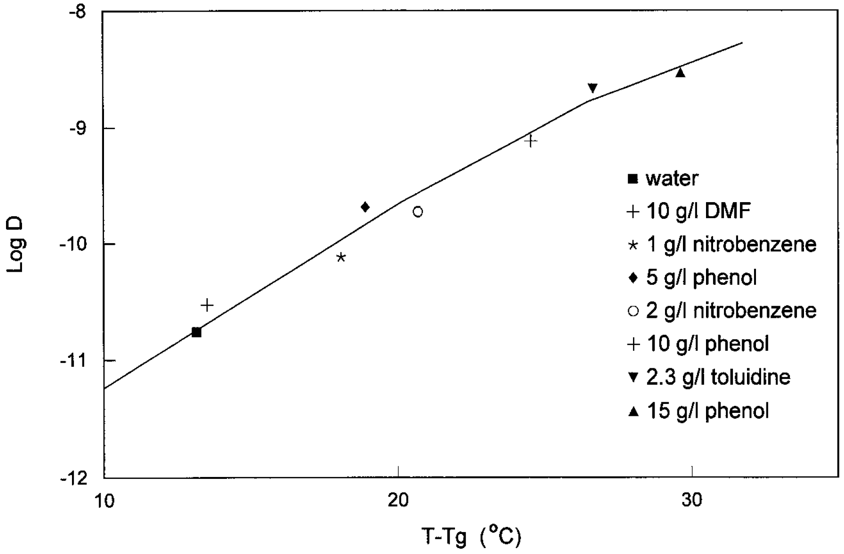


Figure 1.13 Effect of carriers on the diffusion coefficient of *p*-aminoazobenzene in Acrilan fibre at 70°C as a function of $(T-T_g)$ [243]
(Reproduced with permission from R.H. Peters and the Society of Dyers and Colourists)

of phenol in aqueous solution (Figure 1.12). These workers [242] also demonstrated that the diffusion coefficient of *p*-aminoazobenzene at 70°C in PAN filaments increased in the presence of several carriers and was related to the variable $(T - T_g)$ (Figure 1.13). Furthermore, Ingamells *et al.* [242] determined the appropriate shift factors (a_T in equation (1.16)) using values of 10.8 for A and 28.5 for B as given by Rosenbaum [237] and appropriate values of $(T - T_g)$ obtained from the measured changes in physical property of the filaments brought about by the presence of different concentrations of phenol. A plot of log $1/a_T$ obtained against $(T - T_g)$ showed that the effects of the carrier upon the measured physical properties of the filaments conformed to the WLF equation and, therefore, that the segmental mobility of Acrilan was enhanced by the presence of phenol (Figure 1.14).

These workers then showed that the diffusion of CI Disperse Red 1 in Acrilan filaments in the presence of different concentrations of phenol also conformed to the WLF equation from the finding that a plot of log D_T (diffusion coefficient of the dye at various phenol concentrations) versus $(T - T_g)$ could be superimposed upon the plot of log $1/a_T$ against $(T - T_g)$ by a vertical shift of the ordinate of the diffusion data (Figure 1.14). Thus, this work [242, 243] clearly demonstrated that the diffusion of the disperse dye in Acrilan was governed by the segmental mobility of

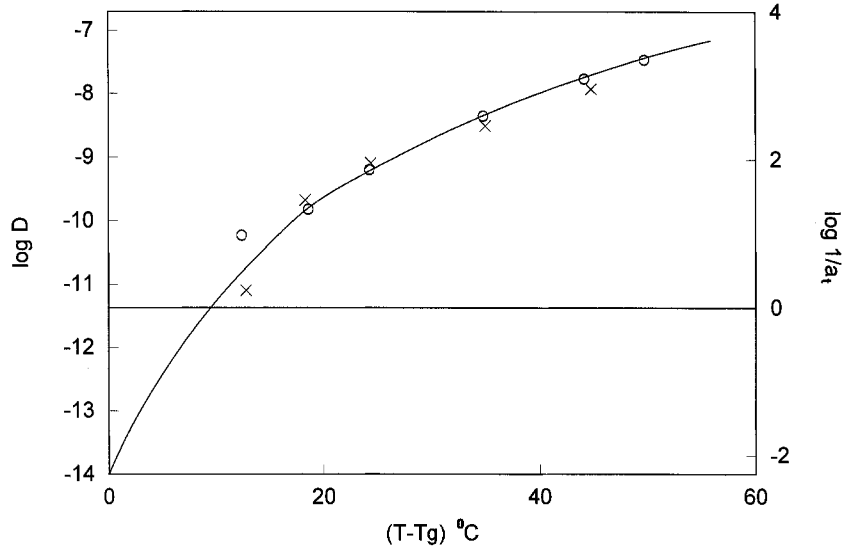


Figure 1.14 Coincidence of the variation of the physical properties of Acrilan filaments (shift factors, ×) and the diffusion data for CI Disperse Red 1 (○) with $(T-T_g)$ [242]

the polymer chains and that the carrier plasticises the fibre thereby increasing the segmental mobility of the polymer chains. Evidence in support of this finding was obtained [242] in terms of the superimposition of a plot of log D_T versus phenol concentration for the diffusion of disperse dyes in PET film in the presence of varying concentrations of phenol in the dyebath on a plot of log $1/a_T$ versus $(T - T_g)$ calculated using equation (1.16) (Figure 1.15).

Gur-Arieh and Ingamells [244] provided further support for these findings in that a plot of log D of CI Disperse Orange 3 into Acrilan filaments in the presence of varying concentrations of benzyl alcohol in the dyebath versus $(T - T_g)$ could be superimposed on a plot of log $1/a_T$ versus $(T - T_g)$. The increase in rate of dye diffusion affected by a carrier can be considered to be equivalent to that obtained by an increase in temperature of $(T_g - T_{g(c)})$ where T_g and $T_{g(c)}$ are, respectively, the glass transition temperatures of the fibre in water and carrier solution [112].

Glenz *et al.* [106] suggested that the activation energy of diffusion (E^*) of disperse dyes in PET was reduced by the presence of carriers. Reductions in E^* with increasing concentration of carrier in the dyebath have been obtained for the diffusion of disperse dyes in PAN filaments in the presence of benzyl alcohol [244] and also phenol [242, 243], that of four disperse dyes in PET fibre in the presence of several carriers [215]

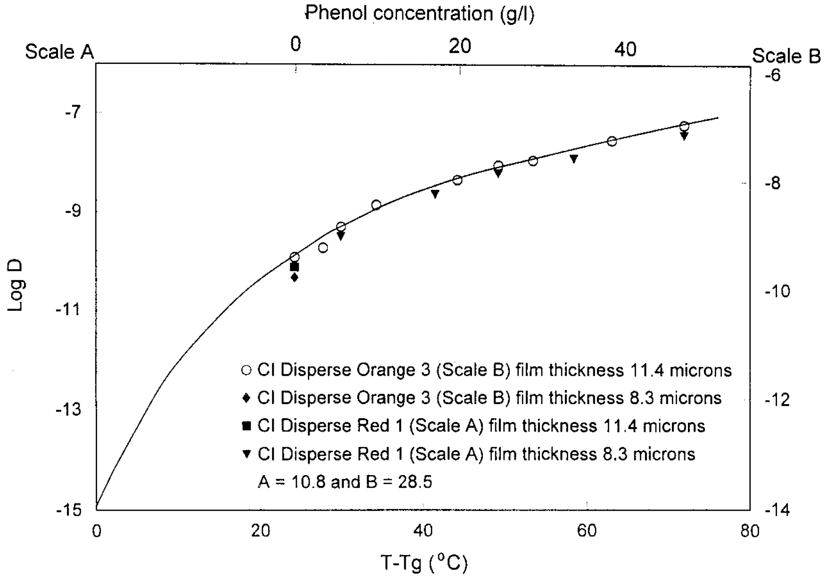


Figure 1.15 Coincidence of the variation of the diffusion coefficient of different disperse dyes and phenol concentration and physical properties of PET films [243]
(Reproduced with permission from R.H. Peters and the Society of Dyers and Colourists)

together with the diffusion of cationic dyes into PAN fibres in the presence of benzyl alcohol [200, 245], *o*-phenylphenol [246], phenol [201, 246], nitrobenzene [201] and other carriers [200]. Roberts and Solanki [213] demonstrated that the presence of carrier within PET fibre reduced the entropy of activation of diffusion (ΔS^*) of four disperse dyes and ΔS^* of CI Basic Green 4 in Courtelle S was also found to be reduced by the presence of varying concentrations of phenol in the dyebath [246]. The observed reduction in entropy of activation of dye diffusion in the presence of carrier can be attributed to the polymer chains having gained entropy, as a result of their increased mobility brought about by the plasticising action of the carrier, which serves to reduce the extent to which the entropy of the dyes must be raised in order for dyeing to occur [214]. The findings that carriers reduce both the activation energy of diffusion and entropy of activation of diffusion provides further confirmation that the increased diffusional behaviour of a dye affected by carriers is related to the corresponding increase in segmental mobility of the polymer chains and, thus, free volume, brought about by plasticisation of the substrate.

Several workers have shown that the extent of plasticisation of a fibre (reduction in T_g), as determined using various methods such as extension in length of filaments, dynamic mechanical analysis (DMA) or differential scanning calorimetry (DSC), increased with increasing concentration of carrier either applied to or present within the fibre [200, 205, 208, 209,

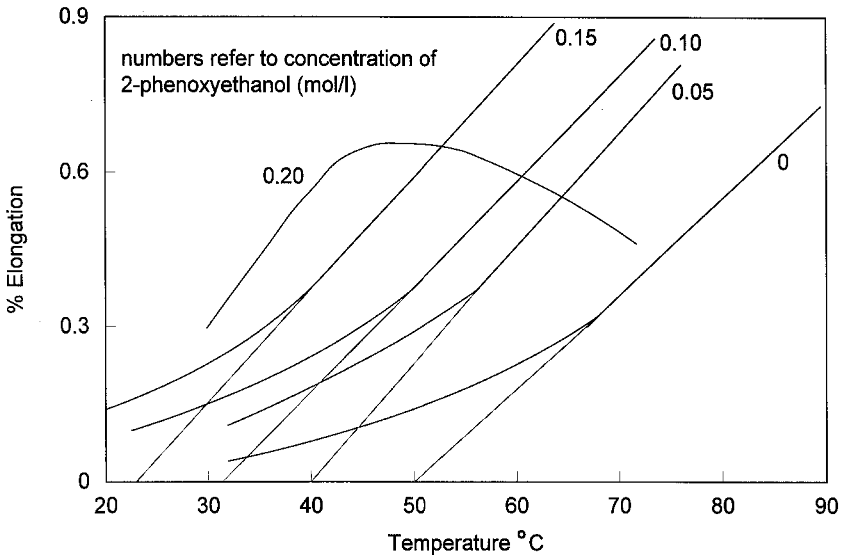


Figure 1.16 Effect of 2-phenoxy ethanol on the T_g of PET filaments [206]
(Reproduced with permission from the Society of Dyers and Colourists)

216, 242–244, 247–252]. Ingamells *et al.* found that the extent of plasticisation of PET filaments, as determined using extension in length, brought about by immersion in aqueous solutions of benzyl alcohol [251] and other carriers [206] reached a maximum value at a certain temperature for a particular concentration of carrier applied to the fibre (Figure 1.16).

Aitken *et al.* [249, 250] employed DMA to demonstrate that the extent of plasticisation of Courtelle S caused by immersion in an aqueous solution of benzyl alcohol reached a maximum value which was found [250], using gas chromatography, to correspond to the maximum uptake of the carrier on to the fibre. This latter work can be considered to lend further support to the theory that carriers plasticise the fibre insofar as the extent of plasticisation will, in general, increase with increasing concentration of plasticiser. Several workers have employed the dyeing transition temperature, T_d, as a reference temperature instead of T_g in describing the plasticizing action of carriers on fibres and its effect on dye diffusion. Commonly, T_d is obtained as the intercept on the ordinate of a plot of dye uptake versus temperature (the dotted lines shown in Figure 1.17).

In a study of the carrier action of phenol on the diffusional character of CI Disperse Orange 3 in PET films, it was concluded [252] that the use of T_d as a reference temperature in place of T_g was justified and Alberti [248, 253] employed T_d in studies of the effects of benzyl alcohol on the short-time dyeing of PAN fibre with CI Basic Green 4. Gur-Arieh and

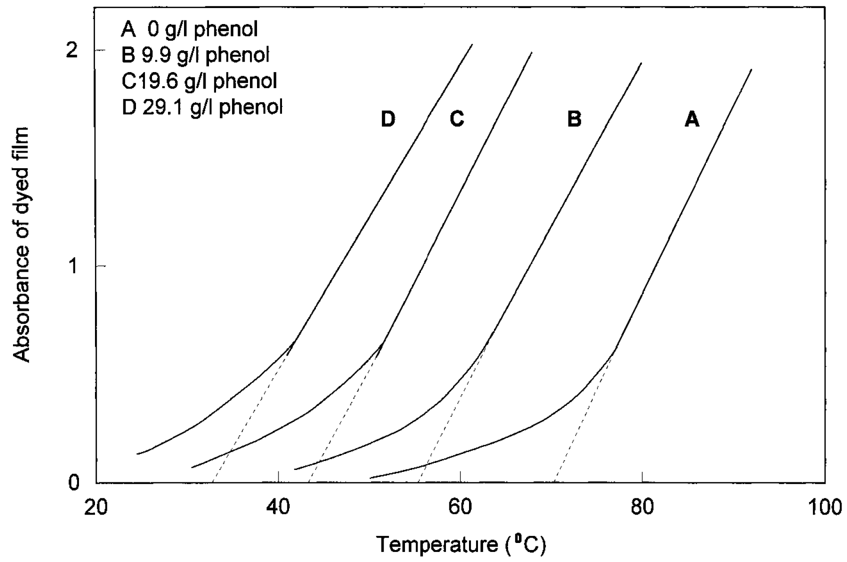


Figure 1.17 Adsorption of *p*-aminoazobenzene on PET film after 10 minutes in the presence of phenol [243]
(Reproduced with permission from R.H. Peters and the Society of Dyers and Colourists)

Ingamells [244], in a study of the effect of benzyl alcohol on the dyeing of Acrilan filaments, observed that whilst a linear relationship existed between T_g of Acrilan filament determined using extension in length and T_d measured from the uptake of CI Disperse Orange 3, the value of T_d was some 12°C higher than T_g, a difference which these workers attributed to the fact that the free volume required for onset of segmental mobility was less than that required for entry of the dye molecule into the fibre. In a study of the effects of four carriers on the dyeing properties of PET, it was also demonstrated [217] that values of T_d determined from the uptake of several disperse dyes were greater than the values of T_g determined using extension in length, and concluded that T_d is influenced by the structure of the dye. In a later study of the effect of benzyl alcohol on PET filaments, Ingamells and Narasimham [251] noted the need for caution when using T_d as a reference temperature to the T_g in the WLF equation (equation (1.16)) insofar as a knowledge of both parameters is required.

In view of the theory that increased dyeability results from the carrier plasticising the fibre, together with the observations that some carriers, such as monochlorobenzene and *m*-cresol [208, 209] can dissolve PET or induce crystallisation of the amorphous polymer [204] or impart considerable disorientation [200, 203, 209, 228], the plasticisation of the fibre has been investigated in terms of the solubility parameter concept, which, as mentioned in section 1.2.2, indicates the potential of interaction between a polymer and a solvent. Lemons *et al.* [204] investigated the plasticising effect of various solvents and carriers on PET and observed that those compounds which plasticised the polymer also accelerated the uptake of Latyl Violet 2R on to the fibre; these workers also demonstrated that the plasticisers had values of cohesive energy densities close to that of PET. Brown and Peters [209] found that although the δ_t values of several halogenated benzenes that exhibit carrier action were similar to that of PET, the correlation between carrier activity and similarity of δ_t of carrier and fibre was not high. Indeed, many aliphatic halogenated solvents of similar δ_t to that of PET were found to have no more than a minimal carrier activity and these workers concluded that factors other than modification of fibre structure contribute to carrier action [209]. Rosenbaum [254] found no correlation between the δ_t values of several plasticisers and their plasticising action on PAN fibre. Furthermore, no correlation was found between δ_t of several carriers and the T_g reduction (determined using extension in filament length) of Acrilan [232] or PET filaments [205]. Ibe [118] observed no relationship between the solubility of several solvents and carriers in PET and coincidence of the δ_t values of the polymer and carriers/solvents but found slightly better correlation between solubility of the compounds and their δ_a values with those of PET. Ingamells and Yabani [206] showed that six carriers reduced the T_g of undrawn PET filaments, as measured using extension in length, and, since the extent of reduction in T_g was found to be the same for equimolar concentrations of the different carriers in the fibre, these workers confirmed the findings of other workers [209, 230] that the controlling influence in plasticisation of PET was independent of the nature of the carrier. Ingamells and Yabani [206] also established no correlation between the δ_a of PET and that of the carrier insofar as although the extent of plasticisation (T_g reduction) of the fibre was the same for equimolar concentrations of the carriers, the δ_a values of the carriers ranged from 4.26 to 7.95 $(\mathrm{cal}^{0.5})\ \mathrm{cm}^{-1.5}$. However, the δ_d values of the carriers, with the exception of phenol, were close to that of the fibre and these workers [206] proposed that this observation supported the earlier suggestion made by Derbyshire and Peters [205] that non-polar forces predominate in the interaction between carriers and PET. Ingamells and Thomas [123] showed that the equilibrium uptake of three monoazo disperse dyes on PET decreased with increasing value of δ_a for several solvents, thus indicating the relative unimportance of the contribution that polar forces make towards dye–fibre substantivity. However, these workers [123] employed the dyeing transition temperature (T_d) as an indication of the effect of equimolar concentrations of various solvents on the dyeing behaviour of a monoazo disperse dye on PET and found that the T_d of the dye reached a minimum value when the ratio (δ_d^2/δ_a^2) of the solvents coincided with that of the polymer. This latter result was considered [123] to demonstrate that although carrier action is dominated by dispersion forces, the association forces also play some part. However, Gur-Arieh *et al.* [255] observed that several carriers reduced the T_g of PAN fibres, as measured using extension in length, and also that the extent of T_g reduction increased with increasing concentration of carrier in the fibre, but, in contrast to their findings with PET [206], the extent of plasticisation varied from carrier to carrier. Although these workers [255] found no correlation between plasticisation of PAN fibres and values of δ_d for the fibre and the various carriers used, maximum plasticisation occurred when the δ_a values of the carrier coincided with that of the fibre. These workers [255] therefore conluded that polar forces only contribute to T_g reduction (plasticisation) of PAN fibre. Consequently, Ingamells and Yabani [206] suggested that the reason for the observed difference in the extent of plasticisation of PAN fibre obtained for equimolar concentrations of different carriers was attributable to the large variation in the δ_a values of the carriers employed. The small variation in the δ_d values of the different carriers was considered to be unimportant since dispersion forces were considered not to contribute to PAN–carrier interaction [206]. Thus, for a compound to exhibit carrier activity on a polar fibre such as PAN, the values of δ_a for carrier and substrate must correspond, whereas for non-polar fibres such as PET, δ_d of the carrier and the fibre correspond [206].

Several workers have demonstrated that the uptake of disperse dyes on to various hydrophobic fibres increased with increasing concentration of carrier applied to or present within the substrate [195, 196, 200, 207–211, 214, 216, 242–245, 249, 250, 253, 256–259]. Rawicz *et al.* [203] found that uptake of Latyl Violet 2R reached a peak at a particular concentration of *o*-phenylphenol in the dyebath. McGregor *et al.* [211] observed that the equilibrium uptake of CI Disperse Red 15 on both PET and cellulose triacetate films increased with increasing concentration of carrier in the dyebath and reached a maximum value at the same carrier concentration; an increase beyond this particular carrier concentration decreased dye uptake. Other workers have observed that enhanced dye uptake brought about by the presence of a carrier reached a maximum value that corresponded to a particular concentration of carrier [162, 195, 198, 200, 206, 214, 251, 257, 258] (Figure 1.18).

Balmforth *et al.* [195] concluded that at carrier concentrations in excess of that which gave maximum dye uptake, undissolved carrier was present in the dyebath as a third phase in which the dye remained dissolved, thereby reducing dye uptake. Balmforth's suggestion has been endorsed by Ingamells and Narasimham [251] from studies of the effect of benzyl alcohol on the dyeing of PET with *p*-aminoazobenzene, although these workers also propose that maximum dye uptake may well represent a change in the molecular structure of the fibre. In a study of the effect of

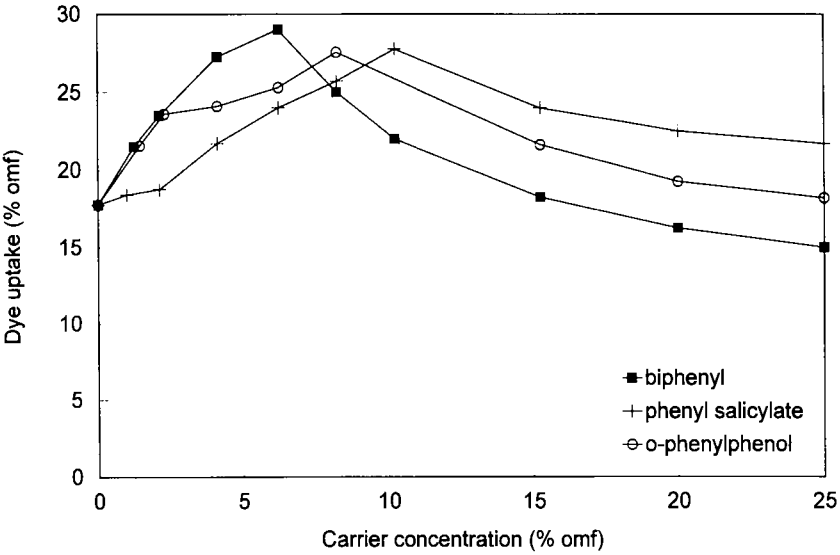


Figure 1.18 Effect of carrier concentration on uptake of CI Disperse Blue 9 on PET fibre at 100°C [195]
(Reproduced with permission from D. Balmforth and the Society of Dyers and Colourists)

varying concentrations of *o*-phenylphenol [246] and also benzyl alcohol [200] on the uptake of several basic dyes on to Courtelle S at 98°C, it was found that for both carriers, dye uptake reached a maximum value that corresponded to the aqueous solubility of the carrier at 98°C. Since an increase in concentration beyond the aqueous solubility of the carrier reduced dye uptake, it was concluded [200, 246] that at concentrations in excess of its aqueous solubility, the carrier was present in the dyebath as a third (liquid) phase for which the dye had greater affinity than either the water or fibre phases, thus concurring with the explanation given by Balmforth *et al.* [195]. Subsequent work by Aitken *et al.* on the effect of several carriers on the uptake of CI Basic Blue 45 [249] and CI Basic Blue 3 [250, 216] on to Courtelle S at 80°C, confirmed the findings [200, 246] that maximum dye uptake coincided with the aqueous solubility of the carriers at the particular temperature used. These workers also used gas chromatography [216, 250] to demonstrate that maximum uptake of CI Basic Blue 3 coincided with the maximum uptake of the carriers on to Courtelle S which, in turn, corresponded to the maximum aqueous solubility of the carriers. Furthermore, it was shown that at concentrations in excess of its water solubility, the uptake of each carrier decreased with increasing concentration, as a consequence of which, the extent of plasticisation (T_g reduction) as determined using DMA, decreased. These workers [216] concluded that the decrease in dye uptake that occurred at concentrations beyond the aqueous solubility of the carriers was primarily due to a reduction in the extent of plasticisation of the fibre, although dissolution of dye in undissolved carrier present in the dyebath as a third phase, as proposed by Balmforth *et al.* [195], may also contribute.

Carriers can also affect a change in the structure of PET fibre; both the crystallinity [228, 251, 252] and degree of orientation [199, 203, 209, 228, 251] of the substrate are altered in the presence of carriers. These structural changes brought about by carriers are similar to those produced as a result of heat setting [212], and it is considered that the extent to which crystallinity is increased by carriers is almost the same as that imparted by HT dyeing, whereas carrier dyeing causes a greater degree of disorientation of the fibre than HT dyeing [212]. Ingamells and Narasimham [252] demonstrated that carrier dyeing induced chain folding in PET fibres and that an increase in the extent of chain folding was accompanied by an increase in the ease of dyeing. In a study of the effects of carriers on the crease recovery of PET after heat setting, Ingamells and Sherkat [260] found that permanent deformations could be easily introduced in fabric containing carrier and that the extent of this phenomenon depended on the concentration and composition of the carrier. It was considered [251, 252] that although the enhancement of dye diffusion in PET fibres caused by carriers can be explained in terms of increased segmental mobility of the polymer chains, changes in the molecular structure of the polymer must also be considered. Several workers [261, 263] have pretreated PET fibres at low temperature with carriers dissolved in an organic solvent so as to introduce the carrier into the fibre as a means of temporarily reducing the T_g of the fibre prior to dyeing. Pretreatment was found to increase the exhaustion of several disperse dyes; Moore and Weigmann [262] observed that pretreatment with methylene chloride/biphenyl gave greater dye penetration of PET filaments than was obtained using a corresponding concentration of emulsified carrier in the dyebath which was attributed to either residual solvent present in the fibre or solvent-induced structural changes having occurred in the fibre.

In conclusion, evidence suggests that carriers function as diluents, their action being attributable to plasticisation of the fibre which reduces the T_g of the polymer, as a result of which the rate of dye diffusion is increased.

1.2.12. Solvent-assisted dyeing

Broadhurst [7] proposes that such processes for PET, in which organic solvents are employed as dyebath additives in order to accelerate the rate of uptake of disperse dyes on the substrate, may be considered as variants of carrier dyeing. Although this particular dyeing system has attracted attention, it has not achieved commercial usage.

Table 1.8 Linear penetration (%) of CI Disperse Red 60 in PET [265]

	Solvent : fibre ratio	100°C		120°C	
		5 min	15 min	5 min	15 min
Water	–	5	5	30	60
o-Dichlorobenzene	0.1:1	50	100	70	100
o-Dichlorobenzene	0.6:1	100	100	100	100
2-Phenoxy ethanol	0.4:1	10	30	100	100
2-Phenoxy ethanol	0.8:1	80	100	100	100

(Reproduced with permission from J. Skelly and the Society of Dyers and Colourists)

Derbyshire *et al.* [264] showed that the use of n-butanol at a concentration of 50 g l^{-1} considerably increased the rates of diffusion of several disperse dyes within PET film, improved the migration characteristics of a slow diffusing dye on PET fabric and also reduced the time of dyeing required to achieve full depths at 130°C. In a study of the effects of solvents on the dyeing of PET and other hydrophobic fibres, in which the concentration of solvent in aqueous dyebaths had been selected so as to give a two-phase system, Skelly [265] demonstrated that the degree of penetration of CI Disperse Red 60 in PET obtained in the early stages of dyeing at both 100 and 120°C was increased by the presence of both 2-phenoxy ethanol and *o*-dichlorobenzene in the aqueous dyebath (Table 1.8).

Furthermore, the presence of these and two other solvents in the aqueous dyebath enhanced the extent of fixation of the dye in the early stages of dyeing at 100°C, whereas enhanced dye fixation was achieved using only 2-phenoxy ethanol and benzyl alcohol in the early stages of dyeing at 120°C.

1.2.13. Solvent dyeing

Much interest has attended the use of organic solvents as alternatives to water for the application of disperse dyes to PET and also other hydrophobic fibres with chlorinated hydrocarbons, notably perchlorethylene (PER), having received most attention. The following account of this topic refers only to the dyeing of PET using disperse dyes from PER; details of the use of other solvents in the dyeing of PET [266, 267] and of PER and other solvents in the dyeing of other hydrophobic fibres are available elsewhere [7, 17, 112, 266, 268–270]. However, the solvent dyeing of PET and other hydrophobic fibres is not used commercially.

Fibres are rapidly and efficiently wetted by PER [268], the solvent being removable by treatment with steam or hot air [269, 271]. It is considered [268] that fibre swelling is lower in PER than in water with the consequence that mechanical deformation will be smaller than in water; treatment of PET with boiling PER causes a change in the morphology of the fibre which appears to involve an increase in the degree of orientation of the fibre [269]. Liquid PER has a lower specific heat and latent heat of vaporisation (0.205 cal g^{-1} C^{-1} [268] and 50 cal g^{-1} [272] respectively) than liquid water (1 cal g^{-1} C^{-1} [268] and 540 cal g^{-1} [272] respectively) so that heating costs are lower for PER dyeing. Although the thermal conductivity of liquid PER (0.11 kcal h^{-1} C^{-1} [268]) is lower than that of water [0.51 kcal h^{-1} C^{-1} [268]) this is considered [268] to be of little significance since heating of PER dyebaths is mostly carried out by convection rather than conduction. Whereas water, which is polar, having both high permittivity and dipole moment, possesses a unique structure that influences the conventional (aqueous) dyeing of PET with disperse dyes, PER is non-polar and aprotic and does not have any of the particular properties of water with the result that, it is considered [269], differences may arise between the dyeing processes in the two solvents. Nevertheless, as discussed below, a close similarity is found between the mechanisms of adsorption of disperse dyes on PET from water and PER. In the context of the role of the solvent in disperse dyeing, Heit *et al.* [273] obtained curvilinear isotherms for the equilibrium adsorption of CI Disperse Red 1 on to cellulose diacetate at 25°C from various organic solvents in which the dye was sparingly soluble and also found that dye uptake varied with the solvent used, which these workers demonstrated was not attributable to differences in fibre swelling caused by the different solvents. The findings of Heit *et al.* [273], together with the observation of Bird and Harris [90], that this particular dye gave a linear isotherm on cellulose diacetate when applied from an aqueous dyebath, suggests that the solvent from which dyeing occurs may be involved in dye–fibre interaction. Thompson [274], from a study of the adsorption of azobenzene on cellulose diacetate, concluded that water does not simply act as a solvent in aqueous dyeing with disperse dyes, but may cause configurational changes in the substrate thus competing allosterically with the dye.

The solubility of disperse dyes in PER, which increases markedly with increasing temperature [268], differs greatly for different dyes [269, 275]; Milicevic [268] found little correlation between solubility in PER at 121°C and partition coefficient on PET for a series of closely related aminoanthraquinone dyes. Linear isotherms are obtained for the adsorption of disperse dyes from PER on PET and, in a manner identical to that of aqueous phase transfer, the partition coefficient decreases and the saturation value increases with increasing temperature [268] (Figure 1.19).

As observed for aqueous dyeing, Datye *et al.* [276] observed that for the application of several disperse dyes from PER on to PET film, the heats of dissolution of the dyes in both the substrate and PER were positive whilst the heat of dyeing was negative. However, owing to the much greater solubility of disperse dyes in PER than in water [276], the parti-

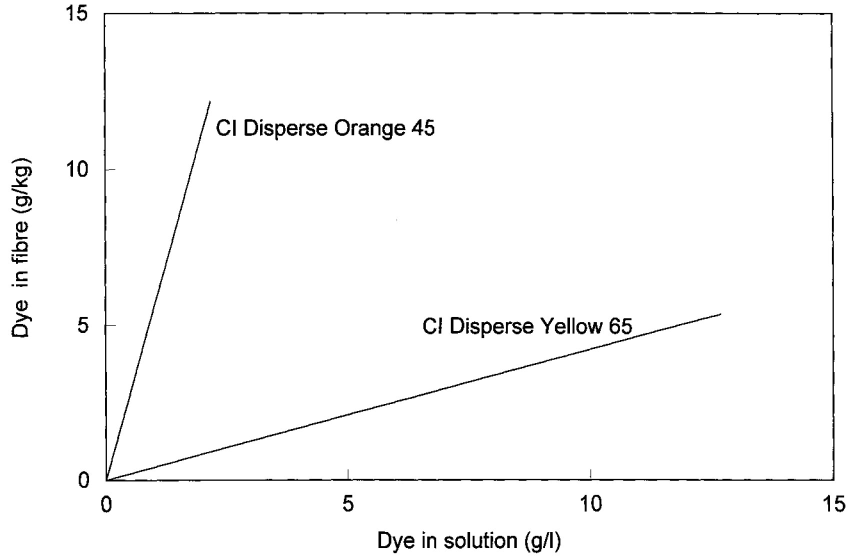


Figure 1.19 Adsorption isotherms of CI Disperse Orange 45, and CI Disperse Yellow 65, on PET from PER at 121°C [268]
(Reproduced with permission from AATCC)

tion coefficients obtained using PER are considerably lower than those obtained for aqueous application [268, 277], typical values for dyeing from PER being less than 10 [276] as opposed to values of between 30 and 800 obtained typically for aqueous dyeing [275]. Harris and Guion [278] demonstrated that the low partition coefficient observed for CI Disperse Violet 1 when applied to PET from PER, was attributable to the close similarity of the total solubility parameter (δ_t) of the dye (12.4 (cal cm^{-3})$^{0.5}$) to that of both the fibre (10.7 (cal cm^{-3})$^{0.5}$) and PER (9.4 (cal cm^{-3})$^{0.5}$), the suggestion being that owing to the similarity of δ_t of both the solvent and fibre, the solubility of the dye in each of these phases is similar in magnitude and the dye therefore has little preference for the fibre. The low partition coefficient of the dyes on PET when applied from PER characteristically result in low dye exhaustion and hence low colour yields; since the characteristic low values for *K* accrue from the high solubility of the dyes in PER, then a reduction in the solubility of the dye in the solvent will therefore increase *K* and hence increase dyebath exhaustion. Consequently, although dyebath exhaustion increases with decreasing liquor to goods ratio [268, 275], little success has been achieved using temperatures in the region of 120°C owing to the very high solubility of the dyes at these temperatures [279].

Datye *et al.* [276] demonstrated that in a manner similar to that observed for diffusion in aqueous systems, the diffusion coefficient of several disperse dyes within PET film from PER was constant and that the rate of diffusion of several disperse dyes within PET film from PER was greater than that from water. Milicevic [269] employed DSC to show that treatment with boiling PER reduced the T_g of PET fibre from 70 to 47°C and concluded that the greater rate of dyeing obtained using PER compared to water could be attributed to this plasticisation of the substrate. The rate of dye adsorption from PER was found to increase with increasing temperature [268, 276], values of the activation energy of diffusion (E^*) obtained for dyeing from PER being comparable to those found for aqueous dyeing [276].

The use of secondary or 'booster' solvents, commonly polar compounds such as dimethylacetamide, methanol and benzyl alcohol [268, 269, 275], improve the solubility of disperse dyes in pad liquors [268, 280]. Gebert [275] demonstrated that the addition of water (10% o.w.f.) to a PER dyebath markedly increased the rate of uptake and extent of penetration of several disperse dyes on PET. The observed increase in rate of dyeing caused by the presence of water in the PER dyebath, which concurs with the findings of McGregor *et al.* [211], that the diffusion coefficient of CI Disperse Red 15 in PET film from iso-octane was increased by the presence of water, may be attributable to the water having lowered the T_g of the fibre [17, 112]. The influence of various solvents on the T_g and other physical characteristics of PET and other hydrophobic fibres, which has been studied by many workers, is reviewed by Ingamells [112].

1.2.14. High-temperature dyeing

As previously mentioned, owing to the low rate of diffusion of disperse dyes in PET at temperatures up to the commercial boil (98°C), the use of high temperatures (in the region 125–135°C) enables the dyeing rate to be increased to a commercially acceptable level. The dramatic effect of temperature on the rate of dyeing of PET with disperse dyes can be demonstrated by the finding of Rochas [281] that dyeings of equal depth could be obtained after 11 seconds at 200°C, 5 minutes at 125°C and 5 days at 60°C and of Merian *et al.* [282] that the rate of dyeing at 130°C was some 200 times greater than at 100°C, showing that dyeing rate increases approximately six-fold for a temperature increase of 10°C.

It is generally considered that HT dyeing in the absence of carrier (in the region 125 to 135°C) offers several commercial advantages over carrier dyeing at 98°C, namely, shorter dyeing times, excellent penetration and coverage of barriness as well as higher colour yield and, in some cases, superior fastness properties of resultant dyeings. Essentially, the greater rate of dyeing and generally superior dye migration obtained in HT dyeing, as compared to dyeing at the boil in the presence of a carrier, can be considered to be a consequence of the higher kinetic energy of the dye molecules, the greater segmental mobility of the less-ordered regions within the fibre and the higher aqueous solubility of the dye at elevated temperatures. However, the use of carriers in HT dyeing also offers several benefits, namely, superior coverage of barré effects in textured PET fabrics and, in some cases, improved levelling. Furthermore, since carriers enable HT dyeing to be expedited at lower temperatures (commonly in the range 110–125°C), the handle and bulk of texturised PET materials is less impaired by dyeing at such lower temperatures, which, in addition, results in reduced liberation of oligomers from the polymer. Also, PET fibres shrink when immersed in hot water, the extent of shrinkage increasing with increase in temperature; shrinkage is promoted by carriers, this effect also increasing with increase in temperature [283]. As a consequence of fibre shrinkage, consolidation of the material can impede liquor flow causing poor dye levelness and penetration, this being of particular significance in, for example, package dyeing. Commonly, specific carriers which are effective in promoting dye migration and which impart low shrinkage to PET under HT dyeing conditions are used [5, 56, 284]. Further, as previously discussed, the propensity to dispersion failure is greatest in the case of HT dyeing; since some non-ionic levelling agents as well as some anionic dispersing agents can have a deleterious effect on dispersion stability, dye makers may recommend specific auxiliaries for use in HT dyeing.

1.2.14.1. Classification of dyes for HT dyeing. The SDC has proposed four tests by which the migration, build-up, diffusion rate and critical dyeing temperature characteristics of disperse dyes on PET fibres under HT conditions can be determined [41]. Many dye makers have adopted their own classification system for their dye ranges; for example, ICI use an A, B, C, D classification system [285–288] for their dyes based on the dyeing and heat (sublimation) fastness of the dyes, according to which, coverage of barré in fabric generally decreases in the order type B > type C > type D [285] whilst heat fastness increases in the same order; type D dyes are predominantly intended for application by HT or Thermofixation (section 1.2.15) dyeing methods [287]. BASF [5] divide their range of Palanil dyes into four groups (A, B, C and D) according to their levelling power and into three groups (I, II and III) in accordance with their ability to cover variations in texturised PET. In very general terms, dyes of high heat fastness tend to possess low diffusion rates within PET and exhibit poor coverage of barré; although such dyes are applicable to PET under HT conditions in both the absence and presence of carrier, often they are not suitable for carrier application at 98°C. Derbyshire [285] considers that from the viewpoint of achieving adequate colour yields, virtually any type of disperse dye can be satisfactorily used in HT dyeing, although attention must be paid to their level dyeing properties, especially with respect to coverage of barré.

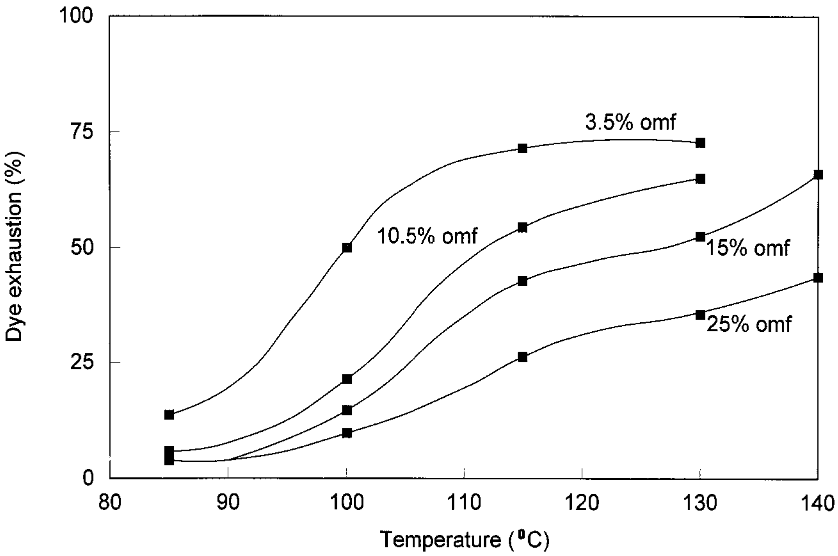


Figure 1.20 Effect of dybath temperature on exhaustion of CI Disperse Orange 3 on PET fibre [295]
(Reproduced with permission from H.R. Hadfield and the Society of Dyers and Colourists)

1.2.14.2. Effects on dye exhaustion and levelling. Although this pressure dyeing method is commonly associated with PET and other hydrophobic fibres, particularly cellulose triacetate, its commercial introduction developed from work initiated by Walter in 1938 on the dyeing of wool [289]. The beneficial effects of using elevated temperatures in the dyeing of PET were demonstrated shortly after the commercial introduction of the fibres [69, 72, 74–77, 79, 199, 290–293]. The extent of exhaustion of disperse dyes on PET fibre increases markedly with increasing temperature up to 130°C [294] and also 140°C [295] (Figure 1.20), the increase in exhaustion being greater for dyes of low diffusional power [457].

Other workers have demonstrated that the rate of dye exhaustion depends on the temperature and duration of dyeing as well as the concentration of dye in the dyebath [43, 296–299]. For a given dye at a given concentration on a given PET fibre, dye exhaustion occurs most rapidly over a particular temperature range; the test method devised by the SDC [41] to determine this 'critical temperature range' of disperse dyes (of approximately 30°C) is based on the temperature-, time- and concentration-dependence of dye exhaustion. The levelling properties of the dyes on PET also increase with increasing temperature up to 140°C and depend on the diffusional behaviour of the dyes, with faster diffusing dyes exhibiting greater levelling at all temperatures [295], and dyes of high sublimation fastness generally exhibiting poor levelling on PET

Table 1.9 Water solubility characteristics of disperse dyes [282]

	Solubility (mg dm^{-3})		
CI Disperse	80°C	100°C	130°C
Orange 13	0.2	~0.3	~0.78
Red 13	4.0	~16	~126
Red 7	21	~93	~640
Blue 14	~2	~5	~15
Blue 3	30	~62	~490
Blue 23	61	~190	~920

(Reproduced with permission from the Society of Dyers and Colourists)

[285]. Merian and Lerch [300], from a study involving several disperse dyes on PET, considered that although dyes of partition coefficient less than 700 exhibited good levelling, those of *K* value in excess of 700 were preferably applied at high temperatures in order to achieve good levelling. Gerber [301] obtained an inverse relationsip between the migration properties of a series of disperse dyes on PET and their molar volume; the propensity to unlevelness was also found to decrease with increasing aqueous solubility of the dyes. Merian *et al.* [282] demonstrated that the aqueous solubilities of six commercial disperse dyes increased, in some cases very markedly, with increasing temperature from 80 to 130°C (Table 1.9). These workers also showed that the diffusion coefficient of several disperse dyes at 130°C was significantly greater than that at 100°C on both unset and heat set PET. Leube [45] considers that at 130°C, especially in pale shades, the dyes can be assumed to be completely in solution.

1.2.14.3. Rapid dyeing processes. Rapid dyeing HT processes are primarily intended to shorten the HT dyeing method, but maximise dye migration, via optimisation of the rate of dyebath exhaustion. Essentially, in such processes, the rate of dye exhaustion is carefully controlled from the start of dyeing by means of temperature control, so that the dyes are adsorbed uniformly during the heating-up phase, with the result that the time required at top temperature (e.g. 130°C) is reduced. Generally, such methods involve quickly raising the temperature of the dyebath to the lowest critical temperature range for the dye combination used, then controlling the rate of temperature rise up to the highest critical temperature range for the particular dye combination; from this temperature up to top temperature, the dyebath is once more rapidly heated and dyeing continued at this temperature for a prescribed time. Details of critical temperature ranges, heating rates and dyeing times at top temperature are usually provided by dye makers and the reader is directed to dye manufacturers' literature for further details of such processes [5, 302, 303]. However, in the context of rapid dyeing HT processess, from a study of the effect of dye penetration on visual colour yield, Dawson and Todd [288] concluded that, for disperse dyes on PET, an increase in colour yield can occur as dyeing proceeds without a corresponding increase in dyebath exhaustion and proposed that rapid dyeing methods for PET may cause problems associated with ring-dyeing, unless care is exercised in dye selection.

1.2.14.4. Dispersant-free dyeing. As a means of overcoming the problems caused by the characteristic poor dispersion stability of disperse dyes under HT dyeing conditions – namely, inadequate levelling and poor reproducibility – an HT dyeing method has been devised [304] that involves the use of dispersant-free dyes dissolved in the presence of surfactants and recycling of the residual liquor. Navratil [304], using CI Disperse Red 169, CI Disperse Red 50 and CI Disperse Blue 125 and textured PET, demonstrated that dye dissolution was best affected using a non-ionic/anionic surfactant mixture and that high surfactant concentrations (between 28 and 72 times greater than the dye concentration) were required to dissolve the dyes and that this surfactant mixture increased the diffusion coefficient of the dyes within PET. The degree of exhaustion of the dispersant-free dyes was found to be virtually temperature- and concentration-independent at a given surfactant concentration, the rate of dye exhaustion in the presence of surfactant being independent of dye concentration and also slower than that obtained for dyeing from dispersion [304, 305], from which it was proposed [305] that level dyeings could be obtained without recourse to special time/temperature programs. Navratil [304] developed a mathematical model that was shown to describe accurately the exhaustion kinetics of the three dispersant-free dyes in the presence of surfactant. This author [304, 305] showed that for dispersant-free dyes in the presence of surfactant, the exhaustion curves and dye distribution within the fibre were independent of dye concentration, from which it was concluded [305] that for given dyeing conditions on a given substrate, each dye has only one exhaustion curve with the result that on-tone build-up can be achieved over a variety of concentrations and shades. Furthermore, Navratil [305] demonstrated the feasibility of HT dyeing of PET with true solutions of dyes in the absence of surfactant, showing that the rate of dye exhaustion obtained for such a system was much greater than that obtained for dye dispersions. This author [305] concluded that although such a system would present no problems with dispersion stability, yield on-tone build-up over a range of dye concentrations and shades and probably shorten dyeing cycles, high rates of liquor circulation would be required to ensure an acceptable levelness of dyeing.

1.2.15. Thermofixation

This dyeing process, introduced by Du Pont in 1949 under the trade name 'Thermosol' [306–309] utilises the high rate of dyeing achieved at high temperatures (commonly in the region of 210°C [7]; indeed, a dyeing achieved in less than one hour at 130°C can be obtained after 20 to 60 seconds at about 200°C [310]. Essentially, in this continuous pad-bake process, which, although applicable to non-ionic colourants (namely, vat and azoic colourants) other than disperse dyes and to hydrophobic fibres other than PET [308, 309], but in practice is nowadays mostly restricted to disperse dyes on polyester and polyester/cellulosic blends, the fibre is padded with dye dispersion, dried and then baked for between 5 and 90 seconds at a temperature in the region of 175 to 225°C depending on fibre type, dye class and heat source used [308]. Meunier [309] cites that on PET, dyeing is typically achieved in 60 seconds using dry air, 10 seconds with contact heating or some 3 seconds using infrared heating. Amongst advantages cited [286, 310–313] for this process are that owing to the high dye diffusion rate at the very high temperatures used no carrier is necessary, heat setting and dyeing can be simultaneously effected, no pressurised equipment is required, high volumes of material can be economically processed owing to the continuous nature of the process and dye fixation in the region of 75 to 90%. However, since Thermosol dyeing is a continuous process and high-volume usage of PET was rare during the initial years of PET dyeing, it did not obtain great commercial importance until 1958 [310] when the popularity of PET/cotton blend rainwear fabrics warranted continuous production; the increasing popularity of PET/cotton blends, which occurred in the early 1960s [315] and has persisted to the present time, stimulated further demand for high-volume, continuous dyeing. Although, several dye classes and dyeing conditions can be employed for the cellulosic component, the application of disperse dyes to the PET component comprises, essentially, of padding with dye dispersion, drying and baking. Although a considerable amount of work has attended the thermofixation of dyes on PET blends, only the transfer of disperse dyes to PET under thermofixation conditions is considered herein, the reader being directed elsewhere [7, 17, 285, 310, 314–324] for discussions of the dyeing of PET/cotton blends using this process.

Thermofixation of disperse dyes on 100% PET fibres is mostly restricted [247] to narrow fabric dyeing [310, 325] although the process has been applied to the dyeing of texturised PET fabrics. In the latter case, migration inhibitors must be added to the pad liquor in order to reduce dye migration during drying [5, 285]. Furthermore, to reduce stiffness and loss of bulk of the goods, the temperature of fixation may be reduced to between 160 and 180°C, depending on fibre type [5] and the addition of

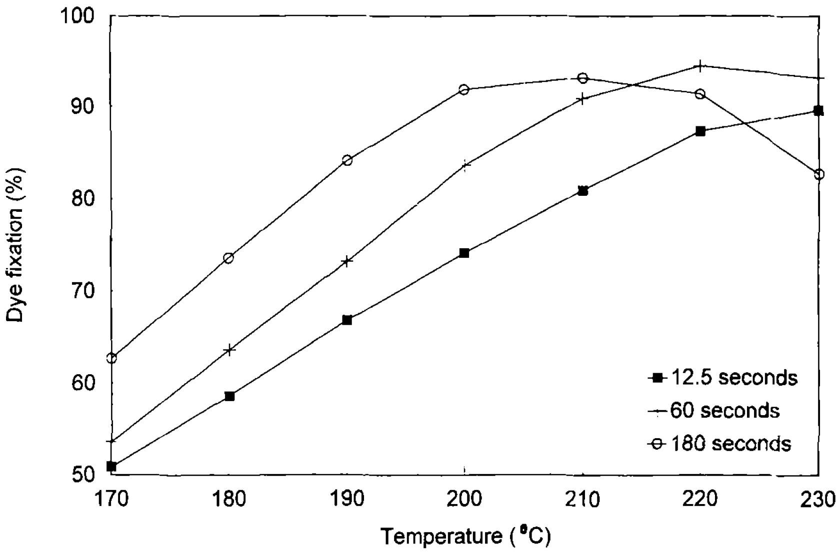


Figure 1.21 Effect of temperature and time on the fixation of CI Disperse Red 86 on PET fabric (310)
(Reproduced with permission from the Society of Dyers and Colourists)

urea to the pad liquor increases the rate [285] and extent [323] of dye fixation. Also, at such reduced fixation temperatures, superheated steam often yields more rapid dye fixation than does dry heat [5].

Keaton and Preston [310] demonstrated that the quantity of disperse dye fixed to PET fibre varied for different dyes and was also dependent upon the duration and temperature of heating (Figure 1.21). For long periods of heating, the extent of fixation increased with increasing temperature, reaching a maximum value at a particular temperature and thereafter decreased with further temperature increase as a result of excessive dye sublimation (Figure 1.21). Furthermore (Figure 1.21), the temperature at which maximum fixation occurred was found to decrease with increasing time of heating [310]. Datye *et al.* [136] observed that both the rate and extent of dye fixation on PET at 210°C decreased with increasing time of heating. Somm [320] showed that the time required for dye fixation on PET at a given temperature increased linearly with increase in concentration of dye and that the maximum achievable yield decreased with increase in dye concentration.

Keaton and Preston [310] concluded that the optimum thermofixation conditions for a given disperse dye were dictated by the rate of diffusion, and thus the molecular size, of the dye. Somm [320] demonstrated that the diffusion coefficient of low sublimation dyes were only some 2 to 8 times greater than those obtained for dyes of high sublimation fastness at

200°C in PET film and that the values of diffusion coefficient were approximately doubled for a temperature rise of 10°C. Datye *et al.* [131, 132] demonstrated that the diffusion coefficient of disperse dyes within PET at temperatures up to 210°C were concentration-independent; these workers concluded that dye adsorption occurs from the vapour phase, the rate-determining step being diffusion of dye within the fibre. Datye and Pitkar [145] observed that sigmoidal plots of M_t/M_∞ versus $t^{1/2}$ were obtained for the rate of uptake of 1-amino-2-methoxy-4-(p-toluene-sulphonyl) aminoanthraquinone on PET at 210°C, such non-linearity in the initial stages contrasting with the linearity predicted by Fick's equation for constant boundary conditions and a concentration-independent diffusion coefficient. Sigmoidal plots had also been obtained by Jones [147] for the rate of adsorption of saturated azobenzene vapour on to secondary cellulose acetate and by Jones and Seddon [89] for the adsorption of saturated vapours of several model compounds and disperse dyes on this fibre. It is considered [89, 145] that curvature of the rate plots accrues from a two-stage adsorption process, the first stage, corresponding to the initial curvature being due to to a surface concentration that increases with time and the second stage, that corresponds to the linear portion of the curve, being due to steady-state diffusion in which the surface concentration remains constant.

Merimond [326] demonstrated that the extent of fixation of two disperse dyes on PET at 180°C was greater when a non-ionic agent rather than an anionic surfactant had been included in the pad liquor. Datye *et al.* [136] found that the saturation value of dye uptake at 210°C on PET decreased with increasing concentration of dispersing agent present in the pad liquor; in a similar manner, the observation [320] that the fixation yield of a dye dispersed with different amounts of dispersing agent on PET was found to decrease with increasing concentration of dispersing agents was considered to support the use of liquid forms of dyes rather than powder brands.

1.2.16. Afterclearing

Commonly, the dyed PET is cleared of surface-deposited dye as well as auxiliaries (e.g. carriers, surfactants) by means of treatment with detergent or reductive or oxidative treatments, in order to secure optimum fastness of the dyeing to, for instance, rubbing, washing, light and heat setting and also to improve the brightness of shade.

Dyeings on PET, especially in medium and heavy depths [5], are often reduction cleared; the treatment is given to some forms of PET materials, regardless of depth of shade, since it removes surface-deposited oligomers which otherwise, would impair the subsequent spinning performance of the fibre [7]. When the reduction-clearing process was devised [218] the dyeing of PET was predominantly carried out using carriers at 98°C and the dispersion quality of the available dyes was such that their tendency to aggregate and deposit on the fibre surface was much greater than with modern disperse dye preparations [285]. However, although the importance of the process has receded in recent years owing to the current predominance of high-temperature dyeing methods together with the superior dispersion properties of modern disperse dyes and the excellent liquor exchange enjoyed with modern dyeing machines [285], the process continues in use especially for circulating-liquor dyeing processess [7]. The process typically consists of treating the rinsed, dyed material for 20 to 30 minutes at between 50 and 70°C in an aqueous bath comprising 2 g l^{-1} sodium hydroxide (flake), 2 g l^{-1} sodium dithionite and 1 g l^{-1} nonionic surfactant, followed by rinsing and, if necessary, neutralisation with dilute aqueous acetic acid; for some types of PET fibre that are sensitive to alkaline attack, NaOH may be replaced by ammonia [7]. The reduction-clearing process relies on the marked hydrophobicity of PET which prevents the penetration of water-soluble substances at temperatures below the boil, as a consequence of which, virtually complete destruction of surface-deposited dye can occur without harm to dye that has penetrated the fibre.

In the cases of pale and medium-depth dyeings or for those dyes which cannot withstand reduction-clearing, the dyed fibre can be given an alkaline scour [5, 18]; residues of anthraquinone dyes which may remain after reduction-clearing, may be removed using an oxidative treatment [7].

1.3. Azoic colorants

In the conventional application of azoic colorants to cellulosic fibres [8], namely, application of the coupling component followed by subsequent development with the diazotised base, the two components are applied, as ions, generally at low temperature under alkaline conditions. However, as observed by Waters in 1950 [8], although such a process is unsuitable for PET fibres, successful results can be achieved by using a 'concurrent' azoic process in which the aromatic amine and coupling component are applied together as aqueous dispersions at the boil, with subsequent development being carried out by immersion in hot nitrous acid or by means of a 'reversed' azoic process in which application of the amine is followed by that of the coupling component and subsequent development [7, 327]. The use of azoic colorants on PET fibres was discussed in the early 1950s [8, 69, 74, 75, 78, 218, 290, 328]; initially, only simple, low M_r amines and naphthols were employed [8, 285] that possessed adequate diffusional behaviour within the fibre at the boil, enabling deep, maroon, scarlet and red shades to be obtained [218]. With the advent of carrier and HT dyeing methods, the range of coupling components increased [218, 285] and the use of CI Disperse Black 1 became of importance for the production of blacks [285]. However, as both the range of disperse dyes and the use of HT dyeing increased, the use of azoic colorants to produce deep shades on PET diminished, owing to the length of the azoic dyeing process and the propensity of many azoic combinations to 'blinding' [285]. The dyeing of PET with this class of colorant is nowadays little used commercially, with the exception of the HT application of CI Disperse Black 1 and CI Coupling Component 18 for the production of strong black [7, 285].

1.4. Vat dyes

Although dyes of this class can be applied to PET fibres, their use is nowadays mostly restricted to the dyeing of PET/cotton blends [324]. The application of this dye type to PET was described as early as 1950 [329]; although selected dyes can be applied using both continuous [72, 73] and HT [7, 68, 69, 330] dyeing methods, the dyes are rarely applied by exhaustion methods [7]. The dyes can be applied from dispersion or as a dispersion of the vat acid [7, 76], suitable dyes being of small molecular size, belonging to the indigoid, thioindigoid and AQ classes [7]. The sulphuric acid ester derivatives of vat dyes can also be applied to PET [7, 76].

References

1. J G Cook, *Handbook of Textile Fibres*, Vol. 3, 4th edn, Merrow, Watford, 1968.
2. J S Ward, *Rev. Prog. Col.*, **14** 98 (1984).
3. K W Hillier in *Man-made Fibres Science and Technology* (ed. H F Mark, S M Atlas and E Cernia), Vol. 3, Interscience, New York, 1968, p. 1.
4. E V Martin and C J Kibler in *Man-made Fibres Science and Technology* (ed. H F Mark, S M Atlas and E Cernia), Vol. 3, Interscience, New York, 1968, p. 83.
5. *Dyeing and Finishing of Polyester Fibres*, B 363e, BASF, Germany, 1975.
6. J K Thimm, *Text. Chem. Col.*, **2** 69 (1970).
7. R Broadhurst in *The Dyeing of Synthetic-Polymer and Acetate Fibres* (ed. D M Nunn), Dyers Co. Pub. Trust, Bradford, 1979.
8. E Waters, *JSDC*, **66** 609 (1950).
9. J D H Hall, J R Whinfield and ICI, USP 2,590,402 (1952).
10. N J Gajjar and Du Pont, USP 2,828,528 (1958).
11. K D Houser, *Text. Chem. Col.*, **15** 70 (1983).
12. C G G Namboori, *Text. Chem. Col.*, **1** 50 (1969).
13. A A-M Gorrafa, *Text. Chem. Col.*, **12** 83 (1980).
14. R T Shet, S H Zeronian, H L Needles and S A Siddiqui, *Text. Chem. Col.*, **14** 233 (1982); H L Needles, S Holmes and M-J Park, *JSDC*, **106** 385 (1990).
15. *Colour Terms and Definitions*, 1988 edn, Society of Dyers and Colourists, Bradford, 1988.
16. S R Sivaraja Iyer in *The Chemistry of Synthetic Dyes*, Vol. VII (ed. K Venkataraman), Academic Press, New York, 1974.
17. R H Peters, *Textile Chemistry*, Vol. III, Elsevier, Amsterdam, 1975.

18. S M Burkinshaw in *The Chemistry and Application of Dyes*, (ed. D R Waring and G Hallas), Plenum, New York, 1990, pp. 237–379.
19. W M Gardner, *JSDC*, **38** 171 (1922).
20. A G Green and K H Saunders, *JSDC*, **39** 10 (1923).
21. A G Green and K H Saunders, *JSDC*, **40** 138 (1924).
22. G H Ellis, *JSDC*, **40** 285 (1924).
23. G H Ellis, *JSDC*, **41** 95, 98 (1925).
24. G H Ellis, *JSDC*, **42** 184 (1926).
25. G H Ellis, *JSDC*, **57** 353 (1941).
26. G H Ellis and British Celanese Ltd, BP 219,349 (1924).
27. J Baddiley, A Sheperdson and British Dyestuff Corporation, BP 211,720 (1923).
28. A J Hall and The Silver Springs Bleaching and Dyeing Co. Ltd, BP 222,001 (1923).
29. J Baddiley, A Sheperdson, H Swann, J Hill, L G Lawrie and British Dyestuff Corporation, BP 246,984 (1926).
30. P Gregory in *The Chemistry and Application of Dyes* (ed. D R Waring and G Hallas), Plenum, New York, 1990.
31. I D Rattee and M M Breuer, *The Physical Chemistry of Dye Adsorption*, Academic Press, London, 1974.
32. L A Shuttleworth and M A Weaver in *The Chemistry and Application of Dyes* (eds. D R Waring and G Hallas), Plenum, New York, 1990, pp. 107–163.
33. J F Dawson, *Rev. Prog. Col.*, **3** 18 (1972); **9** 25 (1978); **14** 90 (1984).
34. O Annen, R Egli, R Hasler, B Henzi, H Jacob and P Matzinger, *Rev. Prog. Col.*, **17** 72 (1987).
35. C V Stead in *The Chemistry of Synthetic Dyes*, Vol. III (ed. K Venkataraman), Academic Press, New York, 1970, pp. 385–462.
36. R K Fourness, *JSDC*, **72** 513 (1956).
37. H E Shroeder and S N Boyd, *Text. Res. J*, **27** 275 (1957).
38. D Blackburn in *The Dyeing of Synthetic-polymer and Acetate Fibres* (ed. D M Nunn), Dyers Co. Pub. Trust, Bradford, 1979.
39. *JSDC*, **80** 237 (1964).
40. *JSDC*, **81** 209 (1965).
41. *JSDC*, **93** 228 (1977).
42. W Beckmann, *Text. Chem. Col.*, **2** 350 (1970).
43. J Carbonell and U Lerch, *Colorage*, (1) 23 (1972).
44. E Schoenpflug and P Richter, *Text. Chem. Col.*, **7** 136 (1975).
45. H Leube, *Text. Prax. Int.*, **33** 733 (1978); *Text. Chem. Col.*, **11** 106 (1979).
46. C H A Schmitt, *Amer. Dyest. Rep.*, **51** 974 (1962).
47. J Carbonell and V Sanahuja, *Textilrundschau*, **17** 529 (1962).
48. E F Shnider, *Amer. Dyest. Rep.*, **52** 370 (1963).
49. P Richter and D Wergerle, *Proc. Int. Wool Text. Res. Conf., Aachen*, **5** 273 (1975).
50. J F Leuck, *Amer. Dyest. Rep.*, **68** (11) 49 (1979).
51. G T Clark, M A Weaver and H W Somers, *Text. Chem. Col.*, **13** 238 (1981).
52. H Braun, *Rev. Prog. Col.*, **13** 62 (1983).
53. S Heimann, *Rev. Prog. Col.*, **11** 1 (1981).
54. J K Skelly, *JSDC*, **96** 618 (1980).
55. T M Baldwinson in *Colorants and Auxiliaries*, Chapter 10 (ed. J Shore), SDC, Bradford, 1990.
56. A N Derbyshire, W P Mills and J Shore, *JSDC*, **88** 389 (1972).
57. T M Baldwinson in *Colorants and Auxiliaries*, Chapter 12 (ed. J Shore), SDC, Bradford, 1990.
58. J Shore in *Colorants and Auxiliaries*, Chapter 3 (ed. J Shore), SDC, Bradford, 1990.
59. A Murray and K Mortimer, *JSDC*, **87** 173 (1971).
60. K A Thakore, N C Shah and R M Mittal, *Amer. Dyest. Rep.*, **76** (9) 58 (1987).
61. R Clavel, *Rev. Gen. Matiere Col.*, **28** 145,167 (1923), **29** 95 (1924).
62. H H Burns and J K Wood, *JSDC*, **45** 12 (1929).
63. V Kartaschoff, *Helv. Chim. Acta*, **8** 928 (1925).
64. T Vickerstaff and E Waters, *JSDC*, **58** 116 (1942).
65. H E Millson and L H Hurl, *Text. Res. J*, **21** 685 (1951).

66. C L Bird, F Manchester and P Harris, *The Faraday Society Discussion on Dyeing and Tanning*, 85 (1954).
67. C L Bird, H K Partovi and G Tabbron, *JSDC*, **75** 600 (1959).
68. P L Meunier, *Amer. Dyest. Rep.*, **40** 51 (1951).
69. C G Lyle, J J Iannarone and R J Thomas, *Amer. Dyest. Rep.*, **40** 585 (1951).
70. R J Thomas and P J Meunier, *Amer. Dyest. Rep.*, **38** 925 (1949).
71. *Du Pont Technical Bulletin* **5** (2) 82 June 1949.
72. P J Choquette, *Amer. Dyest. Rep.*, **40** 681 (1951).
73. G Carmichael, *Text. Age*, **15** 32 (1951).
74. A P Roy, *Amer. Dyest. Rep.*, **41** 35 (1952).
75. S G Turnbull, *Amer. Dyest. Rep.*, **41** 75 (1952).
76. E H Gamble and W G Parks, *Amer. Dyest. Rep.*, **41** 223 (1952).
77. W R Remington, *Amer. Dyest. Rep.*, **41** 859 (1952).
78. *The Dyeing of Terylene Polyester Fibre*, ICI, Manchester, 1952.
79. J E Reith and R J Andres, *Amer. Dyest. Rep.*, **42** 35 (1953).
80. M J Schuler and W R Remington, *The Faraday Society Discussion on Dyeing and Tanning*, 201 (1954).
81. E H Daruwalla and K Turner, *JSDC*, **69** 240,440 (1953).
82. J R Aspland and C L Bird, *JSDC*, **77** 9 (1961).
83. C L Bird and J M Firth, J. *Text. Inst.*, **51** T1342 (1960).
84. T. Vickerstaff, *The Physical Chemistry of Dyeing*, Oliver and Boyd, London, 1954.
85. D Patterson, *The Faraday Society Discussion on Dyeing and Tanning*, 247 (1953).
86. D Patterson and R P Sheldon, *JSDC*, **76** 178 (1960).
87. T G Majury, *JSDC*, **70** 442,445 (1954).
88. F Jones and R Seddon, *Text. Res. J.*, **34** 373 (1964).
89. F Jones and R Seddon, *Text. Res. J.*, **35** 334 (1965).
90. C L Bird and P Harris, *JSDC*, **73** 199 (1957).
91. K Hoffmann, W McDowell and R Weingarten, *JSDC*, **84** 306 (1968).
92. E Merian, *Text. Res. J.*, **36** 612 (1966).
93. J Wegmann, *Can. Text. J.*, **79** 37 (1962).
94. B Lipp-Symonowicz and G W Urbancyk, *Mell. Text.*, **55** 59 (1974).
95. R Kuehni, *Text. Chem. Col.*, **7** 112 (1973).
96. C H Giles, A Yabe and C D Shah, *Text. Res. J.*, **38** 467 (1968).
97. C H Giles, D P Johari and C D Shah, *Text. Res. J.*, **38** 1048 (1968).
98. C H Giles in *The Theory of Coloration of Textiles*, 2nd edn (ed. A Johnson), Dyers Co. Pub. Trust, Bradford, 1989.
99. C H Giles, *Chemistry and Industry*, 137 (1966)
100. W McDowell and R Weingarten, *JSDC*, **85** 589 (1969).
101. F Jones, *Rev. Prog. Col.*, **1** 15 (1969).
102. M M Allingham, C H Giles and E L L Neustadter, *Disc. Far. Soc.*, **16** 248 (1954).
103. F M Arshid, C H Giles and S K Jain, *J. Chem. Soc.*, 1227 (1956).
104. C H Giles, *Text. Res. J.*, **31** 141 (1961).
105. C L Bird, *Palette* (15) 25 (1964).
106. O Glenz, W Beckmann and W Wunder, *JSDC*, **75** 141 (1959).
107. E A Grulke in *Polymer Handbook*, 3rd edn (ed. J Brandrup and E H Immergut), John Wiley, New York, 1989.
108. J H Hildebrand and R L Scott, *The Solubility of Nonelectrolytes*, 3rd edn, Reinhold, New York, 1950.
109. E Burrel in *Polymer Handbook*, 2nd edn, Wiley, New York, 1973.
110. G Scatchard, *Chem. Rev.* **8** 321 (1931).
111. C M Hansen and A Beerbower in *Kirk-Othmer Encyclopedia of Chemical Technology*, Supplement **2**, Interscience, New York, 1971, p. 889.
112. W C Ingamells in *The Theory of Coloration of Fibres*, 2nd edn (ed. A Johnson), Dyers Co. Pub. Trust, Bradford, 1990.
113. W R Moore, *JSDC*, **75** 500 (1957).
114. P A Small, *J Appl. Chem.*, **3** 71 (1953).
115. K L Hoy, *J. Paint Tech.*, **42** 76 (1970).
116. A Urbanik, *Text. Chem. Col.*, **15** 36 (1983).

117. H Gerber, *JSDC*, **94** 298 (1978).
118. E C Ibe, *J Appl. Poly. Sci.*, **14** 837 (1970).
119. S A Siddiqui, *Text. Res. J.*, **51** 527 (1981).
120. S A Siddiqui, *Amer. Dyest. Rep.*, **72** 30 (1983).
121. S A Siddiqui and H L Needles, *Amer. Dyest. Rep.*, **72** 22 (1983).
122. R B Chavan and A K Jain, *JSDC*, **105** 73 (1989).
123. W C Ingamells and W C Thomas, *Text. Chem. Col.*, **16** (3) 55 (1984).
124. C A Abbot, PhD Thesis, University of Leeds, 1989.
125. S A Siddiqui, *Amer. Dyest. Rep.*, **72** (4) 36 (1983).
126. D M Koenhen and C A Smolders, *J. Appl. Poly. Sci.*, **19** 163 (1975).
127. R C D Kaushik and S D Deshpande, *Ind. J Text. Res.*, **14** 119 (1989).
128. D Patterson and R P Sheldon, *Trans. Far. Soc.*, **55** 1254 (1959).
129. M Sekido and H Kojima, *J Soc. Fiber Sci. Technol. Jap.*, **21** 644 (1965); **22** 33 (1966).
130. J Cegarra and P Puente, *Text. Res. J.*, **37** 343 (1967).
131. K V Datye and R Rajendran, *Indian J. Technol.*, **4** 101 (1966).
132. K V Datye, S C Pitkar and R Rajendran, *Indian J. Technol.*, **4** (7) 202 (1966).
133. R H Peters in *Diffusion in Polymers* (ed. J Crank and G S Park), Academic Press, London, 1968.
134. F Jones in *Theory of Coloration of Textiles*, 2nd edn (ed. A Johnson), SDC, Bradford (1989).
135. J G Blacker and D Patterson, *JSDC*, **85** 598 (1969).
136. K V Datye, P J Kangle and B Milicevic, Pub. 97, Ciba Res. Centre, India.
137. J Cegarra and P Puente, *Text. Res. J.*, **36** 134 (1966).
138. C L Bird, F Manchester and D F Scott, *JSDC*, **72** 49 (1956).
139. C H Giles, *Brit. Polymer J.*, **3** 279 (1971).
140. J Cegarra and P Puente, *Text. Res. J.*, **41** 170 (1971).
141. I Marshall and A Todd, *Trans. Far. Soc.*, **49** 67 (1953).
142. J Militky, *JSDC*, **95** 329 (1979).
143. J N Etters and A Urbanik, *Text. Chem. Col.*, **7** 157 (1975).
144. T Shibusawa, *JSDC*, **104** 28 (1988).
145. K V Datye and S C Pitkar, *Indian J. Technol.*, **8** 6 (1970).
146. P Gruner and J Janousek, *JSDC*, **85** 3 (1969).
147. F Jones, *JSDC*, **77** 57 (1961).
148. T Shibusawa, *Sen-i-Gakkaishi*, **42** T671 (1986).
149. C L Bird, *JSDC*, **72** 343 (1956).
150. J N Etters and R McGregor, *Text. Chem. Col.*, **11** 202 (1979).
151. W Biedermann, *JSDC*, **87** 105 (1971).
152. J A Shenai and M C Sadhu, *J. Appl. Poly. Sci.*, **20** 3141 (1976).
153. F Jones, *JSDC*, **85** 569 (1969).
154. F Jones and K Patterson, *JSDC*, **92** 442 (1976).
155. F Jones and L Flores, *JSDC*, **87** 304 (1971).
156. F Jones and L Flores, *JSDC*, **88** 101 (1972).
157. J A Shenai and M C Sadhu, J. *Appl. Poly. Sci.*, **22** 2069 (1978).
158. A Manning, PhD Thesis, Leeds University, 1975.
159. E H Daruwalla and V R Limaye, *JSDC*, **74** 464 (1958).
160. P Richter and M Vescia, *Mell. Text.*, **46** 621 (1965).
161. J K Skelly, *JSDC*, **89** 349 (1973).
162. W Beckmann and H Hamacher-Brieden, *Text. Chem. Col.*, **5** 118 (1973).
163. J Carbonell, *Amer. Dyest. Rep.*, **51** 83 (1962).
164. P Dilling, *Text. Chem. Col.*, **18** (2) 17 (1986).
165. J Dawson, *Rev. Prog. Col.*, **14** 90 (1984).
166. G Prazak and P Dilling, *AATCC Nat. Tech. Conf. Book of Papers*, 283 (1979).
167. G T Clark, M A Weaver and H W Somers, *AATCC Nat. Tech. Conf. Book of Papers*, 72 (1980).
168. P Dilling, *Text. Chem. Col.*, **20** (5) 17 (1988).
169. S Y Yin, *Text. Chem. Col.*, **13** 261 (1981).
170. J Skoufis, *Text. Chem. Col.*, **11** 106 (1979).
171. C L Bird, *JSDC*, **70** 69 (1954).

172. C L Bird, P Harris and F Manchester *JSDC*, **71** 139 (1955)
173. C L Bird and F Manchester, *JSDC*, **71** 604 (1955).
174. E Schoenpflug, *Text. Chem. Col.*, **11** 166 (1979).
175. S Cohen, *Amer. Dyest. Rep.*, **66** (9) 40 (1977).
176. D Fiebig and H Herlinger, *Text. Prax. Int.*, **38** (8) 785 (1983).
177. H Herlinger, D Fiebig, E Hindias and M Bohn, *Mell. Text.*, **68** (1) 52 (1987).
178. H Herlinger, D Fiebig and M Bohn, *Text. Prax. Int.*, **39** (12) 1282 (1984).
179. H J White, *Text. Res. J.*, **30** 329 (1960).
180. E Merian, J Carbonell, U Lerch and V Sanhuja, *JSDC*, **79** 505 (1963).
181. F Jones and J Kraska, *JSDC*, **82** 333 (1961).
182. C H Giles, *Text. Res. J.*, **31** 141 (1961).
183. T Vickerstaff, *JSDC*, **59** 92 (1943).
184. A Johnson, R H Peters and A S Ramadan, *JSDC*, **80** 129 (1964).
185. C L Bird and P Rhyner, *JSDC*, **77** 12 (1961).
186. H R Hadfield and W M Sokol, *JSDC*, **74** 629 (1958).
187. BP 428,767, *JSDC*, **51** 340 (1935).
188. BP 654,551, *JSDC*, **67** 467 (1951).
189. BP 764,439, *JSDC*, **73** 178 (1957).
190. I Goodman and B F Nesbitt, *J Poly. Sci.*, **48** 423 (1960).
191. I Goodman and B F Nesbitt, *Polymer*, **1** 384 (1960).
192. E S Calhoun, K C Brafford and W H Holden, *Text. Chem. Col.*, **7** 141 (1975).
193. A Murray and K Mortimer, *Rev. Prog. Col.*, **4** 1 (1973).
194. F Fortess and V S Salvin, *Text. Res. J.*, **28** 1009 (1958).
195. D Balmforth, C A Bowers, J W Bullington, T H Guion and T S Roberts, *JSDC*, **82** 405 (1966).
196. V S Salvin *et al.*, AATCC Piedmont Section, *Amer. Dyest. Rep.*, **48** (22) 23 (1959).
197. C R Jin and D M Cates, *Amer. Dyest. Rep.*, **53** 64 (1964).
198. K Fugino, N Fujimoto and K Eto, *Text. Mach. Soc., Jap. Ed.*, **14** 49 (1961).
199. T Vickerstaff, *Mell Text.*, **35** 765 (1954).
200. J P Kim, PhD Thesis, University of Leeds, 1990.
201. A Tokaoka and M Aki, *Sen-i Gakkaishi*, **21** Y-437 (1965).
202. A Tokaoka and M Aki, *Sen-i Gakkaishi*, **21** 425,432 (1965).
203. F M Rawicz, D M Cates and H A Rutherford, *Amer. Dyest. Rep.*, **57** 284 (1968).
204. J H Lemons, S K Kakar and D M Cates, *Amer. Dyest. Rep.*, **66** 76 (1966).
205. A N Derbyshire and R H Peters, *JSDC*, **71** 530 (1955).
206. W C Ingamells and A Yabani, *JSDC*, **93** 417 (1977).
207. W C Ingamells and N Yanumet, *Brit. Ploy. J.*, **27** (3) 12 (1980).
208. A H Brown and A T Peters, *Amer. Dyest. Rep.*, **57** 281 (1968).
209. A H Brown and A T Peters, *Amer. Dyest. Rep.*, **57** 284 (1968).
210. M J Schuler, *Text. Res. J.*, **27** 352 (1957).
211. R McGregor, R H Peters and C R Ramamchandran, *JSDC*, **84** 9 (1968).
212. D Herlinger, D Fiebig, S Koch and D Schnaitmann, *Text. Prax. Int.*, **33** 583 (1983).
213. G A F Roberts and R K Solanki, *JSDC*, **95** 226 (1979).
214. W C Ingamells and A Yabani, *J Appl. Poly. Sci.*, **22** 1583 (1978).
215. G A F Roberts and Solanki, *JSDC*, **95** 427 (1979).
216. D Aitken and S M Burkinshaw, *JSDC*, **98** 219 (1992).
217. M L Gulrajana and R K Saxena, *JSDC*, **95** 330 (1979).
218. A S Fern and H R Hadfield, *JSDC*, **71** 840 (1955).
219. E Elod, *Mell. Text.*, **41** 195 (1960).
220. E Elod and A Vinh, *Text. Prax.*, **16** 718 (1961).
221. P Senner and H Bessel, *Mell. Text.*, **48** 75 (1967).
222. P Senner and A Rezk, *Mell. Text.*, **50** 64 (1969).
223. C L Zimmerman, J M Mecco and A J Carlino, *Amer. Dyest. Rep.*, **44** 296 (1955).
224. S M Burkinshaw and J P Kim, *J Korean Fibre Soc.*, **28** 549 (1991).
225. T Vickerstaff, *Haxagon Digest*, **20** (7) (1954).
226. P J Choquette, *Text. Res. J.*, **24** 387 (1954).
227. C Millson, *Amer. Dyest. Rep.*, **44** 417 (1955).

228. V Ravichandran, M Wilde, D R Gadoury, A T Lemley and S K Obendorf, *Text. Chem. Col.*, **19** (11) 35 (1987).
229. H Hendrix, *Mell. Text.*, **43** 258 (1962).
230. H Hendrix, *Z. Ges. Textilind.*, **62** 921 (1960).
231. R Asquith, H S Blair and N Spence, *JSDC*, **94** 49 (1978).
232. Z Gur-Arieh and W C Ingamells, *JSDC*, **90** 12 (1974).
233. V S Salvin, *Amer. Dyest. Rep.*, **49** 600 (1960)
234. P Rochas, *Teintex*, **24** 825 (1959).
235. P Rochas, *Chemifasern*, **10** 394 (1960).
236. P Rochas and M Courmont, *Bull. Inst. Text. France*, **86** 15 (1960).
237. S Rosenbaum, *J. Poly. Sci., Part A*, **3** 1949 (1965).
238. J F Bell and T Murayama, *J. Appl. Poly. Sci.*, **12** 1796 (1968).
239. J P Bell, *J. Appl. Poly Sci.*, **12** 627 (1968).
240. J H Dumbleton, J P Bell and T Murayama, *J. Appl. Poly. Sci.*, **12** 2491 (1968).
241. R Fujino, W Kuroda and F Fujimoto, *J. Soc. Fibre Sci. Technol. Japan*, **21** 573 (1965).
242. W C Ingamells, R H Peters and S R Thornton, *J Appl. Poly. Sci.*, **17** 3733 (1973).
243. W C Ingamells and R H Peters, *JSDC*, **89** 397 (1973).
244. Z Gur-Arieh and W C Ingamells, *JSDC*, **90** 8 (1974).
245. G Alberti, A Cerniani and M R de Giorgi, *Ann. Chim.*, **74** 429 (1984).
246. S M Burkinshaw and J P Kim, *J Korean Fibre Soc.*, **28** 565 (1991).
248. G Alberti and A Loi, *Mell. Text.*, **69** 365 (1989).
249. D Aitken, S M Burkinshaw, J Catherall, R Cox and D M Price, *J. Appl. Poly. Sci., Appl. Poly. Symp.*, **47** 271 (1991).
250. D Aitken, S M Burkinshaw and D M Price, *Dyes and Pigments*, **18** 23 (1992).
251. W C Ingamells and K V Narasimham, *JSDC*, **93** 306 (1977).
252. W C Ingamells and K V Narasimham, *J. Appl. Poly. Sci.*, **20** 2271 (1976).
253. G Alberti, *Amer. Dyest. Rep.*, **71** 46 (1983).
254. S Rosenbaum, *J. Appl. Poly. Sci.*, **9** 2085 (1964).
255. Z Gur-Arieh, W C Ingamells and R H Peters, *J. Appl. Poly. Sci.*, **20** 41 (1976).
256. G Alberti, M R de Giorgi and G Sen, *Ann. Chim.*, **74** 421 (1984).
257. R C D Kaushik and S D Deshpande, *Ind. J. Text. Res.*, **14** 125 (1989).
258. R C D Kaushik and S D Deshpande, *Ind. J Text. Res.*, **14** 130 (1989).
259. W C Ingamells, *JSDC*, **96** 466 (1980).
260. W C Ingamells and H Sherkat, *JSDC*, **93** 448 (1977).
261. R D Matowsky, H D Weigmann and M G Scott, *Text. Chem. Col.*, **12** 55 (1980).
262. R A F Moore and H D Weigmann, *Text. Chem. Col.*, **13** 70 (1981).
263. R J Papuga, C D Livengood and G N Mock, *Text. Chem. Col.*, **15** 91 (1983).
264. A N Derbyshire, E D Harvey and D Parr, *JSDC*, **91** 106 (1975).
265. J K Skelly, *JSDC*, **91** 177 (1975).
266. M Capponi, H Gerber and F Somm, *Text. Chem. Col.*, **3** 266 (1971).
267. H R Byland, M Capponi, H Gerber and F Somm, *Text. Chem. Col.*, **3** 210 (1971).
268. B Milicevic, *Text. Chem. Col.*, **2** 87 (1970).
269. B Milicevic, *JSDC*, **87** 503 (1971).
270. G S Dodd and W C Ingamells, *JSDC*, **93** 74 (1977).
271. G L Brodman, *Text. Chem. Col.*, **7** 80 (1975).
272. J J Willard, *Text. Chem. Col.*, **4** 62 (1969).
273. C Heit, M Moncrief-Yeates, A Palin, M Stevens and H J White, *Text. Res. J.*, **29** 6 (1959).
274. J Thompson, PhD Thesis, Leeds University, 1969.
275. K Gebert, *JSDC*, **87** 509 (1971).
276. K V Datye, S C Pitkar and U M Purao, *Textilveredlung*, **6** 593 (1971).
277. B Millicevic, *Text. Res. J.*, **39** 677 (1969).
278. J A Harris and T H Guion, *Text. Res. J.*, **42** 626 (1972).
279. *AATCC Sympos. Solvent Tech., Atlanta*, 127 (1973).
280. G M Gantz and G Siegrist, *Text. Chem. Col.*, **1** 70 (1969).
281. P Rochas, *Chemiefarsen*, **10** 666 (1960).
282. E Merian, J Carbonell, U Lerch and V Sanahuja, *JSDC*, **79** 505 (1963).

283. H T Pratt, *Text. Chem. Col.*, **2** 26 (1969).
284. J K Skelly and D G Evans, *Textilveredlung*, **8** 3 S102 (1973).
285. A N Derbyshire, *JSDC*, **90** 273 (1974).
286. ICI Technical Information D 1389.
287. C B Stevens in *The Dyeing of Synthetic Polymer and Acetate Fibres* (ed. D M Nunn), Dyers Co. Pub. Trust, Bradford, 1979.
288. T L Dawson and J C Todd, *JSDC*, **95** 417 (1979).
289. H T Pratt, *Text. Chem. Col.*, **21** (9) 61 (1989).
290. P Roy, *Amer. Dyest. Rep.*, **441** 844 (1952).
291. C L Zimmerman, *Amer. Dyest. Rep.*, **42** 627 (1953).
292. J J Ianarone, O S Larson and R J Thomas, *Amer. Dyest. Rep.*, **43** 650 (1954).
293. I M S Walls, *J. Text. Inst.*, **45** (6) P258 (1954).
294. A S Fern, *JSDC*, **71** 502 (1955).
295. H R Hadfield and R Broadhurst, *JSDC*, **74** 387 (1958).
296. W Beckmann, *Text. Chem. Col.*, **2** 350 (1970).
297. W Beckmann and H Brieden, *Chemifasern*, **20** 553 (1970).
298. P Richter, *Text. Prax.*, **28** 71 (1973).
299. Wolf and Ruttiger, *Mell. Text.*, **55** 876 (1974).
300. E Merian and U Lerch, *Mell. Text.*, **43** 845,965 (1962); *Amer. Dyest. Rep.*, **51** 695 (1962).
301. H Gerber, *JSDC*, **94** 298 (1978).
302. Sandoz pattern card *Foron RD*, 0282, 1980.
303. *Serene Dyes Pattern Card*, Serene Dyestuff Industries Ltd.
304. J Navratil, *JSDC*, **106** 283 (1990).
305. J Navratil, *JSDC*, **106** 327 (1990).
306. Anon, *Du Pont Tech. Bull.*, No. 5, 82 (1949).
307. J W Gibson, USP 2,663,612; 2,663,613 (1958).
308. J W Gibson, *Text. Chem. Col.*, **11** 241 (1979).
309. P L Meunier, *Text. Chem. Col.*, **2** 386 (1970).
310. J Keaton and D T Preston, *JSDC*, **80** 312 (1964).
311. J J Iannarone, P L Speakman, O S Larson, R C Hunt and E H Hinton, *Amer. Dyest. Rep.*, **46** 674 (1954).
312. M Santymire, *Amer. Dyest. Rep.*, **48** (12) 45 (1953).
313. J J Iannarone and W J Wyland, *Amer. Dyest. Rep.*, **49** 81 (1960).
314. V S Salvin, *Amer. Dyest. Rep.*, **56** (12) 31 (1967).
315. K V Datye and S C Pitkar, *Proc. Symp. Contributions to Chem. Synthetic Dyes and Mech. of Dyeing*, University of Bombay, 1968, p. 47.
316. K V Datye, S C Pitkar and R Rajendran, *Proc. Symp. Contributions to Chem. Synthetic Dyes and Mech. of Dyeing*, University of Bombay, 1968, p. 57.
317. C J Bent, T D Flynn and H H Sumner, *JSDC*, **85** 606 (1969).
318. K V Datye, *Textilveredlung*, **4** 562 (1969).
319. M Fox, *Text. Chem. Col.*, **1** 566 (1969).
320. F Somm, *Colorage*, 28 June, 31 (1973).
321. J Shore, *Rev. Prog. Col.*, **10** 33 (1979).
322. P W Leadbetter and A T Leaver, *Rev. Prog. Col.*, **19** 33 (1989).
323. C W Taylor and R L Denyer, *JSDC*, **81** 300 (1965).
324. J Shore in *The Dyeing Of Synthetic-Polymer and Acetate Fibres* (ed. D M Nunn), Dyers Co. Pub. Trust, Bradford, 1979.
325. J Park, *Rev. Prog. Col.*, **13** 37 (1983).
326. J P Merimond, *Can. Text. J.*, **80** (11) 15 (1963).
327. C C Wilcock and J L Ashworth, *Whittaker's Dyeing with Coal-tar Dyestuffs*, 6th edn, Ballière, Tindall and Cox, London, 1964.
328. J F Laucius, *Amer. Dyest. Rep.*, **42** 792 (1953).
329. *Du Pont Tech. Lab. Bull.*, 930 43 (1950).
330. E R Trotman, *The Dyeing and Chemical Technology of Textile Fibres*, 3rd edn, Griffin, London, 1964.

2. Nylon

2.1. Introduction

In 1938 [1] Du Pont publicly announced the discovery, made by W H Carothers, of 'super-polyamides' to which the general term *nylon* had been ascribed; as a result of successful experimental-scale production and assessment, nylon 6.6, the first commercially available wholly synthetic textile fibre, was marketed in 1939 [2 8]. The term *nylon* now refers to members of a generic class of synthetic polyamides derived predominantly from aliphatic monomers and, as such, distinguishes such polymers from other polyamides, namely proteinaceous polyamino acids (such as silk and wool), lower melting point resins as well as wholly aromatic polyamides (aramids), which also can be classified as [2–4] *polymers whose structural units contain amide groups* (—CONH—) as recurring integral parts of the main polymer chain.

Commonly, commercial nylons are manufactured using processes related to either of three basic approaches [2–5], namely:

(i) *poly condensation of diamines and dibasic acids*, as exemplified by hexamethylene diamine and adipic acid (nylon 6.6);
(ii) *poly condensation of* ω-amino acids, as typified by 11-aminoundecanoic acid (nylon 11);
(iii) *ring-opening polymerisation of lactams*, such as ε-caprolactam in nylon 6.

Nylons obtained from diamines and diacids are generally referred to as AABB types whilst those derived from ω-amino acids or from lactams are referred to as AB types; the polymers are labelled either by numbers which correspond to the number of carbon atoms in the monomer(s) (two numbers for the AABB type polymers, *diamine.diacid* for the AABB types, such as nylon *4.6*, nylon *6.6* and one number for the AB type polymers, for example nylon *6*, nylon *12*) or sometimes by letters for certain types of monomers (e.g. *MXD6*, *TMDT*) [2 5].

Although a variety of polyamides are now manufactured and are marketed under various trade names, the two most important nylon textile fibres are nylon 6.6 and nylon 6; other polyamides, with the exception of the high temperature-resistant nylon 4.6 whose recent consideration as a textile fibre [9] has augmented its long-established commercial use in many engineering plastics applications, are of little importance from a textile

Table 2.1 Some physical properties of nylon 6.6 and nylon 6

	Nylon 6	Nylon 6.6
T_g at 65% RH (°C)[a]	60	74
Moisture regain (21°C; 65% RH)[a]	4.0–4.5	3.5–4.0
Water shrinkage (%; 15 mins; 98°C)[a]	10	5.3
Melting point (°C)[b]	215–220	250
Softening point (°C)[b]	170	235

[a] ref 9.[b] ref. 8

viewpoint. As a consequence of the predominance of nylons 6 and 6.6 as textile substrates, this chapter mainly concerns the dyeing of these two types of polyamide fibre.

Both nylon 6 and nylon 6.6 polymers are converted into yarn by melt spinning [3, 7, 8], the yarn being produced either as continuous filament or converted into staple fibre; depending on the intended use of the yarn, it may also be texturised. Both nylon 6 and 6.6 are linear, partially amorphous materials; nylon 6.6 exists in two crystalline forms, α and β, the latter form representing an intermediate stage in the formation of the triclinic α form [4, 5, 10] whilst nylon 6 can crystallise in either the more predominant α or the γ forms, the two being interconvertible [11–13]. Although generally very similar, nylon 6.6 has a more compact and crystalline structure than nylon 6, this being manifest in differences in both the physical properties (Table 2.1) and dyeing behaviour of the two types of fibre. The chemical characteristics of both types of fibre are determined by the functional end groups ($-NH_2$ and $-COOH$) and chain amide groups ($-CONH-$) present, the hydrocarbon chain portions of the polymer being relatively inert [10]. The amounts of the various groups present in a typical nylon 6.6 sample (Table 2.2) shows that the quantities of acidic ($-COOH$) and basic ($-NH_2$) groups are not equivalent owing to the use of 'chain stoppers', such as acetic acid, to control the degree of polymerisation of the polymer.

Table 2.2 Typical analysis of nylon 6.6 [14]

Group present	Amount (m-eq. kg^{-1})
Terminal amino ($-NH_2$)	45
Terminal carboxylic ($-COOH$)	75
Chain amide ($-NHCO-$)	1×10^4
Terminal acetylamino ($-NHCOCH_3$)	4–5

CHEMICAL CHARACTERISTICS. The retention of water by nylon 6 and nylon 6.6 depends on the degree of orientation of the fibre, especially at high humidities [15], water absorption occurring predominantly at the strongly hydrophilic terminal amino groups and to those amide groups that are accessible [16]. In conjunction with their relatively low moisture regain (Table 2.1), both types of fibre swell very little when immersed in water [17] and are relatively stable to water at temperatures up to the boil, but are hydrolysed at temperatures above 150°C [2, 3, 9]. Whilst the polymers exhibit high resistance to aqueous alkalis, although severe hydrolysis of the amide link occurs at high temperatures, they are more sensitive to acids, being rapidly degraded by strong inorganic and organic acids [18]. It has been shown [19] that whilst the extent of degradation of nylon 6 fibres at temperatures of 70 and 100°C was independent of pH over the range 2 to 7, an increase in fibre degradation occurred at pH values of less than 2 in the presence of H_2SO_4; furthermore, a marked increase in hydrolysis of the fibre occurred below a pH of 2.5 at a temperature of 130°C. Such acid degradation is of significance in dyeing as several types of dye are applied to the fibre under acidic conditions. Marfell [19] observed that ammonia and both amino caproic acid and amino percaproic acid were released from nylon 6 films during dyeing with an acid dye, the amino end group (AEG) content of the film increasing with increase in concentration of dye. Kyllo and Ladisch [20] demonstrated that simulated acid rain conditions of pH 3 and below degraded nylon 6.6 fabric, the physical and chemical damage that occurred being primarily a function of the apparently synergistic action of light on the acid hydrolysis of the polymer. Both nylon 6 and nylon 6.6 are soluble in phenols, mineral acids and formic acid at room temperature and are dissolved by unsaturated alcohols and nitro alcohols at higher temperatures [2, 3, 10].

Nylon fibres are prone to oxidation when heated in air at high temperature [21], as a consequence of which the rate of dyeing with anionic dyes is reduced [22] due to a corresponding decrease in AEG content [19, 22] and an increase in carboxylic acid end group content [23] caused by chain scission [19, 22]. The AEG content of nylon fibres is also reduced as a result of oxidative degradation when exposed to direct sunlight [24]; the photo- and thermal degradation of nylon has been studied by many workers [19, 25–32], various positions having been proposed for bond scission of nylon by UV light [25].

FIBRE MODIFICATION. The fibres can be modified in several ways so as to achieve end-use variation. The copolymerisation of polyamide homopolymer with either other homopolyamides or different monomers to those used in the polyamide have been employed to achieve modified moisture adsorption, dyeability, T_g and bulk, using block, random and

Table 2.3 AEG contents of anionic-dyeable nylon 6.6 fibres [14]

Fibre type	AEG content (m-eq. kg^{-1})
Ultra deep	99
Deep	84
Regular	45–50
Low	25–30

also graft polymerisation methods, such modifications having involved both bicomponent and biconstituent fibres [7, 8]. The presence of terminal amino groups accords nylon fibres substantivity towards several classes of anionic dye, namely acid (including metal-complex), mordant, direct and reactive. The polar and relatively hydrophobic characteristics of the substrate also serve to impart substantivity towards disperse dyes; azoic colorants and vat dyes can also be applied to the substrates although these two particular colorants are nowadays little used. The substantivity of anionic dyes towards the fibre can be modified by altering the concentration of amino end groups in the substrate. By increasing the AEG content [33–36], dye–fibre substantivity is enhanced [37] and both the rate and extent of dye uptake are enhanced [36]; anionic-dyeable variants for differential dyeing are commonly referred to as *ultra-deep*, *deep*, *regular* or *low* dyeing (Table 2.3).

The introduction of carboxylic or sulphonic acid groups, for example by the use of 3,5-dicarboxy-benzene-1-sulphonic acid [7, 8, 14, 33], imparts substantivity for cationic dyes and, at the same time, the *cationic-dyeable* fibre exhibits reduced substantivity towards anionic dyes [34, 35]. Hence, differential-dyeable nylon fibres are available [33, 38]; both anionic and cationic-dyeable types of fibre are dyeable with disperse dyes. In the context of regular nylon, the most widely used dye classes are acid and disperse, the latter being confined mostly to hosiery. In this account of the dyeing of nylon, each of the various types of dye used is considered individually.

2.2. Anionic dyes

As mentioned, although five types of anionic dye (non-metallised acid, pre-metallised acid, mordant, direct and reactive) are substantive towards nylon fibres, acid dyes (both non-metallised and pre-metallised types) enjoy greatest use and also have attracted most attention from the viewpoint of the mechanism of their interaction with the substrate and, of this, focus has been placed on non-metallised acid dyes. Essentially, the substantivity of anionic dyes towards nylon fibres arises primarily by virtue of ion–ion forces of interaction operating between the anionic (usually sulphonate) groups in the dye and the protonated terminal amino groups in the substrate. Other forces of interaction, such as hydrogen bonding, dispersion forces and polar van der Waals' forces can also be expected to contribute to dye–fibre substantivity.

2.2.1. *Barré effects*

All anionic dyes are sensitive to both chemical and physical variations in the substrate and vary in their ability to cover such fibre irregularities [22, 39–43]; disperse dyes, in contrast, cover fibre irregularities well. Physical variations are of two types, namely *fine*, which are introduced during fibre processing (drawing, setting) and *gross*, which are due to variations in the count of the fibre or crimp whilst chemical variations in the fibre are introduced during polymer spinning or blending of yarns of differing AEG contents [24, 44]. Each of these variations affects both the rate and extent of anionic dye uptake resulting in barré dyeing, which has been defined [45] as a *continuous visual barred pattern or stripiness parallel to the yarn direction in a knit or woven fabric that is caused by physical, optical or dye differences in the yarns or geometric differences in the fabric structure acting either singly or in combination to produce the barred pattern.* Holfeld and Hallada [46] propose that chemical variations in nylon fibres are nowadays rare and it is generally agreed [44, 46–49] that barré dyeing problems are almost always due to physical variations in the substrate. Such physical variations, which tend to be emphasised by high M_r anionic dyes, are mostly associated with continuous filament yarns rather than staple yarns as the blending stages involved in the manufacture of the latter type of yarn minimise such dye-affinity variations. Diagnostic dyeing tests have been developed to detect the causes of both chemical and physical variations in nylon fibres [22, 40, 41, 43, 50].

Holfeld and Shepard [51] consider that physical variations alter the 'porosity' of the substrate which determines the accessibility of dye sites and that such 'porosity' is determined by the total temperature–tension history of the fibre. Many workers have demonstrated that the various heat treatments to which nylon yarns are subjected affect the dyeing behaviour of the yarns and that inadequate control of such processes result in unlevel dyeings [22, 39, 40, 43, 45, 46, 48, 51–59]. The effect of both dry heat and steam setting on the dyeability of nylons 6 and 6.6 has been elegantly reviewed by Holfeld and Shepard [60]. In essence, although both dry heat and steam setting increase fibre crystallinity, the modulus of the fibre is decreased by setting in steam and increases on dry heat setting. Steam setting increases dye uptake whilst dry heat setting decreases dye uptake. Although dry heat setting has been shown to reduce the

AEG content of nylon 6.6 as a result of oxidative degradation [22], as steam treatment does not markedly alter the AEG content nor the M_r of the fibre, it is generally accepted that the enhancement of dye uptake imparted by steam setting is attributable to changes in fibre structure, notably decreased orientation [60]. It has been shown that steam or hot water treatment decreases the number of bonds between the composite molecular chains in the fibre, whereas dry heat setting results in the formation of additional interchain bonds. Thus, whilst saturated steam and water increase dyeing rate, superheated steam is more like dry heat in terms of its effect on dyeability [60].

In a study of the effects of water on the physical properties of nylon, the following findings were included:

- the T_g of nylon 6.6 was reduced from 80°C at 0% RH to between −10 and −20°C at 100% RH;
- moisture dramatically reduces the modulus of the fibre but markedly increases the crystallinity of undrawn fibre;
- water reduces the melting point of nylon 6.6 from 250–255°C to 160–170°C and imparts shrinkage;
- nylon can be set with steam at 93–121°C whereas dry heat setting must be carried out at 196–219°C.

From such findings, Holfeld and Shepard [51] considered that water is a potent carrier for nylon, providing some 100°C of thermal energy in its effects on fibre properties and that the dyeing of nylon in water is equivalent to dyeing polyester fibres in 100% carrier. These workers [51] also proposed that the structural changes imparted by water are reversible below about 75°C and irreversible above about 95°C, and that physical barré is caused by differences in accessibility rather than differences in crystallinity.

The effect of different draw ratios on the dyeability of nylon fibres has been studied by several authors [47, 61–66] who have shown that whilst the rate of acid dye diffusion into nylon substrates is generally decreased by increasing draw ratio, equilibrium dye uptake was little affected by differences in draw ratio. Greider [47], in a study of the dyeability of nylon 6 of normal and high draw ratios with four non-metallised acid dyes, found that the ratio of the dye diffusion coefficients in the two substrates was independent of both the dye used and the concentration of dye adsorbed by the fibre and concluded that the higher the diffusion coefficient of the dye, the better the coverage of barré.

Nylon fibres are radially non-uniform insofar as they have a core/sheath structure resulting from the processing conditions employed during melt spinning. Temperature gradients, polymer viscosity and stress variations during yarn formation, as well as variations in stress during drawing [67], all contribute to the surface (sheath) of the fibres differing to the interior regions (core) of the fibre in terms of properties such as orientation and crystallinity. The existence of such a core/sheath arrangement in nylon fibres has been shown by several workers, this having been comprehensively reviewed by Duscheva *et al.* [67]. It is considered that in polyamide, three layers are present which differ in their orientation, namely a surface layer of high orientation, a layer immediately beneath this of lower orientation and a central layer which has a highly ordered uniform structure. Other workers propose that a fourth, thin layer exists between the central layer and the layer immediately above it which binds the sheath and core together [67]. The presence of this sheath/core structure in nylon has been discussed in the context of the barré dyeing of nylon. Heidemann [68] employed ATR IR spectroscopy to reveal orientation and crystallinity differences between the sheath and core of nylon 6.6 fibres and concluded, from a study of streakily dyed yarns, that the streakiness was caused by differences in skin orientation and that the orientation of the sheath determined the diffusion of dye into the core of the fibre. Garasimova *et al.* [69] showed that the core and sheath in nylon was dyed more rapidly than the core and, using tracer diffusion studies of Cl^{35}-labelled HCl and of S^{35}-labelled CI Food Yellow 3 in nylon 6.6 filaments, Coates *et al.* [70] demonstrated that the surface layer acted as a barrier to diffusion of both types of anion. Holfeld and Pike [71] demonstrated the contribution that the uniformity of the surface of nylon made towards barré dyeing.

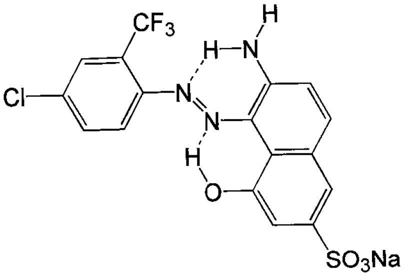
Duscheva *et al.* [67] argue that, in nylon fibres, the sheath contains many pores, interstices and other defects that are created during drawing and especially during texturising; such pores and defects are also distributed radially from the centre to the surface of the fibre such that the core contains none and that such defects can give rise to unlevel dyeing. These authors [67] consider that this difference in structure and dyeability of the sheath and core of the fibre can lead to unlevel dyeing.

In general, physical variations can, in the case of acid dyes, be greatly reduced or even eliminated by the use of dyes of high migrating power, elevated dyeing temperatures (110–115°C for nylon 6 and 110–120°C for nylon 6.6) and/or proprietary auxiliaries [72]; the latter approach is discussed in section 2.2.2.1.1.

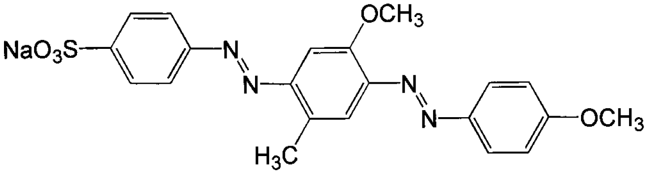
2.2.2. *Acid dyes*

The term *acid dye* derives from the use of acidic dyebaths that were originally employed for the application of the dyes to wool and silk. However, although some members of this dye class now require acidic conditions for their application to these two protein fibres and also nylon, many acid dyes exhibit considerable substantivity towards these substrates from neutral dyebaths. Early studies [73–75] clearly established the suitability of acid dyes for the coloration of nylon fibres, this being not unexpected owing to the similar chemical nature (i.e. the possession of primary amine groups) of nylon and both wool and silk fibres for which this particular dye type had been developed. Although in the *Colour Index* [76], pre-metallised acid (metal-complex) dyes are included within this application class, as both dyers and dye chemists nowadays consider pre-metallised acid dyes to be distinct from their non-metallised counterparts [72, 77], the two types of acid dye will now be separately considered.

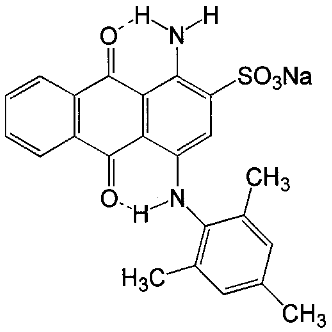
2.2.2.1. Non-metallised acid dyes. The characteristic water-solubility of these dyes is commonly conferred by the presence of one or more sulphonate groups (–SO_3Na). Of the several chemical classes of dye to which non-metallised acid dyes belong [72], azo dyes are by far the largest representative, providing an extremely wide gamut of hues and, of these, monoazo types, such as CI Acid Red 266 (I) predominate although



I



II



III

disazo types, as exemplified by CI Acid Orange 156 (II), are also represented; the traditional provision, by anthraquinone dyes such as CI Acid Blue 129 (III), of bright green to violet hues has in recent years been eroded by the introduction of bright monoazo types. In addition to the traditional powder form, the dyes are also available in liquid form [78].

CLASSIFICATION. Owing to the variability of non-metallised acid dyes in terms of their application and fastness properties on nylon fibres, it is common for dye makers to classify their range of dyes into subgroups; Stevens [79] employed a I to III system for classifying non-metallised acid dyes on nylon in terms of the relationship between the M_r and degree of sulphonation of the dyes and their dyeing behaviour and wet-fastness properties.

GENERAL APPLICATION CONSIDERATIONS. Generally, highly sulphonated dyes exhibit low substantivity, high migration power but low fastness to wet treatments and are applied at lower pH values than their less sulphonated counterparts. Also, the saturation values of the dyes decreases with increasing degree of sulphonation. Large M_r dyes of low water-solubility possess high substantivity under neutral pH dyeing conditions and display high wet fastness but poor coverage of fibre irregularities. Due to the higher crystallinity and more compact structure of nylon 6.6, the rate of dye uptake on to this fibre will generally be lower than than on to nylon 6. In general, the dyes are applied to nylon in the pH range 4 to 8 on which they provide a wide range of bright shades of low to moderate wet fastness and moderate to very good light fastness. The particular pH value employed for dyeing depends on both the type of dye used and the depth of shade applied (higher pH values are used for pale depths and lower values for heavy depths). Two general methods can be used to apply the dyes to nylon, namely by maintaining the dyebath pH at a value within a narrow pH range (or at a constant value) and controlling the rate of dyeing and thus levelling, by means of temperature control or by using a constant (or near constant) temperature for most of the dyeing process and employing a change in dyebath pH. As the former approach requires strict control of dyebath pH throughout the dyeing cycle, recourse is often made to buffer systems such as CH_3COOH/CH_3COONa for the pH range 4–5, NaH_2PO_4 for pH 5.5, NaH_2PO_4/Na_2HPO_4 for the range pH 6 to 8 and $Na_4P_2O_7$ for the range pH 8 to 9. The second approach, that of securing level dyeing by initially applying the dyes at high pH followed by a controlled lowering of dyebath pH, can be achieved using various systems. Ammonium sulphate or acetate can be employed for the temperature-dependent reduction of dyebath pH, as their decomposition at the boil liberates acid and ammonia. However, whilst this particular system may be adequate when open dyeing vessels are used, the desired lowering of dyebath pH will not occur in enclosed vessels as the ammonia liberated during decomposition of the ammonium salt cannot escape. Consequently, recourse can be made to hydrolysable esters [80] such as γ-butyrolactone [81] or 2-hydroxyethyl chloroacetate [82]; at high temperature the lactone hydrolyses to yield 4-hydroxybutyric acid. In this particular approach, the initial pH of dyeing is adjusted to 8–9 using, for example, borax, Na_2CO_3, NaOH or NH_4OH [82, 83] and, after a predetermined time at 98°C, the hydrolysable ester is added to gradually lower the pH by 3 units in the later stages of dyeing [83].

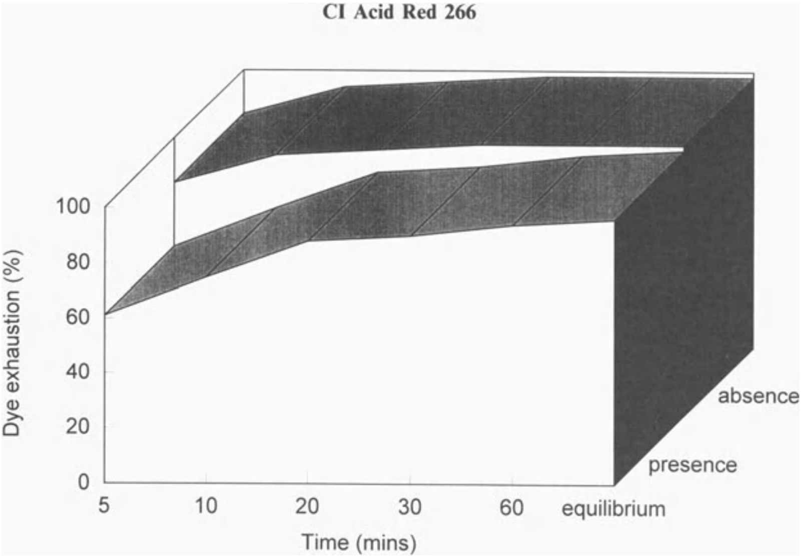
Although a dyeing temperature of 98°C is commonly used for both nylon 6 and 6.6, many dyes, especially those of low and medium substantivity [24], display optimum exhaustion at lower temperatures. Elevated temperatures (110–115°C for nylon 6 and 110–120°C for nylon 6.6 [24]) can be employed to achieve level dyeing of very barré material; the enhanced fibre swelling that arises under such high temperatures expedites dye penetration, promotes dye migration and also improves the compatibility of the dyes when applied in admixture. However, as nylon fibres are prone to oxidative degradation at such elevated temperatures, it is recommended [24] that anti-oxidants such as thiourea or hydroxylamine sulphate are added to the dyebath. Selected dyes can be applied at low temperature (65°C) in the presence of a suitable auxiliary although, as little dye migration occurs at such a temperature, levelness must be achieved during the initial stages of dyeing [84]. Some anthraquinone dyes are prone to oxidation during dyeing, especially in the presence of Fe^{III} and Cu^{II} ions [85] and it has also been shown that the azo linkage in some azo dyes can be reduced during dyeing, the rate of reduction increasing rapidly above pH 7 [86]. Many dyes, especially blues, are prone to ozone fading, this being prevalent in warm, humid conditions and particularly marked in the case of dyeings of pastel shades. Moore *et al.* [87] showed that the ozone fading of acid dyes in nylon is influenced by the rate of dye migration to the filament surface and proposed that, to minimise the effect, the morphology of the fibre should be manipulated so as to secure a compact structure and thereby minimise dye mobility and also to employ dyes (i.e. of large M_r) that either diffuse slowly or, ideally, are esentially immobile. Proprietary agents are available which, when employed as an aftertreatment of the dyed fibre, improve the fastness to ozone [88]; in this context, an aftertreatment with either the full backtan or a syntan is reported to be effective, as is the addition of ammonium thiocyanate to the dyebath [89]. The light fastness of acid dyes on nylon can be improved by the use of proprietary UV absorbers or metal salts, these being applied towards the end of dyeing [89]. Also, as dyeings of some dyes are dulled by the presence of certain metal ions such as calcium, iron and copper, sequestering agents may be required.

2.2.2.1.1. Levelling agents. Although both pH and temperature control will promote level dyeing, these measures are not sufficiently effective in overcoming barré dyeing; consequently, dyeing auxiliaries are also used in nylon dyeing.

For all dye–fibre systems, level dyeing problems can be divided into either *gross unlevelness throughout the substrate* which is related to the dyeing process or *localised unlevelness* which is related to non-uniformity of the substrate [90]. Barriness in nylon is an example of the latter type of level dyeing problem and, as mentioned previously, since all anionic dyes are sensitive to both chemical and physical irregularities in the substrate, considerable attention has been focused on both the causes and cures of barré dyeing; much research has also attended the overall level dyeing behaviour of acid and other anionic dyes on nylon. The level dyeing behaviour of acid dyes on nylon has become of especial interest in recent years owing to the trend towards dyeings of higher wet fastness and the attendant problem that, in general, the higher the wet fastness of a dye the less easy it is to apply the dye evenly.

ANIONIC LEVELLING AGENTS. Earlier methods that were used to apply acid dyes to nylon employed both temperature and pH control in order to promote dye levelling. However, such techniques were not especially effective in overcoming barré [91] and thus, in the 1950s, recourse was made to the use of anionic levelling agents [48, 92–96] either as an addition to the dyebath or as a pretreatment of the nylon substrate, prior to dyeing, to promote both levelness and coverage of fibre irregularities. The latter technique. namely the application of an anionic 'blocking' agent to the undyed substrate, was employed to achieve maximum effectiveness of the anionic surfactant and, as all the acid required for dyeing was added with the anionic agent, to also eliminate gross pH changes that could occur if acid was added during dyeing; the rate of dyeing was then controlled by means of temperature [91]. In the case of such anionic agents, careful dye selection is also necessary in order to achieve level dyeing [92].

The mechanism by which such anionic levelling agents work is that, as they are substantive towards the fibre, they compete with the anionic dye for sites both within the substrate and on the fibre surface [24, 97]. However, their effect is temporary [24] in that once adsorbed on to the fibre they are displaced by the dye anion. Thus, such agents reduce the rate of dye uptake and, because their occupation of dye sites reduces the total number of available dye sites in the fibre, they increase the relative saturation of the fibre S_{rel} (the ratio of the number of dye anions in the system to the number of dye sites in the fibre), thereby improving dye levelling [97]. Hughes *et al.* [98] demonstrated that when applied prior to the dye, the anionic 'blocking' agent *Lissapol D* (ICI) (cetyl-oleyl sodium



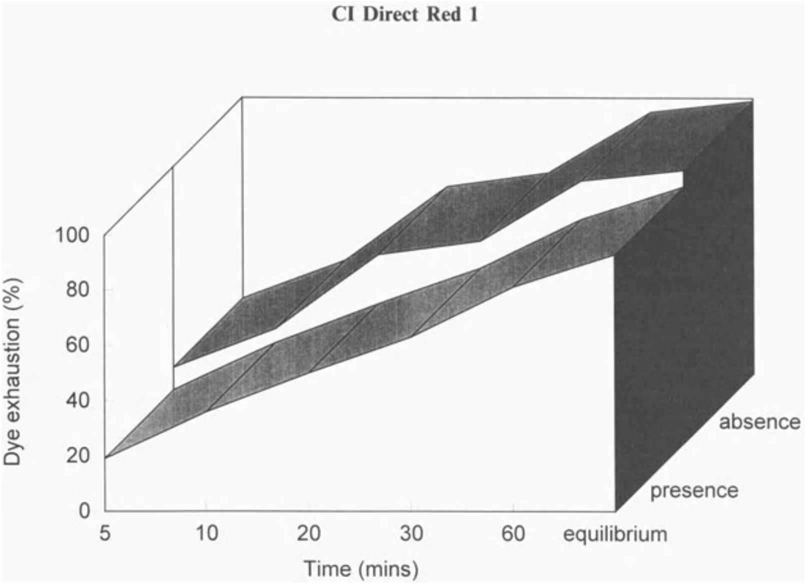
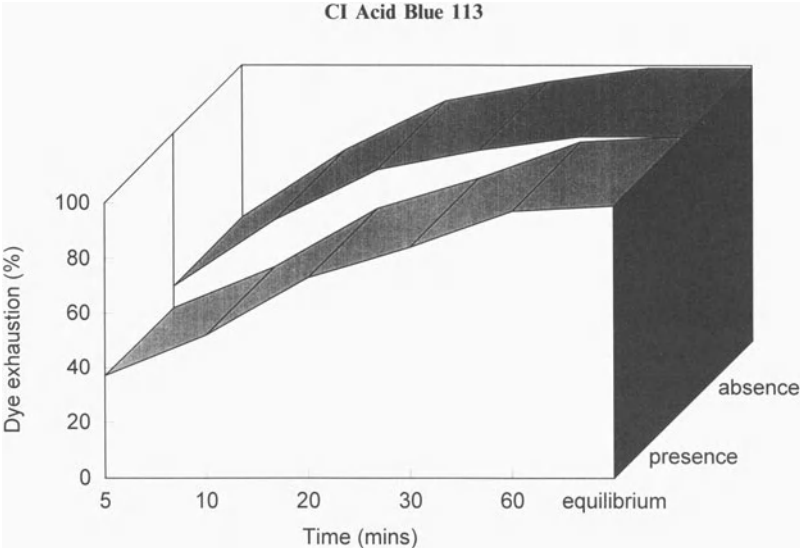


Figure 2.1 Rate of dyeing curves for three anionic dyes (1% o.m.f.) on nylon 6.6 (pH 6.8, 95°C) in the absence and presence of 2% o.m.f. Lissapol D [98]
(Reproduced with the permission of H.H. Sumner and the Society of Dyers and Colourists)



sulphate) was very rapidly adsorbed on to nylon 6.6 under typical dyebath conditions. Calculation of the affinity from this revealed that the value obtained for the anionic agent was similar to that of one of three non-metallised acid dyes used in the study (Table 2.4). Furthermore, it was observed [98] that whilst equilibrium uptake of the surfactant on to nylon 6.6 was achieved in 30 minutes under the particular application conditions used, that of four non-metallised anionic dyes took 3 hours. The difference in rates of adsorption of the anionic agent and three of the dyes is reflected in the $t^{1/2}$ values displayed in Table 2.4. These workers [98] also showed that the presence of the adsorbed anionic surfactant on the substrate markedly reduced the initial rate of dye uptake (strike) and that the extent of this retardation in dyeing rate decreased with increasing

Table 2.4 Affinities and times of half-dyeing of Lissapol D and three anionic dyes on nylon 6.6 (95°C; pH 6.8) [98]

Agent or dye	$-\Delta\mu^0$ (kcal mol^{-1})	$t^{1/2}$ (min)
Lissapol D	13.8	~2
CI Acid Red 266	13.9	18
CI Acid Red 138	18.4	24
CI Acid Blue 113	20.7	23

(Reproduced with the permission of H.H. Sumner and the Society of Dyers and Colourists) duration of dyeing, with the result that after 60 minutes dyeing the final extent of dye uptake was little affected by the levelling agent [98] (Figure 2.1).

Hughes *et al.* further showed that as soon as the pretreated fabric came into contact with dye solution, simultaneous adsorption of dye and desorption of the levelling agent occurred, clearly demonstrating the temporary nature of the anionic 'blocking' agent [98]. As previously discussed, nylon fibres are radially non-uniform and comprise a sheath/core structure. In this context, from Heidemann's finding [68] that streakily dyed nylon 6.6 yarns had a higher orientation than non-streakily dyed yarns and the facts that orientation-sensitive (rate-sensitive) disulphonated non-metallised acid dyes tend to ring dye nylon fibres, possibly by 'cross-linking' adjacent polymer chain segments in the fibre surface, Holfeld and Pike [71] considered that pretreatment of the fibre surface with an anionic levelling agent should block the terminal amino end group sites for dye adsorption and thereby reduce the tendency to ring dyeing. This was indeed achieved using only a small concentration of levelling agent (0.05 to 0.08% o.m.f.) applied at low temperature (27°C), analysis of the pretreated fibres revealing that the levelling agent behaved as a colourless, disulphonated acid dye as it did not form a surface layer but rather its sorption was diffusion-controlled in that uptake was governed by AEG site stoichiometry. In essence, the levelling agent 'blocked' the most accessible dye sites in the fibre sheath, thus making the dye sites more uniformly accessible. These workers [71] employed a variety of levelling agents in conjunction with both non-metallised and pre-metallised acid dyes and observed that the levelling agents varied in their ability to promote level dyeing, from which it was concluded that the affinity of the levelling agent and dye must be matched in order to achieve optimum results; furthermore, it was demonstrated that different yarns may require different temperatures for application of the levelling agent owing to differences in fibre dyeing transition temperature, T_d (see Chapter 3 for a discussion of this parameter). Typical anionic agents are ethoxylated alkyldisulphonates [99] although the use of a polycarboxylic acid levelling agent has been described [100]. Anionic blocking agents, such as Matexil LA-NS (ICI), are applied at 40°C in the pH range 4.5 to 6.5 for nylon 6.6 and 5.5 to 7.5 for nylon 6 [101].

CATIONIC LEVELLING AGENTS. Although both the high substantivity of cationic surfactants towards nylon fibres [102] and the use of such agents to control the levelling of direct dyes on the fibre [103] had been reported in 1945, it was not until 1956 [92, 104] that cationic surfactants were introduced to promote the level dyeing of nylon fibres with acid dyes. Earlier examples of such agents were strongly cationic, careful dye selection being necessary for success using these cations [104]. It had been early recognised that cationic agents formed complexes with anionic dyes [105, 106] and it was initially proposed [104] that the ensuing acid dye–cationic surfactant complex present in the dyebath was adsorbed on to the nylon substrate as a non-ionic disperse dye. However, it was subsequently shown [92] that the dye–cationic agent complex was not adsorbed as a non-ionic species, but rather, the cationic surfactant reduced the rate of dye uptake via the formation, in the dyebath, of an anionic dye–cationic agent complex which dissociated with increasing temperature, thereby gradually releasing dye anions for adsorption on to the fibre. In order to obviate precipitation of the dye–cationic agent complex, the presence of a non-ionic surfactant in the dyebath can be employed [96, 107] to solubilise the anionic dye–cationic agent complex. Weakly cationic agents, typically obtained by the polyethoxylation of alkylamines [108], are commonly employed to avoid precipitation of anionic dye–cationic agent complexes [91, 109, 110], such cationic surfactants, in effect, acting as a mixture of a cationic and a non-ionic surfactant, in that the oxyethylene chain of the cationic surfactant functions as a solubilising agent for the dye–agent complex. It has been shown that the sulphonate groups of acid dyes interact with the quaternary groups of such agents [111, 112] and that dye–agent complexes are formed, the constitution of which depends on the dye:agent ratio employed [112]. Hughes *et al.* [98] demonstrated that a complex was formed between a weakly cationic levelling agent (ethylene oxide amine condensate) and several non-metallised acid dyes and also that, in the initial stages of dyeing from a dyebath that contained an excess of dye, very little complex formation occurred. However, as the extent of dye exhaustion increased, the concentration of the cationic agent, which was not fibre-substantive, in the dyebath increased as did the concentration of the anionic dye–cationic agent complex. The result of this was that in the early stages of dyeing, the rate of dye uptake was little affected whereas in the later stages of dyeing, the cationic agent exerted an increasing restraining effect on dye adsorption. These workers [98] also showed that during the dyeing of nylon 6.6, using a constant temperature method in which an anionic levelling agent was used either prior to or simultaneously with the above weakly cationic levelling agent, the anionic agent readily complexed with the cationic surfactant and reduced the formation of the anionic dye–cationic agent complex to an extent that varied for each of the dyes used. Furthermore, these workers demonstrated that in this particular dyeing method, two variables influenced the rate of dyeing and thus levelling, namely a retarding effect resulting from reduced dye–fibre substantivity imparted by the anionic agent and a restraining effect imparted by the cationic agent; low dye–fibre substantivity and high dye–cation agent complex stability resulted in maximum retarding and restraining effects, respectively [98]. Blackburn and Dawson [91], in a study of this particular anionic–cationic surfactant mixture in a practical dyeing process using non-metallised acid dyes, concluded that the agent–mixture approach was more effective in terms of levelness and coverage of barré than the use of the agents alone for the constant temperature dyeing process. However, owing to the different response of different dyes to the agents, the problem of dye compatibility was not, in general, overcome using this particular approach and it was therefore suggested that dyes of good compatibility should be selected [91].

NON-IONIC LEVELLING AGENTS. Non-ionic surfactants are also employed as levelling agents in the dyeing of nylon with anionic dyes [97, 103]; several workers have established that complexes are formed between acid dyes and non-ionic surfactants [97, 114–117]. Datyner and Delayney [118] showed that three non-ionic surfactants retarded the rate of uptake of several disulphonated non-metallised acid dyes on nylon 6.6, greatest retardation of dye uptake having been achieved for the most hydrophobic dye; the retarding effect of the three surfactants was found to increase with increasing length of the oxyethylene chain of the surfactant. It was proposed that such non-ionic surfactants functioned by reducing the concentration of dye in solution through the formation of a dye–surfactant complex which contained more surfactant than dye [118]. Datyner *et al.* [119], in a study of the effects of a nonylphenol polyoxyethylene condensate on the uptake of two monoazo non-metallised acid dyes on nylon 6, reported that the real diffusion coefficient of the dyes was reduced in the presence of surfactant owing to a corresponding reduction in the concentration of dye in solution. However, non-ionic agents alter the compatibility of acid dyes and, by the use of the correct amount of levelling agent, the compatibility of otherwise incompatible dyes is enhanced [97]. Bayer have developed the *Telon S* [97, 120] process for dyeing nylon substrates; this utilises temperature control to optimise the rate of dye uptake in the presence of a non-ionic auxiliary to enhance dye compatibility [97].

2.2.2.1.2. Aftertreatment. Owing to the higher crystallinity and more compact structure of nylon 6.6, the wet fastness of a given dye on nylon 6.6 will, in general, be higher than that on nylon 6. Nevertheless, as the wet-fastness properties of many non-metallised dyes on nylon leaves much to desired, an aftertreatment, using a syntan (synthetic tanning agent) or, less commonly, a natural tanning agent (the full backtan), can be given to the dyeing to improve its wet fastness.

NATURAL TANNING AGENTS. The conversion of putrescible animal skin to leather of improved chemical and biological resistance is one of man's oldest known crafts [121]. Seguin [122] first recognised that water-soluble agencies were present in certain vegetable tissues, such as oak bark, which precipitated gelatin and combined with skin to form leather and he applied the term *tannin* to such agents. The vegetable tanning process, which has remained essentially unchanged since its inception many thousands of years ago, consists, in essence, of steeping the de-haired and flayled skin in an infusion of natural tannins, thereby rendering the collagen protein of the hide stable to decomposition. The natural vegetable tannin extracts form a heterogeneous group of generally amorphous materials which contain large M_r polyphenolic *tannins* as well as less complex *non-tans*, such as saccharides, flavones and gums which, although devoid of direct tanning ability, nevertheless contribute to the overall tannage of the skin. The natural tannins can be classified [123] as *Hydrolysable (pyrogallol) tannins* of which there are two types, namely **gallotannins** as represented by 'tannic acid' and **ellagitannins** and *Condensed (Catechol) tannins*.

The earliest textile applications of natural tannins included the dyeing of cotton with dyewoods, which, owing to their insignificant substantivity towards the fibre, required the use of a metal salt, such as $CuSO_4$ [124] in the case of Logwood Black, as mordant, the purpose of the tannin being to 'fix' the metal salt by the formation of a metal tannate and, thereby, enhance the wet fastness of the resulting dyeing, the tannin being applied either before the metal salt prior to dyeing or after the dyeing of the mordanted fabric [125]. Also, following the introduction of Mauveine in 1856, Perkin and Pullar [126, 127] utilised tannins as mordants to enhance the uptake of cationic dyes on cotton; in this 'tannin-metal' dyeing method, the tannin mordant was 'fixed' prior to dyeing by the subsequent application of a metal salt (sodium stannate [126–128]) to the tannin-treated fabric which resulted in the formation of a metal tannate, this process being necessary to impart adequate wash and light fastness to the dyeing [124]. Of various metals (Sn, Al, Fe), salts of antimony were found to yield dyeings of highest fastness [124, 128] and, in 1882, Dale discovered that, of these, potassium antimonyl tartrate (tartar emetic) was the most appropriate [124, 126, 127]. To improve the fastness of the dyeing, the dyed material was aftertreated using either tannin alone or tannin with tartar emetic (back tanning) or with other metal salts such as $SnCl_4$ [129]. Tannins were also used in the weighting of silk to restore the loss in mass that accompanied de-gelatination of the fibre; however, although silk adsorbed appreciable quantities of tannin, the low fastness of the adsorbed tannins to water was overcome by treatment of the tannin-treated silk with metal salts such as those of tin [130] or antimony [131].

FULL BACKTAN. The *full backtan* aftertreatment that was originally developed to improve the wet fastness of acid dyes on nylon entailed successive treatments with tannic acid, potassium antimonyl tartrate and stannous chloride [132, 133], this method being simplified by the omission of the use of stannous chloride [132]. The aftertreatment is carried out by applying tannic acid to the rinsed, dyed fibre at pH 2.5 (acetic or formic acid) for 30 minutes at 70°C for nylon 6 and 90°C for nylon 6.6 [24]; the higher application temperature employed for nylon 6.6 is attributable to the lower rate of diffusion of tannic acid within such fibres [134, 135]. The tanned fabric is then treated with potassium antimonyl tartrate for a further 20 minutes at the appropriate temperature for nylon 6 and nylon 6.6 and the material is then thoroughly rinsed.

It is currently believed that in the full backtan process, the tannic acid behaves as a high M_r acid which binds to the protonated amino end groups in the substrate, and that subsequent treatment with tartar emetic results in the formation of a surface *skin* of the sparingly water-soluble antimonyl tannate which possesses lower diffusional characteristics and undergoes oxidative degradation to a lesser extent than the un-complexed tannic acid [125, 132]. The presence of aggregates of the complex at the periphery of the dyed nylon reduce the rate of diffusion of dye out of the dyed substrate and hence not only reduces the transfer of dye to adjacent materials during subsequent washing [125, 132, 133, 136] but also retards uptake of dye on to pretreated material [132, 133, 137]. Support for this mechanism is provided by the absence of interaction between the anionic dye and the antimonyl tannate complex or either of its precursors during the full backtan aftertreatment [132, 133, 138].

Although pure tannic acid is colourless, it is relatively expensive and normal commercial grades can contain impurities which impart a yellow colour to the acid; these coloured impurities are adsorbed by the dyed fibre and cause a marked flattening of shade. Shore [139] has suggested that under warm, alkaline conditions, such as those encountered in domestic washing or the ISO C06/C2 wash test, tannic acid is oxidatively degraded to give yellow quinonoid compounds. Ashworth and Blackburn [140] observed that maximum yellowing of undyed adjacent nylon as well as minimum staining of adjacent fibres, were achieved, conjointly, when the tannic acid was applied to dyed nylon 6 at 70°C and at a concentration of less than 2% o.m.f. The nature of the antimonyl tannate complex is not clearly understood [125]; it has been suggested that 5 moles of tartar emetic are required to precipitate 1 mole of gallotannin from solution [132] and that a 1:1 complex is formed between tannic acid and potassium antimonyl tartrate in solution [141], although the interaction between the two components in the presence of fibre appears not to obey this stoichiometry [132].

Whilst the full backtan can significantly improve the wet-fastness properties of acid dyes on nylon, several disadvantages inherent in the process have nullified its use, namely:

- potassium antimonyl tartrate is toxic;
- treatment can reduce the light fastness of the dyeing;
- the treated dyeings can undergo a distinct change of shade;
- the two-stage treatment is expensive in terms of the costs of both chemicals and duration [141];
- tannic acid oxidises under alkaline conditions, resulting in discoloration of treated fabric, especially in the case of pale shades [139];
- the treatment is not stable to steam or heat treatments owing to degradation of tannic acid [139];
- the process imparts a harsh handle to the fibre [135].

SYNTHETIC TANNING AGENTS. As mentioned above, although the full backtan aftertreatment can significantly enhance the wet-fastness properties of acid dyes on nylon, owing to the various disadvantages inherent in the process its use has largely been superseded by that of synthetic tanning agents or *syntans*. As their name implies, syntans were first developed as alternatives to natural tannins in the tanning of leather; subsequent developments lead to products that were specifically intended for use as an aftertreatment of dyed nylon. In this context, although the term *syntan* was originally used to describe synthetic compounds that possessed skin-tanning ability, with regards to the aftertreatment of dyed nylon, this same term applies to synthetic compounds that serve as replacements to the full backtan. However, whilst a syntan that has skin-tanning ability may be capable of improving the wet fastness of dyed nylon, a syntan that was specifically designed for aftertreating dyed nylon may not necessarily be effective as a tanning agent for leather.

Although, by dehydrating arylsulphonic acids, Schiff, in 1875, as well as other workers [125], obtained synthetic compounds by dehydrating arylsulphonic acids, that exhibited the general properties of a tanning agent for leather, it was Stiasny, in 1911 [142], who first described the preparation of synthetic compounds which possessed hide-tanning ability and which now are referred to as *syntans*. Early examples of such syntans for use on leather, as exemplified by the first such commercial product introduced by BASF in 1912 [143], were derived from the acidic condensation of phenols and their sulphonic acids with aldehydes (commonly formaldehyde). Considerable development attended such water-soluble novolac resins [144–148] including, in the 1930s, syntans derived from the condensation of arylsulphonic acids and dihydroxydiaryl sulphones with aldehydes [145, 148, 149]; thiophenolic syntans (sulphurised phenols) [150] were also developed for leather tanning.

In the context of application to textiles, although the thiophenolic and some of the arylsulphonic acid polycondensate syntans were used in the weighting of silk [151], the mordanting of cotton dyed with cationic dyes [152, 153] and also as dye-resist agents for wool [154], the largest and most important use of this type of compound is in the improvement, by aftertreatment, of the wet fastness of predominantly non-metallised acid dyes on nylon.

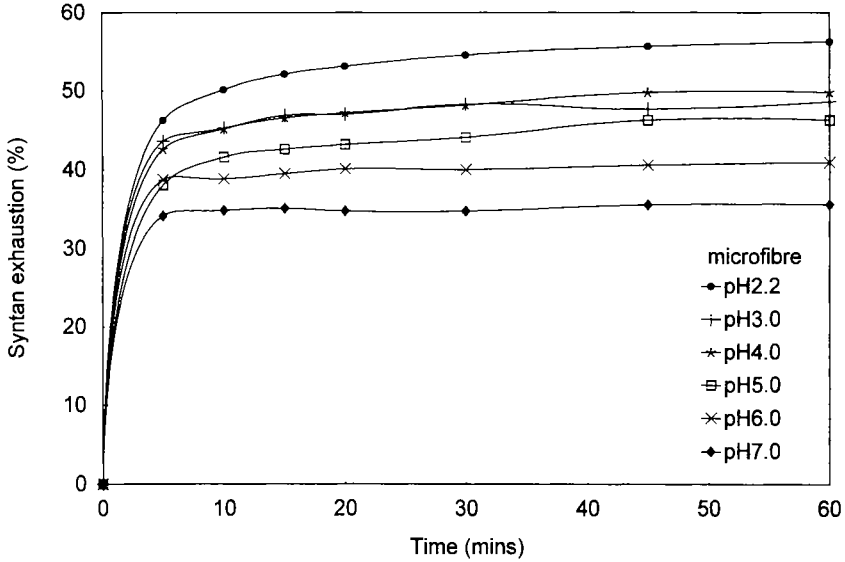
The general chemistry of syntans has been discussed by several authors [125, 139]; however, little published work concerning the composition of syntans for use on dyed nylon exists and the preparation of such compounds is confined to patent literature. However, Kelson and Holt [129], using HPLC, recently showed the diverse composition of several commercial synthetic tanning agents. Syntans for nylon are, typically, water-soluble, anionic formaldehyde polycondensates of arylsulphonates and sulphonates of dihydroxydiaryl sulphones (typically dihydroxydiphenylsulphone [155]); for example, Matexil FA-SNX (ICI) is described as a *sulphonated high* M_r *product based on phenol sulphone* [101].

Current theories regarding the mechanism of wet fastness improvement of anionic dyes on nylon by aftertreatment with these agents has been reviewed by Cook [125]. It has been suggested that the desired M_r of such polycondensates is below 10^3 as larger M_r compounds tend to be insoluble in water [156], the preferred compounds exhibiting a minimum of branching and cross-linking [156, 157]. Although the syntans are commonly marketed as sodium sulphonates, other metal cations have been used, including NH_4^+, K^+ and Li^+ [158]. The solubility of the polycondensates depends on the anion used, the concentration of hydrophilic (sulphonate, methylol) groups present, the M_r of the polycondensate as well as the degree of cross-linking of the condensate; some syntans contain additional polar groups such as carbonamide, sulphonamide or ureido [132, 155, 158]. It is considered that condensation products in which each repeat unit contains only one sulphonate group are more effective than corresponding products in which each repeat unit contains two or more sulphonate groups. Also, the syntan becomes more effective as the ratio of repeat units containing sulphonate groups: units that are devoid of sulphonate groups increases [158].

It has been proposed [125] that syntans are adsorbed at the periphery of the dyed polyamide fibre and that their ability to improve the wet-fastness properties of non-metallised acid dyes on nylon fibres is attributable to this peripheral 'layer' of syntan molecules reducing the diffusion of dye out of the dyed, treated fibre during wet treatments; ion–ion repulsion effects operating between the anionic syntan and the anionic dye also contribute to reduced dye diffusion. However, the precise mechanism by which syntans improve the wet fastness properties of dyed nylon fibres remains unclear in view of the varied composition of the polycondensates.

SYNTAN-FIBRE SUBSTANTIVITY. Syntans are applied to dyed nylon by a single-stage process under acidic conditions, as exemplified by the application of Matexil FA-SNX (ICI), which is carried out either in the

(a)



(b)

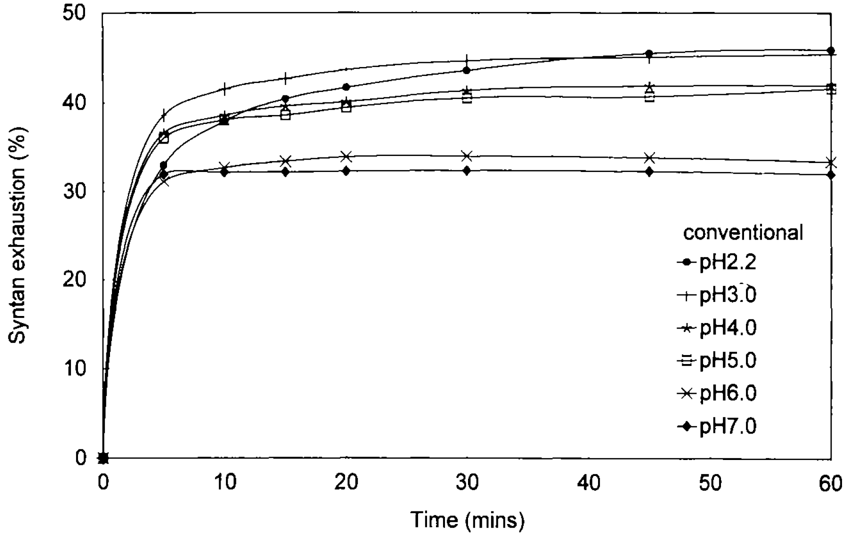


Figure 2.2 Effect of pH on uptake of Matexil FA-SNX on to micro (0.92 dtexpf) and conventional (1.69 dtexpf) nylon 6.6 fabrics at 80°C using a 50:1 liquor ratio [161]

(Presented at the 1994 AATCC International Conference and Exhibition, Charlotte, NC. Reprinted with permission from AATCC)

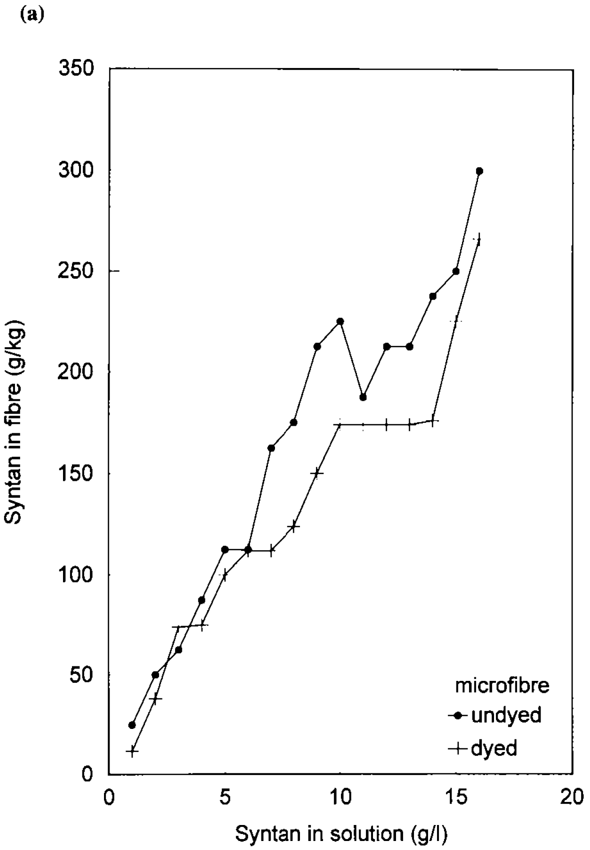
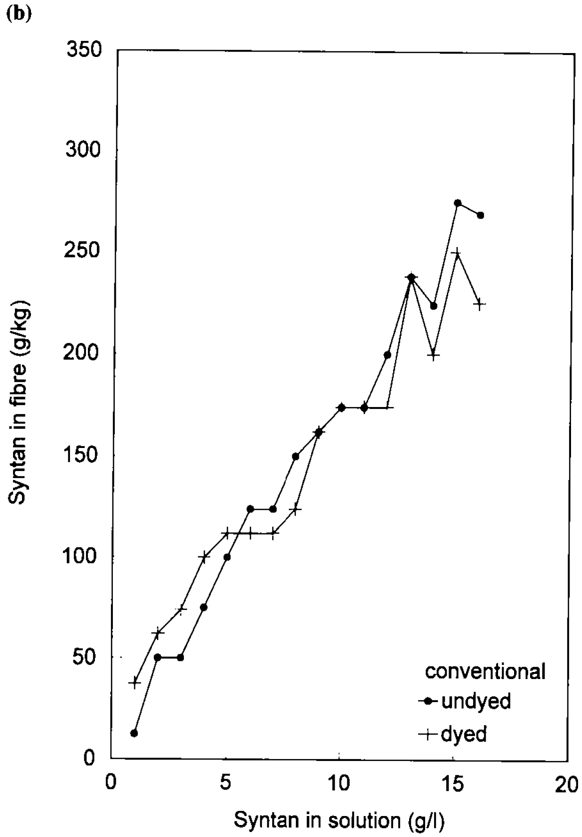


Figure 2.3 Adsorption isotherms for Matexil FA-SNX on undyed and dyed (1% o.m.f. CI Acid Blue 25) micro (0.92 dtexpf) and conventional (1.69 dtexpf) nylon 6.6 fabrics at 80°C using a 100:1 liquor ratio [161]
(Presented at the 1994 AATCC International Conference and Exhibition, Charlotte, NC. Reprinted with permission from AATCC)

exhausted dyebath for 30 minutes or in a fresh bath using 4% o.m.f. HCOOH at 95°C for nylon 6.6 or 70°C for nylon 6 [101]. Under such acidic conditions, ion–ion interaction, operating between the protonated amino groups in the fibre and sulphonate groups in the syntan, as well as hydrogen bonding are considered [125, 132, 158, 159 161] to contribute towards syntan–fibre substantivity.

The importance of ion–ion interaction in syntan fibre substantivity was demonstrated [160, 161] by the finding that the uptake of two different commercial syntans on to nylon 6.6 increased with decreasing pH in the region pH 2 to 7, these observations concurring with those [162 164] for the adsorption of several commercial syntans on wool. This is illustrated by the results shown in Figure 2.2. It has also been shown [161] that the



rate and extent of adsorption of a commercial syntan on both conventional and microfibre nylon 6.6 increased with decreasing liquor ratio. It was proposed [161] that this result was attributable to a corresponding increase in the effective concentration of syntan in the treatment bath that accompanied the reduction in liquor ratio. Although no information was available concerning the precise chemical composition and M_r of the particular syntan used, it was suggested that aggregation of the syntan would occur in solution by virtue of both polar and non-polar forces operating between the large molecular size syntan molecules. Thus, the increased effective concentration of syntan that accompanied a decrease in liquor ratio could be expected to increase the degree of syntan aggregation in solution which, in turn, would result in greater uptake of the tanning agent [161–164]. The observation that both the rate and extent of adsorption of the syntan on to conventional and microfibre nylon 6.6 increased with increasing application temperature was attributed to the higher kinetic energy of the syntan molecules and their consequent greater diffusional power within the substrate, together with the higher extent of fibre swelling that accompanied an increase in application temperature [161]. It was shown [161] that both the rate and extent of syntan uptake were greater on microfibre nylon 6.6 fabric than on its conventional decitex counterpart, irrespective of the pH value, liquor ratio and temperature of application, this being attributed to the greater surface area of the microfibre nylon 6.6 fabric.

The equilibrium adsorption isotherms of the syntan on undyed conventional and undyed microfibre nylon 6.6 revealed [161] that uptake on to both types of fibre followed a BET mechanism (Figure 2.3), which implied that uptake involved the formation of multilayers of adsorbed syntan molecules. Although these results agreed with those obtained for the adsorption of various syntans on wool [162–164], they disagreed with those of Cook and Guthrie [165] who found that the adsorption of both the commercial syntan *Cibatex PA* (Ciba-Geigy) and a novel sulphonated novolac syntan on to nylon 6 followed a Freundlich mechanism. This disagreement between the Freundlich mechanism proposed by Cook and Guthrie [165] and the BET mechanism obtained on wool [162–164] and on nylon 6.6 [161] was attributed [161] to differences in the concentration ranges employed by the different workers. In the case of the adsorption isotherms of various syntans on wool [162–164], a concentration range of between 0.5 and 14 g l^{-1} was used and concentrations of between 1 and 16 g l^{-1} were employed using nylon 6.6 [161]; in contrast, the concentration range used by Cook and Guthrie for each of the two syntans employed in their study [165] was 0.05 to 0.25 g l^{-1}. Thus, it was postulated [161] that the Freundlich isotherms obtained by Cook and Guthrie might, owing to the low concentration of syntan used, constitute the initial region of BET isotherms. Nevertheless, the results obtained on nylon 6.6 [161], wool [162–164] and nylon 6 [165] indicate that syntan adsorption on to undyed nylon and wool fibres does not occur simply by virtue of ion–ion interaction operating between the anionic syntan molecules and specific sites (namely, the protonated amino groups) in each fibre and, therefore, that other forces of interaction, for example, hydrogen bonding, ion–dipole as well as hydrophobic interaction operating between the aromatic centres in the syntan molecules and hydrophobic regions of the fibre, contribute towards syntan–fibre interaction. In view of the BET adsorption mechanism obtained on nylon 6.6 (Figure 2.3) [161], such forces can also be considered to contribute towards multilayer adsorption of the syntan, which will also contribute towards syntan–fibre substantivity.

In an attempt to further determine the influence that ion–ion interaction made towards syntan adsorption, as it is widely held that the adsorption of a small molecular size, anionic dye on to nylon 6.6 is confined to the amino end groups within the polymer, then the presence of such a dye on the fibre should markedly affect the adsorption of a syntan if uptake of the tanning agent occurred mainly by virtue of ion–ion forces of interaction at the terminal amino groups in the substrate employing this approach. It was demonstrated [161] that the presence of 1% omf CI Acid Blue 25 on nylon 6.6 fabric reduced the extent of adsorption of a commercial syntan on to both conventional and microfibre nylon 6.6. However, as Figure 2.3 shows, adsorption of the syntan on to each type of dyed nylon 6.6 fibre also occurred by a BET mechanism and, therefore, the presence of the dye had not affected the mechanism of adsorption of the syntan. From these results, it was concluded that in addition to ion–ion interaction, other polar and non-polar forces contribute towards syntan-fibre substantivity [161]. Further support for the proposal that adsorption of syntans on nylon 6.6 occurs by a combination of both polar and non-polar forces of interaction has been obtained from the observation [160] that a commercial syntan was adsorbed on to basic-dyeable nylon 6.6 and also on to acid-dyeing nylon 6.6, the latter fibre having been chemically modified such that all available amino end groups were replaced with sulphonic acid groups, to an extent that was not substantially different to that secured on regular acid-dyeing nylon 6.6 fibre.

ENHANCEMENT OF EFFECTIVENESS. In the context of the effectiveness of syntans in improving the wet fastness of non-metallised acid dyes on microfibre nylon 6.6, it was shown [161] that when the same concentration of syntan was applied to dyed conventional and microfibre, each of which contained the same quantity of CI Acid Blue 25, the extent of dye loss that occurred during an ISO C06/C2 wash test was greater from the dyed microfibre. As it had been demonstrated that this observed lower effectiveness of the syntan aftertreatment on dyed microfibre was not due to a difference in the mechanism by which the syntan was adsorbed on to the microfibre fabric and, in addition, as the uptake of the syntan had been shown to be greater on dyed microfibre than on dyed conventional fibre, the observed lower effectiveness of the syntan aftertreatment on dyed microfibre was attributed to the greater surface area of the microfibre, this resulting in a greater surface area from which dye loss occurred [161].

The effectiveness of the commercial syntan, Matexil FA-SNX, in improving the wash fastness of various non-metallised acid dyes on both conventional and microfibre nylon 6.6 was enhanced [161, 166] using a technique analogous to that of the full backtan. As mentioned above, the full backtan process comprises the sequential application of tannic acid and potassium antimonyl tartrate to the dyed material. In this sequential process, the potassium antimonyl tartrate insolubilises the anionic, water-soluble tannic acid, resulting in the formation of a large M_r, sparingly water-soluble, potassium antimonyl tannate complex situated at the surface of the dyed fibre which reduces diffusion of dye out of the substrate during wet treatments. Matexil FA-SNX and other syntans marketed for use as an aftertreatment of dyed polyamide fibres are, typically, water-soluble, anionic formaldehyde polycondensates of sulphonated dihydroxydiaryl sulphones. Thus, it was argued [161] that by analogy with the full backtan process, the effectiveness of the syntan aftertreatment of dyed nylon might be enhanced if it were possible to subsequently treat syntanned, dyed nylon and form a sparingly water-soluble, high M_r complex on the dyed nylon; as the syntan is strongly anionic then a suitable cationic compound should be capable of forming such a complex. Hence, various cationic compounds were used in conjunction with the syntan and their ability to enhance the effectiveness of the tanning agent assessed [161]. It was found that whilst aftertreatment with either of two cationic agents, each of which was intended for use as an aftertreatment of cotton dyed with direct dyes, increased the wash fastness of dyed microfibre nylon 6.6 fabric, the subsequent application of the two cationic agents to syntanned, dyed nylon 6.6 microfibre markedly enhanced the effectiveness of the syntan in improving wash fastness. Other cationic agents were found to be effective in this context, the enhanced effectiveness achieved for the sequential syntan–cationic agent system being attributed to the formation of a large $\mathrm{M_r}$, sparingly soluble, syntan–cationic agent complex [161]. As it is considered that syntans are adsorbed at the periphery of dyed polyamide fibre, it was proposed that the syntan–cationic agent complex will also be situated at the periphery of the dyed substrate; consequently, the ability of the complex to improve the wash-fastness properties of non-metallised acid dyes on nylon 6.6 fabric was attributed to this peripheral 'layer' of the complex reducing diffusion of the dye out of the dyed, treated fibre during washing [161]. The light fastness (ISO A02) of microfibre which had been dyed with three commercial shades and aftertreated with a commercial syntan was not affected by a subsequent treatment with various cationic agents [161].

2.2.2.1.3. Thermodynamics of dyeing. As previously mentioned, the presence of terminal amino groups in nylon confers substantivity for acid and other types of anionic dye. Although five types of anionic dye can be used on nylon (non-metallised acid, pre-metallised acid, mordant, direct and reactive), most attention has been given to the mechanism of the adsorption of acid dyes on the substrate and, of this, greatest focus has been on non-metallised acid dyes. However, as the procedures employed for the application of all five types of anionic dye to nylon are very similar, in that acidic or slightly alkaline pH values are used to exhaust the dyes on to the substrate, the following account of the thermodynamics of the adsorption of acid dyes on nylon can be considered as being generally applicable to all types of anionic dye used on nylon.

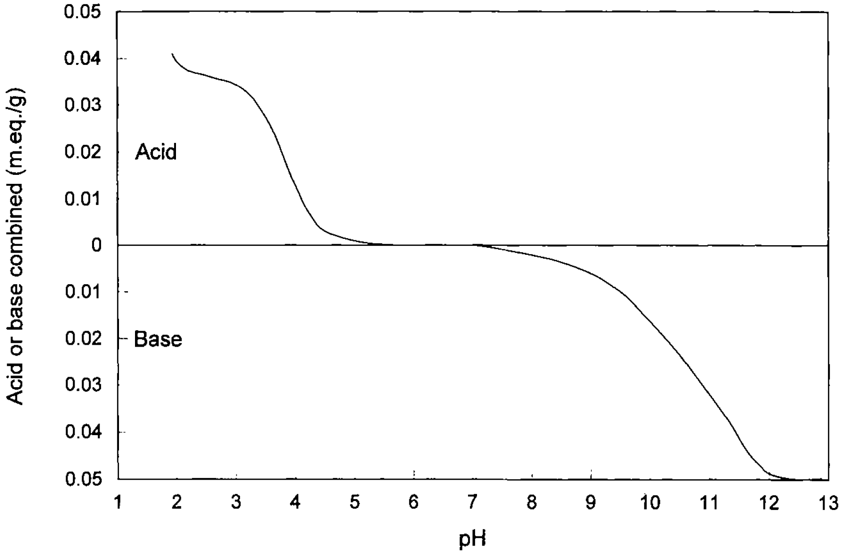


Figure 2.4 Titration curve of nylon 6.6 with HCl and NaOH at 21.5°C [172] (Copyright © 1964 John Wiley & Sons, Inc. Reprinted by permission)

TITRATION CURVES. The adsorption of both simple acids, namely HCl [167–172], HBr [173], H_2SO_4 [173, 174] and also more complex acids [172, 174] as well as NaOH [172, 175], have been used as a basis for describing the adsorption of dye anions. Elöd and Schachowsky [167] first observed the dependency of acid adsorption by nylon on pH as well as the steady increase in acid adsorption at low pH values which increased without limit.

In the case of the adsorption of HCl, the titration curve obtained using nylon 6.6 fibres exhibits an inflection point at a pH of between 2 and 3 [168, 169, 171], at which point uptake of the acid corresponds approximately to the AEG content of the fibre (Figure 2.4). At lower pH values, acid adsorption increases, without limit, this being attributable to adsorption of the acid on to the chain amide groups of the polymer [168, 169, 171, 172, 174, 176]. The dependency of acid adsorption on AEG content was demonstrated by the finding [172] that nylon 6.6 fibres in which the terminal amino groups had been chemically modified adsorbed very little acid.

The addition of electrolyte (KCl) shifts the HCl titration curve to higher pH values [172] (Figure 2.5) whilst an increase in temperature slightly reduces the extent of acid adsorption [171, 172]. The titration of nylon 6.6 fibres with more complex acids, such as benzene sulphonic acid [172, 174] and naphthalene-2-sulphonic acid [172], exhibits similar behaviour to that of HCl, except that the titration curves move to higher pH

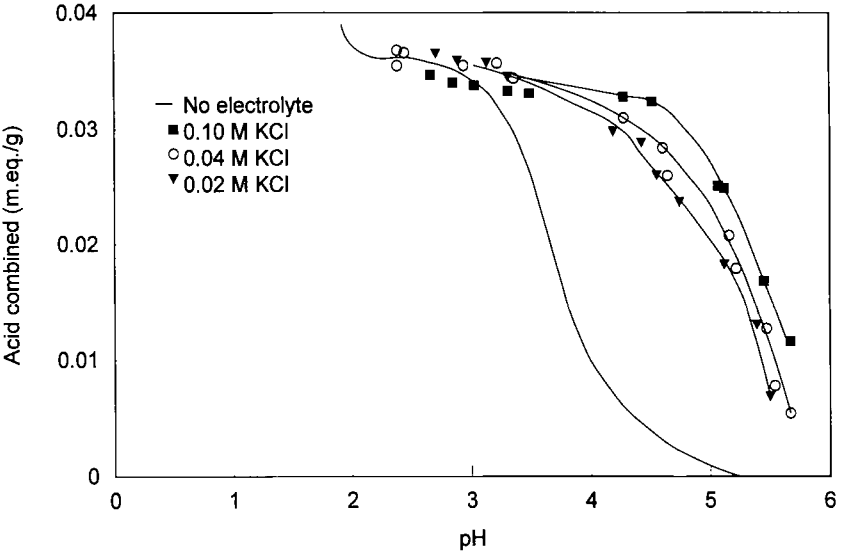


Figure 2.5 Titration curves of nylon 6.6 with HCl at 21.5°C in the absence and presence of KCl [172]
(Copyright © 1964 John Wiley & Sons, Inc. Reprinted by permission)

values as the complexity of the acid anion increases [172, 174]. In the case of titration with alkali, the adsorption of NaOH was found to decrease with decreasing pH in the range 12 to 7 with an inflection in the curve occurring in the pH range 6 to 7, which corresponds to the isoelectric point of the polymer (Figure 2.4].

The above results of titrations of nylon with both simple and more complex acids, as well as with alkalis, have been interpreted using two approaches, namely one based on a specific site (Langmuir) model proposed by *Gilbert and Rideal* in 1944 [177] and various modifications of the *Donnan membrane* (ion exchange) theory as first proposed by Peters and Speakman in 1949 [178], in a manner similar to that employed in the case of the titrations of wool although modifications are necessary in the case of nylon because, unlike wool which contains an equal number of amino and carboxylic groups, many commercial nylon fibres contain an excess of carboxylic acid groups. As both the principles underlying these various theories and critical assessments of the applicability of the theories with regards to nylon have received considerable attention from several authors [179–182], the following account serves only as a general overview of these theoretical treatments of the titration of polyamides.

GILBERT-RIDEAL. This theory [177], which was developed to interpret the titration curves of wool, assumes that the fibre has an equal number of positive and negative charges, these constituting adsorption sites; the cationic sites are assumed to behave identically in their interaction with anions and the anionic sites are likewise identical. All anions are considered as being able to be adsorbed on to any cationic site in the fibre and all cations are able to be adsorbed on to any anionic site. The activities of both cations and anions are equated to $\theta/(1-\theta)$ where θ represents the fractional occupation of sites. The substrate is also assumed to be ideally stable in that the aqueous solution from which adsorption occurs contains only protons and anions from the acid.

$$\frac{-\Delta\mu^0}{4.606RT} = \log\left(\frac{\theta}{1-\theta}\right) + \mathrm{pH_S} \tag{2.1}$$

According to this theory, in the case of acid only (no other added electrolyte) equation (2.1) can be derived [168, 179] from which a plot of log $\theta/(1-\theta)$ versus pH of the external solution ($\mathrm{pH_S}$) should yield a straight line of negative unit slope. The value of affinity is related to the pH at which half-saturation occurs (i.e. when $\theta = 0.5$) (equation (2.2)) where R is the gas constant.

$$-\Delta\mu^0 = 4.606RT.\mathrm{pH} \tag{2.2}$$

However, in the case of the titration of wool with HCl [182], the log $\theta/(1-\theta)$ versus pH plot was found to be not linear but slightly sigmoidal and also of lower slope (0.87) than theory predicted [168]; this was also found in the case of the adsorption of HCl on nylon 6 [184]. In the presence of added electrolyte (KCl), equation (2.2) is transformed into equation (2.3) from which a plot of log $\theta/(1-\theta)$ versus $\mathrm{pH_S}$ at constant $[\mathrm{Cl}\ ]_S$ should give a straight line of slope 0.5, which will be displaced to higher pH values with increasing $[\mathrm{Cl}^-]_S$.

$$\frac{-\Delta\mu^0}{2.303RT} = 2\log\left(\frac{\theta}{1-\theta}\right) + \mathrm{pH_S} - \log\,[\mathrm{Cl}^-]_S \tag{2.3}$$

Vickerstaff [168] observed that in the case of wool, although straight lines were obtained which were displaced to higher pH values with increasing electrolyte concentration, the slopes varied from −0.4 to −0.5. The reasons for the discrepancy of the theoretically predicted and observed results have been attributed to the assumption made in the theory that the substrate is ideally stable, which is not the case for wool or nylon; also, such discrepancies may have their source in the actual theoretical treatment [180]. Rattee and Breuer [181] point out that there is no way of experimetally distinguishing between internally adsorbed and adsorbed ions, the experimentally determined θ not being the same as the θ used in the theory to describe the activities of the adsorbed ions. Furthermore, these authors [181] note that the value of affinity secured using equation (2.1), wherein $\theta = 0.5$, bears little resemblance to that obtained for values of θ other than 0.5.

The Gilbert–Rideal theory has also been employed to interpret the titration of nylon with NaOH [175, 185] although, as Peters [179] comments, this particular approach suffered the disadvantage that it was assumed that Na^+ ions were adsorbed on to undissociated carboxylic acid groups.

DONNAN MEMBRANE. Several variations of this model have been proposed, each being classifiable as a theory based on ion exchange. By using equations for equilibria at semi-permeable membranes devised by Donnan and Guggenheim [186], Peters and Speakman [178] developed equations that enabled internal concentrations, including the 'internal pH' within the fibre, to be calculated. Although, in the Peters–Speakman [178] theory, as in the Gilbert–Rideal theory, the water-swollen fibre is considered to constitute an equipotential volume that contains fixed, charged groups, in this particular theory [178] the sorption of ions from solution occurs in accordance with a Donnan distribution in which the solution within the fibre is considered separately from both the fibre itself and the external (bulk) solution. In this model, whilst protons are adsorbed on to anionic sites in the fibre, the anions are present only in the internal aqueous solution (of volume $V\ \mathrm{l\,kg^{-1}}$) and are not able to interact directly with the cationic sites in the fibre (i.e. the anion has no affinity for the substrate).

$$\frac{\Delta\mu^0}{2.303RT} - \log\frac{S_H}{V} = \log\left(\frac{\theta^2}{1-\theta}\right) + 2\mathrm{pH_S} \qquad (2.3)$$

In the case of a simple acid in the absence of other added electrolyte, equation (2.3) is obtained [168, 180, 181], where $\mathrm{pH_S}$ is the pH of the external solution, from which a plot of log $[\theta^2/(1-\theta)]$ versus $\mathrm{pH_S}$ should yield a straight line of slope −2; however, in the case of wool, a line of slope −1.4 was obtained [168]. The reasons for the discrepancy between the theoretically predicted and observed results can, as was the case with the Gilbert–Rideal treatment, be attributed to fibre decomposition and possible wrong assumptions in the theoretical treatment.

Equation (2.4) is that for the internal pH ($\mathrm{pH_I}$) in the absence of added electrolyte where a is the total concentration of H^+ ions adsorbed by the fibre:

$$\mathrm{pH_I} = 2\mathrm{pH_S} + \log\frac{a}{V} \qquad (2.4)$$

The effect of added electrolyte (KCl) in this model is explained in terms of the internal pH through equation (2.5).

$$\mathrm{pH_I} = \mathrm{pH_S} + \log\frac{a}{V} - \log\,[\mathrm{Cl^-}]_\mathrm{S} \qquad (2.5)$$

In the case of the titration of wool with HCl alone, when $\theta = 0.5$ (when the fibre is half-saturated with acid) the $\mathrm{pH_S}$ and thus the pK of the carboxylic acid groups was found to be 2.1 [168], this being much lower than the value of pK for free amino acids. In the cases of both wool and, as mentioned previously, nylon fibres, the effect of adding neutral electrolyte during the titration with acid was to shift the titration curves to higher pH values which, in turn, implies that different pH values were operating in the presence and absence of added electrolyte; this should not be so as, for a given amount of acid adsorption, a fixed electrical potential and thus a fixed pH must operate. The main purpose of employing Donnan membrane theory [178] was to resolve this situation. In the case of the pK of the carboxylic acid groups in wool, the use of $V = 0.3$, $a = 0.4$ and $\mathrm{pH_S} = 2.1$ in equation (2.4) gave a pK of 4.3, a value that closely agrees with that of free amino acids [168, 180, 181]. Furthermore, whereas when the amount of acid adsorbed by wool, in both the absence and presence of added electrolyte, was plotted against external pH ($\mathrm{pH_S}$), two curves were obtained, when the amount of acid adsorbed by wool was plotted against internal pH ($\mathrm{pH_I}$), the curves were superimposed [178]; this has also been obtained for the titration of nylon 6 with HCl in the presence and absence of KCl [183]. However, whilst the Donnan treatment does give a satisfactory explanation of the effect of electrolyte on the acid titration curve, in the context of the pK of the carboxylic acid groups in wool, it should be pointed out that the Gilbert–Rideal theory also provides a reasonable interpretation of the effect of electrolyte on the titration curve:

$$\mathrm{p}K = 2\mathrm{pH_S} \tag{2.6}$$

Equation (2.6) can be derived from equation (2.2), from which it follows that in the case of HCl, as $\mathrm{pH_S}$ was 2.1, at $\theta = 0.5$ [187], the value of pK obtained using equation (2.6) is 4.2 which not only closely agrees with that of free amino acids but also closely resembles the value for pK, namely 4.3, obtained using equation (2.4) of the Donnan treatment.

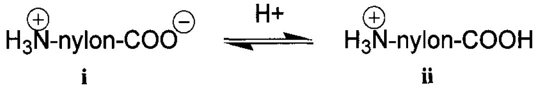
By considering that the Gilbert–Rideal and Peters–Speakman theories were extreme cases of the same adsorption mechanism, Peters [188] subsequently developed a more general model that incorporated features of both and enabled affinities and titration curves to be calculated. As in the earlier Peters–Speakman model, in the *Unified* theory [188] the fibre has an internal aqueous solution of volume V which has the same properties of the external (bulk) aqueous solution; however, whereas in the Peters–Speakman model the ionised groups within the internal solution were considered as being immobile, in the generalised model, the ionised groups within the internal aqueous phase are considered to be in solution. Whilst, in effect, the same equations were used as in the Peters–Speakman theory, unlike this earlier theory, the Unified model enabled both the cation and anion affinities to be determined in terms of binding or dissociation constants.

Mathieson and Whewell devised a *Polyelectrolyte* theory [189] based on the titration of charged groups within the substrate and the energy required to overcome electrostatic, osmotic and affinity forces so as to remove adsorbed protons from the fibre to the external aqueous solution. In this model, no assumptions were made as to the degree of association between charged species within the fibre. The fibre and internal solution were considered to constitute a single, homogeneous phase of known volume, thus eliminating the need to determine or deduce an internal volume term which was essential to the Peters–Speakman model. In essence, the Polyelectrolyte theory falls between the Gilbert–Rideal and Peters–Speakman models in that the adsorption of anions on to specific sites which the former postulates and the latter denies, is regarded as occurring to some degree in the Mathieson–Whewell model. Although the model was used to interpret the titration of nylon 6.6 fibres and nylon 6 resins with HCl [189], for which pK values of 4.3 and 4.34–4.45 were obtained, respectively, no allowance was made either of unequal numbers of amino and carboxylic acid groups or of degradation of the substrates; as the theory resembled that of Peters' application of Donnan membrane theory [188], it provides no more reliable an interpretation of the titration curves than those described previously.

The theory devised by Myagkov and Pakshever [170] was developed from the titration of nylon 6 with various acids. According to this theory, which also involved the use of appropriate binding or dissociation constants and made no allowance either of unequal numbers of amino and carboxylic acid groups or of degradation of the substrate, only anions will interact with the amino groups in the substrate, by means of an ion-exchange mechanism, owing to the low extent of dissociation of the carboxylic acid groups.

MECHANISM OF ACID ADSORPTION. Thus, from the foregoing, it can be concluded that none of the theoretical treatments provide a thoroughly satisfactory interpretation of the acid and alkali titration curves of nylons, this being attributable to the lack of allowance made for degradation of the substrate and/or to flaws in the theories themselves. However, the Gilbert–Rideal and the various Donnan theoretical approaches do provide a reasonable interpretation of the effect of electrolyte on the titration curve. Despite these shortcomings, which, in the case of the Gilbert–Rideal theory prompted one pair of authors to conclude that it was *incorrect as a predictive model except in a very approximate sense* [181], many workers have sought to interpret the titration curves of nylon and to calculate acid dye affinity on nylon using the Gilbert–Rideal [168, 171, 173, 175, 179, 180, 185, 190] and Donnan models [170, 180, 185, 189].

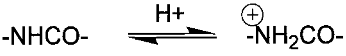
Thus, from the foregoing, it can be considered that at its isoelectric point, the nylon fibre exists as the *zwitterion* (i) [173, 191, 192]. However, as many commercial nylon fibres contain more carboxylic acid groups than amino end groups (Table 2.2), those carboxylic acid groups which are in excess of the number of terminal amino groups will be undissociated at the isoelectric point; if the fibre contained more amino end groups than carboxylic acid groups, the excess terminal amino groups would be capable of being protonated. Thus, although typically, nylon contains more carboxylic end groups than amino end groups, the number of ionised carboxyl groups present will be determined by the number of terminal amino groups present in the substrate.



$$H_3\overset{\oplus}{N}\text{-nylon-COO}^{\ominus} \overset{H+}{\rightleftharpoons} H_3\overset{\oplus}{N}\text{-nylon-COOH}$$

i ii

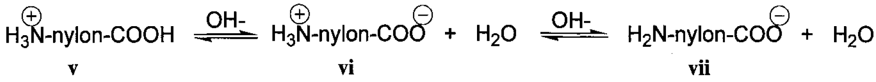
When acid is added, the protons are adsorbed on to the ionised carboxyl groups with the result that the fibre develops an overall positive charge (ii); the adsorption of acid and the consequent development of a positive charge within the fibre should continue until all the ionised carboxyl groups have been protonated. Since, as previously mentioned, the number of ionised carboxyl groups depends on the number of amino groups present, the extent of this protonation of the ionised carboxyl groups (i.e. the adsorption of acid by the substrate) should accord with the AEG content of the fibre, as has been approximately found [168, 169, 173]. However, several workers have observed that acid adsorption on to nylon 6 [193] and nylon 6.6 [171, 172] was less than that expected from the AEG content of the substrates, this having been attributed to obscuration of some of the terminal amino groups in the polymer and that modifications of the polymer structure can alter the extent of acid adsorption [172]. Thus, although the amount of acid bound should equate to the AEG content of the fibre and a limit should, therefore, be reached in terms of acid proton adsorption, the finding that, at low pH, the adsorption of acid does not reach a limit, but, instead increases continuously with decreasing pH [167–169,171, 172] has been attributed to protons being adsorbed on to chain amide groups (iii) under such strongly acidic conditions.



$$\text{-NHCO-} \overset{H+}{\rightleftharpoons} \text{-}\overset{\oplus}{N}H_2\text{CO-}$$

iii iv

As commercial nylons usually contain more carboxylic acid end groups than amino end groups when, to the fibre at its isoelectric point, is added alkali, protons are first removed from the excess undissociated carboxylic acid groups (v) [172, 175], this having been proven by the appearance, in the alkaline (NaOH) titration curve, of an inflection at a value of adsorbed alkali that corresponds to the value of the excess carboxylic acid groups in nylon 6.6 fibre [175].



$$\underset{\textbf{v}}{H_3\overset{\oplus}{N}\text{-nylon-COOH}} \overset{OH^-}{\rightleftharpoons} \underset{\textbf{vi}}{H_3\overset{\oplus}{N}\text{-nylon-CO}\overset{\ominus}{O}} + H_2O \overset{OH^-}{\rightleftharpoons} \underset{\textbf{vii}}{H_2N\text{-nylon-CO}\overset{\ominus}{O}} + H_2O$$

Once the excess undissociated carboxylic acid groups have been ionised, further addition of alkali removes protons from the protonated amino end groups of the zwitterion (vi) resulting in the substrate carrying a negative charge (vii), the amount of alkali adsorbed by the fibre reaching a maximum value that corresponds to the total carboxylic acid end group content of the substrate.

ADSORPTION OF DYE ANIONS. The equilibrium adsorption of acid dyes on nylon fibres as a function of pH closely resembles that of simple acids.

The findings of Peters [176], for the adsorption of several mono- and dibasic, purified and also commercial, non-metallised acid dyes on nylon 6.6 (Figure 2.6) revealed that, at high pH (e.g. 10), dye uptake was very low as the carboxylic acid groups were highly dissociated (vi) and the protonated amino end groups may be deprotonated (vii). As the pH decreased, dye adsorption increased markedly as the extent of dissociation of the carboxyl groups decreased and the amino end groups became protonated. Dye uptake continued to increase with decreasing pH until it reached an approximate constant value that extended over several units of pH (e.g. pH 3 to 7) at which stage the carboxylic acid groups are

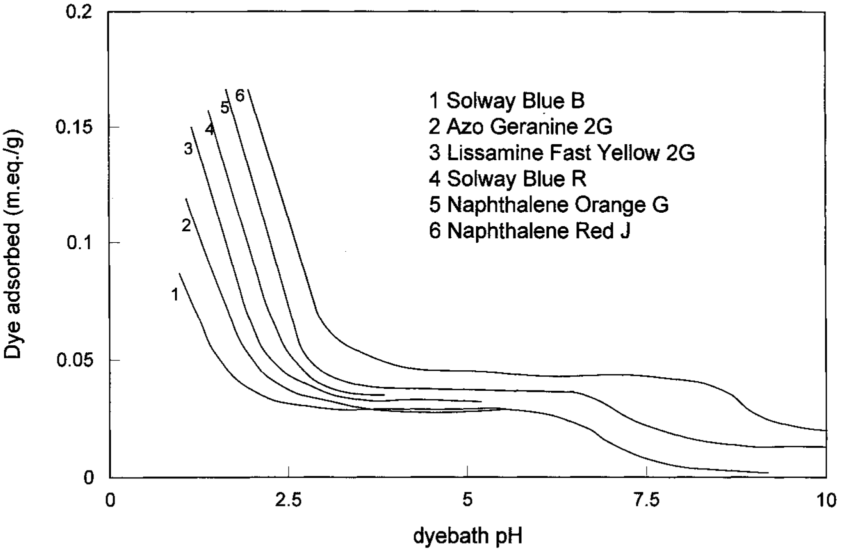


Figure 2.6 Adsorption isotherms of several non-metallised acid dyes on nylon 6.6 [176)]
(Reproduced with permission from R.H. Peters and the Society of Dyers and Colourists)

undissociated and the amino groups protonated (v); in this 'plateau' region, the breadth of which is dye-dependent, dye uptake corresponds to the AEG content of the substrate. Further reduction in pH resulted in a dramatic increase in dye uptake which continued to increase with decreasing pH without reaching a limiting value; this latter phenomenon, namely dye adsorption in excess of the AEG content of the fibre, is referred to as *overdyeing* and, although it has been attributed to dye adsorption on to the protonated chain amide groups of the fibre (iv), other theories of overdyeing have been proposed, as discussed below.

Thus, in essence, these findings imply that within the pH range 3 to 7, wherein acid dye uptake is insensitive to pH, the adsorption of non-metallised acid dyes on regular nylon fibres follows a Langmuir mechanism in which the anionic dye molecules are adsorbed on to the protonated amino end groups in the substrate. This, in turn, suggests that that a stoichiometric relationship should exist between AEG content and dye uptake; this has indeed been obtained, from which the mechanism of dye adsorption was proposed as being one of simple ion exchange [194]. However, several workers [23, 187, 190, 195–197] have observed deviation from this stoichiometry, such non-stoichiometry being related to the basicity of the dye anion, insofar as the uptake of monosulphonated dyes tends to be in excess of the AEG content whilst that of di- and trisulphonated dyes tends to be lower than the terminal amino group content [195, 199]. The lower saturation values achieved using di- and trisulphonated dyes has been attributed to the difficulty of such bulky dye molecules being accommodated at the terminal amine end group sites [190, 195]. Milicevic [200] demonstrated that dye uptake was not determined by the AEG content of the substrate insofar as when 32 different nylon substrates were dyed with the same monosulphonated non-metallised acid dye under identical conditions to 1/1 standard depth, although, as expected, different exhaustion values were obtained for each fibre, there was little correlation between dye uptake and AEG content for the 32 fibres considered. A dual-mode adsorption mechanism has been proposed for acid dyes on nylon [195, 201 207] comprising both a Langmuir or ion-exchange mechanism and a non-specific or Nernst mechanism. Holfeld and Shepard [51] consider that the initial adsorption, on to nylon, of *all* types of dye occurs by a non-ionic mechanism and that, subsequently, ionic dyes ion-exchange with the amino end groups. These workers likened the dyeing of nylon with acid dyes to a 'precipitation reaction' in which the dyed nylon was analogous to a 'precipitate' and that the key role of pH in this mechanism was to convert acid dyes to their non-ionic form which was insoluble in water but soluble in nylon.

MODELS OF DYE ANION ADSORPTION. McGregor and Harris [208] formulated a theoretical model for the equilibrium acid dyeing of nylon fibres based on the generalisation of the Donnan membrane theory, according to which the pH dependence of the sorption of acid dyes on nylon can be explained without invoking the concept of the dye anions binding to sites within the fibre; essentially, in this model, the driving force for dye uptake is the difference in electrical potential between the dye and the fibre. By modifying Guggenheim's expression for the distribution of an ion (i) between two phases (fibre (f) and solution (s)), these workers derived equation (2.7), which shows that the partition of the ion involves changes in chemical potential ($-\Delta\mu^0_i$), electrical potential ($z_iF\Delta\Psi$), internal pressure ($V_i\Delta P$) and activity coefficients (γ_i^f/γ_i^s) as well as a term (χ_i) that takes into account structural factors of the substrate.

$$\frac{C_i^f}{C_i^s} = \exp\left(\frac{-\Delta\mu^0_i + V_i\,\Delta P + z_iF\Delta\Psi + RT\ln(\gamma_i^f/\gamma_i^s) + RT\ln\chi_i}{RT}\right) \tag{2.7}$$

For simplicity, an apparent standard affinity ($-\Delta^*\mu^0_i$) and a partition coefficient K_i are defined as is a Donnan coefficient (λ), enabling equation (2.7) to be written in the simpler form of (2.11).

$$-\Delta^*\mu^0_i = -[\Delta\mu^0_i + V_i\Delta P + RT\ln\left(\frac{\gamma_i^f}{\gamma_i^s}\right) + RT\ln\chi_i] \tag{2.8}$$

$$K_i = \exp\left(\frac{-\Delta^*\mu^0_i}{RT}\right) \tag{2.9}$$

$$\lambda = \exp\left(\frac{-F\Delta\Psi}{RT}\right) \tag{2.10}$$

$$C_i^f = (\lambda_i)^z K_i C_i^s \tag{2.11}$$

In their model, these workers [208] identified two parameters which determined ion adsorption namely, the *valency* (z_i) and the *partition coefficient* (K_i) of the ion. The significance of valency arises from the electrical work term ($z_iF\Delta\Psi$), which, although experimentally immeasurable, is isolated as the Donnan coefficient (λ) in equation (2.10) and, from the term $(\lambda_i)^z$ in equation (2.11), it thus follows that the distribution of the ion between the two phases depends on the valency of the ion. The importance of the partition coefficient of the ion (K_i) stems from its relationship to the apparent standard affinity through equation (2.9), which, from equation (2.8), reveals that K_i represents all factors other than electrical potential difference that contribute to adsorption. According to this model, the acidic and basic groups in the fibre take part in an internal acid–base dissociation equilibria from which the condition for electrical neutrality in the fibre takes the form of equation (2.12) where the subscript 1 ($i = 1$) represents the H^+ ion, A_j is the concentration of the jth acidic group in the fibre, K_{Aj} the dissociation constant of the jth acidic group, B_k the concentration of the *k*th basic group in the fibre and K_{B_k} the dissociation constant of the *k*th basic group.

$$f(\lambda) = \sum_i z_i \lambda^{z_i} K_i C_i^s + \sum_j \frac{\lambda K_1 C_1{}^s A_j}{\lambda K_1 C_1{}^s + K_{Aj}} - \sum_k \frac{K_{B_k} B_k}{K_{B_k} + \lambda K_1 C_1{}^s} = 0 \qquad (2.12)$$

To use this model, numerical values are required for z_i, K_i, A_j, K_{Aj}, B_k and K_{B_k} as well as C_i^s, equation (2.12) must be for the unknown parameter λ and equation (2.11) used to calculate C_i^f. This procedure must be repeated for each change in C_i^s or in any of the parameters in equation (2.12).

Using this model, McGregor and Harris [208] were able to demonstrate, theoretically, the pH dependence of uptake of a monosulphonated dye of varying ‘affinity’ (of *K* values 1, 10, 100 1000 and 10 000) on to a substrate of equal amino end and carboxylic acid end group content (40×10^{-3} m-eq. kg^{-1}) as well as the variation of dye uptake as a function of AEG content (0–200 m-eq. kg^{-1}) at different pH values. These theoretical predictions showed that the shape of the adsorption curves obtained at each of the different *K* values closely resembled that secured for the adsorption of ‘real’ dyes on nylon [176]. The finding that the predicted dye uptake was very high at high pH values was attributed to the high ionic strength of such dyebaths, this latter proposal having been experimentally verified using CI Direct Yellow 12 [208]. Qualitative confirmation of this particular theoretical model has been obtained by Ulery [209] for the adsorption of cationic dyes on the aromatic polyamide, *Nomex*.

2.2.2.1.4. Overdyeing. As discussed above, in the ‘plateau’ region of a plot of dye uptake versus pH (Figure 2.6), which extends over several units of pH (e.g. from pH 3 to 7), dye uptake corresponds approximately to the AEG content of the substrate. Further reduction in pH results in a dramatic increase in dye uptake which continues to increase with decreasing pH, without reaching a limit. This particular phenomenon, namely dye adsorption in excess of the AEG content of the fibre, is referred to as *overdyeing*. Several explanations of this phenomenon have been offered as follows.

It has been considered [39] that at low pH values, overdyeing is attributable to dye being adsorbed on to new amino end groups that were generated by the acid hydrolysis of the chain amide groups; these workers [39] also suggested that such hydrolysis was dye-catalysed, this latter view having gained support from other workers [37–42]. Brody [210] suggested that acid dyes were adsorbed within voids caused by chain folding and that during overdyeing, hydrolysis of polymer chains that bordered these voids provided additional ‘free volume’ for dye adsorption to occur. Valk *et al.* [211] employed an ion-exchange method to determine the AEG content of nylon 6 and showed that the AEG content of the fibre increased as a result of dyeing with several non-metallised acid dyes, the extent of this increased AEG content being dye-dependent and related, in a linear manner, to the relative affinity of the dye. In later work Valk and Stein [212] demonstrated that the extent of fibre hydrolysis that occurred during dyeing depended on the dye, its concentration, as well as the pH and duration of dyeing and also dyebath additives; additionally, a non-linear relationship was obtained between the extent of fibre hydrolysis (AEG content increase) and the relative affinity of the various dyes used. However, Peters [176] and also O'Briain and Peters [213] proposed a converse mechanism. The latter workers [213] proposed that in the low pH region (pH $\approx$ 1.5), whilst dye uptake in excess of the AEG of nylon 6.6 yarn increased at a rate that paralleled that of the generation of new amino end groups formed by fibre hydrolysis, because the rate of increase in the extent of dye uptake was considerably greater than the rate at which new terminal amino groups were being generated, the dye was first adsorbed either as an anion on to the charged chain amide group ($-CON^+H_2-$) or as undissociated dye, this adsorption being followed by hydrolysis of the fibre. However, other workers [214] observed that the dye-catalysed hydrolysis of nylon 6 commenced prior to dye uptake. The concept that amide protonation can result in overdyeing has gained support from other workers [215].

However, as overdyeing is observed at pH values under which no protonation of the chain amide groups is possible [202, 204], it has been suggested that such overdyeing can arise from the high affinity of the dye anion [204, 208, 216, 217] or from the dye being adsorbed in its undissociated form [195, 201–204, 218]. In the context of overdyeing being dependent of the affinity of the dye anion, White [199] observed in the case of the titration of nylon 6 with a homologous series of mono-, di, tri- and tetrasulphonated naphthalene azo naphthol dyes, that over the pH range 2 to 6, the extent of overdyeing achieved increased in the order tri$<$di$<$monosulphonate and that the tetrasulphonated dye overdyed only at pH values of less than 3. Using White's data, Rattee and Breuer [181] proposed that two opposing factors contributed to dye adsorption in excess of the AEG content of the fibre namely, a gain in free energy ($-\Delta\mu^0$) which promotes dye adsorption and a gain in potential energy of the fibre surface (Π) which resists dye adsorption; the driving force for dye adsorption ($-\Delta\mu^{*0}$) is given by equation (2.13), from which when $-\Delta\mu^0 = \Pi$ no adsorption occurs.

$$-\Delta\mu^{*0} = -\Delta\mu^0 + \Pi \tag{2.13}$$

As Π is a function of z^2, where z is the valency of the dye anion, it follows that the propensity of an anionic dye to overdye will decrease with increasing valency of the dye anion and, therefore, dyes of low valency and thus high affinity will exhibit marked overdyeing tendencies, as indeed is found in practice [195, 199]. McGregor and Harris [208] consider that a dual sorption mechanism need not be invoked to explain overdyeing as, according to their theoretical model for the equilibrium acid dyeing of nylon fibres, overdyeing is explained purely in terms of the high tendency of dye anions to be adsorbed by the polymer matrix. Datyner *et al.* [219], from a study of the adsorption of two monoazo non-metallised acid dyes on nylon 6, concluded that overdyeing was due to adsorption of aggregates of the dye; similarly, Kraska and Blus [220], in a study of the dyeing of nylon 6 with fourteen monoazo non-metallised acid dyes, observed that when applied under identical conditions (pH 5), the equilibrium uptake of some of the dyes was in excess of the AEG content of the fibre whilst for other dyes, equilibrium uptake was below the AEG content. From the finding that those dyes which overdyed tended to be hydrophobic and of low water-solubility, these workers [220] argued that under the particular application conditions used (pH 5), the observed overdyeing was not due to hydrolysis of the fibre but, instead was attributable to adsorption of the dyes as aggregates.

2.2.2.1.5. Kinetics of dyeing. Peters *et al.* [66, 221, 222] showed that the diffusion of non-metallised acid dyes in nylon 6.6 film was markedly concentration–dependent in that sigmoidal concentration–distance profiles were obtained (Figure 2.7). Furthermore, Peters *et al.* [66, 222]

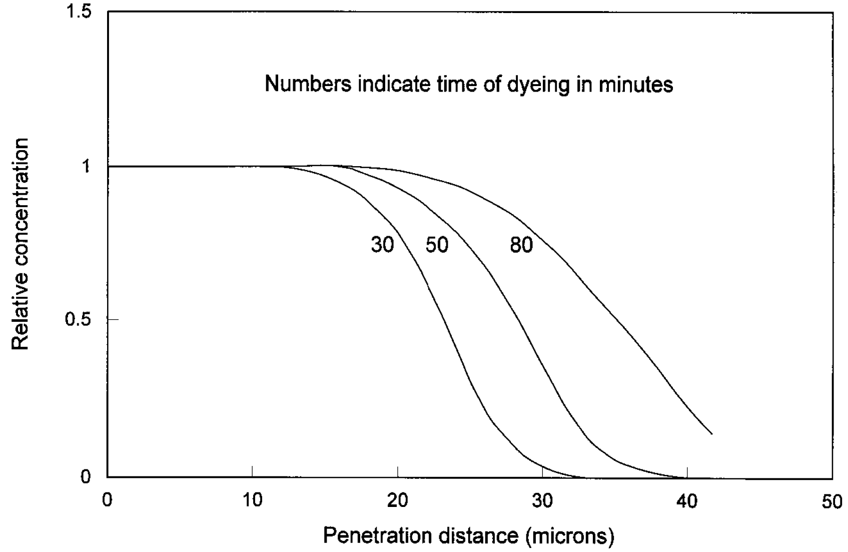


Figure 2.7 Concentration–distance profile for CI Acid Red 18 in nylon 6.6 film at pH 3.2 [222]

(Reproduced with permission from R.H. Peters and the Society of Dyers and Colourists)

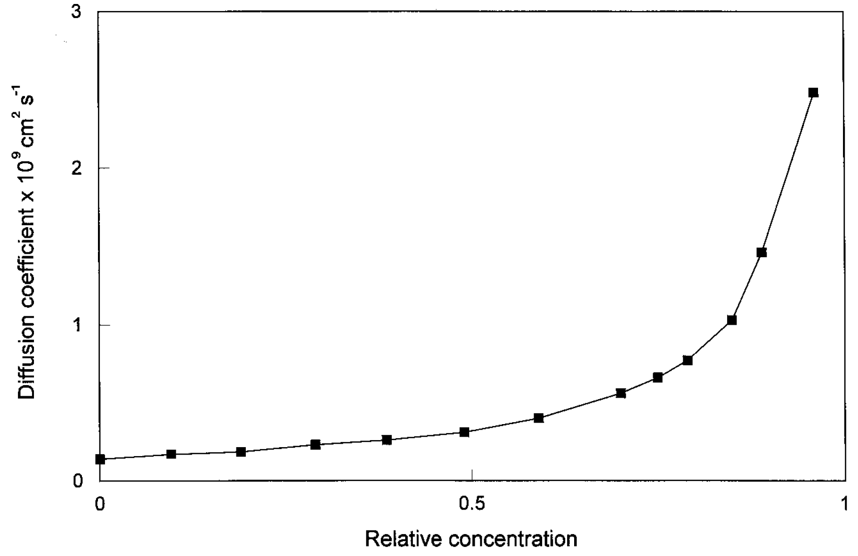


Figure 2.8 Relationship between diffusion coefficient and concentration for CI Acid Red 18 in nylon 6.6 film at pH 3.2 [222]
(Reproduced with permission from R.H. Peters and the Society of Dyers and Colourists)

demonstrated (Figure 2.8) that when CI Acid Red 18 was applied to nylon 6.6 film from a finite dyebath using conditions (pH 3.2) under which the surface was saturated with dye, the real diffusion coefficient ($D(c)$) of the trisulphonated dye increased with increasing dye concentration and, at dye concentrations close to saturation, the value of $D(c)$ increased sharply. Such concentration–dependence of acid dye diffusion has been confirmed by many workers.

As previouly discussed, since many workers have shown that a close correlation exists between the extent of acid dye uptake and the AEG content of nylon fibre, the observed concentration–dependence of acid dye diffusion can be explained in terms of the nature of the interaction between the anionic dye and the protonated terminal amino groups in the substrate. At the start of dyeing, when there are many available dye sites within the substrate and the dye concentration gradient across the substrate is very high, dye uptake on to the surface of the substrate will be rapid. In order for subsequent dye adsorption to proceed, either adsorbed dye molecules must desorb from their original position and become re-adsorbed on to other sites further within the substrate, or new dye molecules must penetrate the dyed surface to become adsorbed at sites further within the substrate. Such a process will depend on the affinity of the dye, the concentration gradient across the substrate, the availability/accessibility of dye sites within the substrate as well as the number of adsorbed dye molecules. During the early stages of dyeing, the dye concentration gradient across the substrate is high and the number of available dye sites within the substrate is also high, with the effect that a large proportion of the diffusing dye molecules become readily adsorbed and therefore immobile so that the rate of dye diffusion and thus *D(c)* will be low; such a situation is reflected in the well-known high strike exhibited by many acid dyes on nylon fibres. As dyeing proceeds, although the dye concentration gradient falls, as does the number of available dye sites, the proportion of the diffusing molecules that are immobile decreases, with the result that, in the later stages of dyeing, as saturation of the substrate is approached, the diffusion coefficient increases markedly, as was observed by Peters *et al.* [66, 222] (Figure 2.8). The importance of AEG content on dye diffusion was further demonstrated by the findings [223] that the rate of dyeing of nylon 6.6 yarn with non-metallised acid dyes was proportional to the AEG content of the fibre and that the rate of dyeing was zero for yarn of zero AEG content.

Peters *et al.* [66] also found that the concentration–distance profiles became less sigmoidal in the cases of both CI Acid Red 18 and CI Acid Red 8 as the pH of application was increased (Figure 2.9) and, in the case of CI Acid Red 18, in the presence of increasing amounts of electrolyte (NaCl) (Figure 2.10). Bell [223] also observed that the presence of NaCl

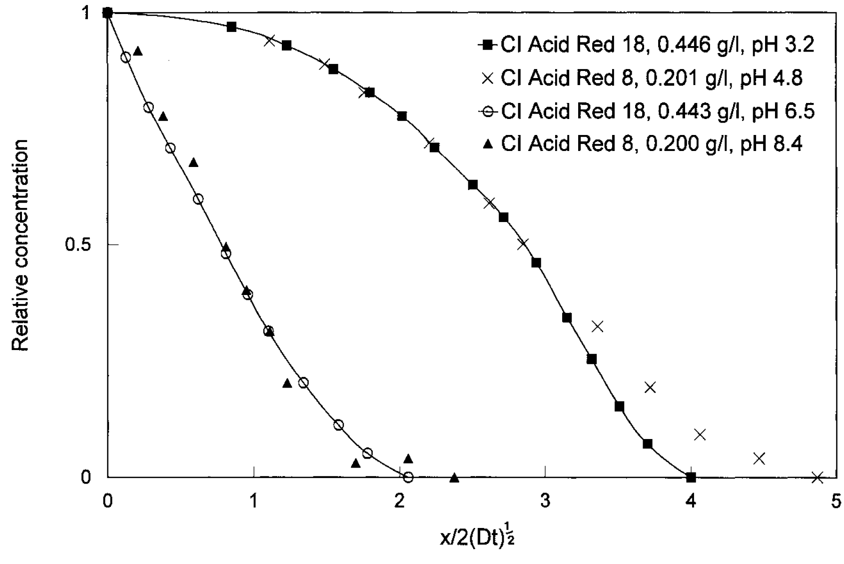


Figure 2.9 Relative concentration versus $x/2(Dt)^{1/2}$ for two acid dyes applied to nylon 6.6 film under different conditions [66]
(Reproduced with permission from R.H. Peters and the Society of Dyers and Colourists)

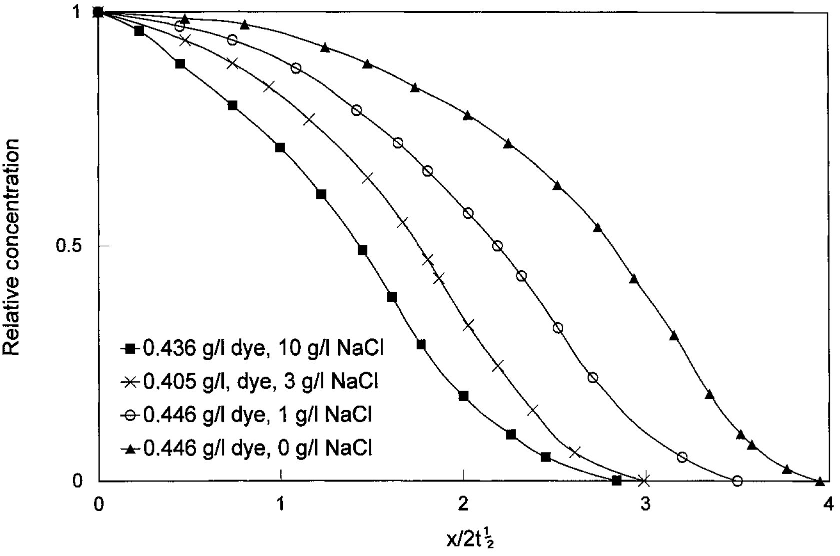


Figure 2.10 Relative concentration versus $x/2(Dt)^{1/2}$ for CI Acid Red 18 applied to nylon 6.6 film at pH 3.2 at different NaCl concentrations [66]
(Reproduced with permission from R.H. Peters and the Society of Dyers and Colourists)

and Na_2SO_4 decreased both the rate of diffusion and the saturation uptake of acid dyes on nylon 6.6 yarns. As each of these effects, namely an increase in dyeing pH and addition of electrolyte, serve to decrease the concentration of dye adsorbed by the fibre, the diffusional behaviour of the dye becomes more Fickian (i.e. $D(c)$ becomes less concentration-dependent). Furthermore, at low pH (1.95), under which conditions, overdyeing is achieved, the concentration–dependence of diffusion of CI Acid Red 18 was reduced in that the variation of $D(c)$ with dye concentration was more gradual [179]. Indeed, several workers have found that during overdyeing, the diffusion coefficient of acid dyes is constant [179, 182, 202], such Fickian diffusional behaviour gaining support from the linear adsorption isotherm observed for acid dyes in the overdyeing region [195].

It was shown [66] that when the same acid dye was applied under identical conditions to different types of nylon film, the rate of dye diffusion differed for each film; furthermore, the diffusion of non-metallised acid dyes in both nylon 6 and 6.6 yarns was found to be related to the time-dependent mechanical properties of the fibres [224]. However, it has been proposed [66, 179] that the diffusion coefficient of acid dyes is determined by the mechanism of dye adsorption rather than fibre structure, although this applies to substrates that are homogeneous in relation to diffusion. It has also been shown [66] that the concentration–distance profiles obtained for a monosulphonated acid dye and a trisulphonated acid dye were independent of dye basicity, insofar as, when made to coincide at $C = 0.5$ (i.e. for the same level of surface saturation), the shapes of the profiles were similar for the two dyes under both acidic and alkaline pH values.

Such non-Fickian diffusional behaviour of acid dyes in nylon is very similar to that found for the diffusion of cationic dyes in acrylic fibres. However, as pointed out by Jones [225], the kinetic behaviour of cationic dyes in acrylic is also temperature-dependent as the T_g of the fibre lies within the practical dyeing temperature range.

The data obtained for the diffusion of acid dyes in nylon has been analysed in terms of the *porous matrix* model of dye diffusion within textiles [168, 179, 181, 182], namely that the nylon substrate is considered to comprise water-filled *pores* in which dye diffusion occurs. Several models have been devised to describe the mechanism of dye transport within the pores [66, 206, 226, 227].

UNIMODAL ADSORPTION. According to Hopper *et al.* [66], the dye anions are adsorbed on to dye sites on the pore walls whilst the inorganic ions, owing to their negligible substantivity towards the substrate, are considered to be dissolved in the pore liquid. Within the pores, the adsorption of the dye anions is described as occurring via a Langmuir mechanism such that the variation of the real (measured) diffusion coefficient, $D(c)$, with dye concentration, C, is expressed by equation (2.14), where θ is the fractional site saturation and $D_0 = D(c)_o$ which represents the influence of polymer structure on diffusion.

$$D(c) = \frac{D_o}{(1-\theta)^2} \tag{2.14}$$

Alternatively, rather than using concentration gradient as the driving force for diffusion as in equation (2.14), either activity gradient or chemical potential gradient can be used [228], according to which, equations (2.14) and (2.16), respectively, are obtained for the concentration–dependent diffusion, the activity of the dye in the substrate (a_D) being given by equation (2.15) [229, 230] in which z is the basicity of the dye anion.

$$a_D = \frac{1}{z}\frac{\theta}{(1-\theta)} \tag{2.15}$$

$$D(c) = \frac{D_0}{(1-\theta)} \tag{2.16}$$

Thus, equations (2.14) and (2.16) show that the diffusion coefficient $D(c)$ depends on the fractional site saturation (θ) namely, the concentration of dye relative to the maximum amount of dye that can be adsorbed by the substrate. However, whilst neither equation (2.14) nor (2.16) gave an exact representation of the experimentally determined variation of $D(c)$ with relative dye concentration for CI Acid Red 18 in nylon 6.6 film [179], it was concluded that the variation of $D(c)$ with θ was better explained using the activity gradient model (equation (2.14)); this view has been confirmed by other workers [231, 232]. As all the amino end groups in the substrate may not be accessible to the dye, improved agreement between experimentally obtained results and theory should be obtained [66, 179] when the fractional site saturation term θ in equations (2.14) and (2.16) is replaced by $\alpha\theta$, where $\alpha = C_\infty$, C_∞ being the equilibrium dye uptake [66, 179]. This results in equations (2.17) and (2.18).

$$D(c) = \frac{D_0}{(1 - \alpha\theta)^2} \tag{2.17}$$

$$D(c) = \frac{D_0}{(1 - \alpha\theta)} \tag{2.18}$$

However, Peters *et al.* [66] argued that an electrical potential gradient is established when the dye anion $({}_{\mathrm{D}})$ exchanges with the chloride ion $({}_{\mathrm{Cl}})$ or $\mathrm{HCOO^-}$ ions inside the substrate and, in the case of $\mathrm{Cl^-}$, derived equation (2.19), where $\alpha_1 = 1 - (zD_{\mathrm{o,D}}/D_{\mathrm{o,Cl}})$.

$$D(c) = D_{\mathrm{o,D}} \frac{1 + (z\text{-}1)\theta}{1 - \alpha_1\theta} \tag{2.19}$$

An analysis of the diffusion data obtained for a monosulphonated and a trisulphonated dye using equations (2.17), (2.18) and (2.19) revealed that equation (2.19) offered the most satisfactory explanation of the practical data.

MULTIMODAL ADSORPTION. Based on the proposal of Back and Zollinger [201] that the adsorption of a 1:2 metal-complex dye on nylon occurred by two mechanisms, namely, uptake on to amino end groups and a 'solution' mechanism, as well as the findings [233, 234] that, with some acid dyes on nylon, maxima were obtained in the variation of diffusion coefficient with dye concentration near to the stoichiometric uptake of the dye on to the amino end groups, Komiyama and Iijima [205] suggested that the concentration–dependence of acid dye diffusion could be explained by considering that the dye was present in the polymer as two thermodynamically distinct states, namely *adsorbed* and *dissolved* dye, in equilibrium (this having an equilibrium constant, K), the adsorption of which were described by Langmuir and Nernst mechanisms, respectively. These workers [205] developed equation (2.20) to describe this bimodal adsorption mechanism wherein K_{P} is the partition coefficient of the 'dissolved' dye molecules, K_{L} the Langmuir sorption constant, and S the saturation value (assumed to be equal to the AEG content) of the fibre.

Equation (2.20) can also be expressed in the form of equation (2.21) in terms of the fractional saturation, θ, where $\theta = zC_L/S$ and $K = K_L/K_P$.

$$C_f = K_P C_s + \frac{K_L S C_s}{z(1 + K_L C_s)} \tag{2.20}$$

$$C_f = \frac{\theta}{K(1-\theta)} + \frac{S\theta}{z} \tag{2.21}$$

In their study of the diffusional behaviour of both a monosulphonated non-metallised acid and a monosulphonated 1:2 pre-metallised acid dye within nylon 6 film, these workers [205] derived equation (2.22) (wherein $\alpha = KS$), which explained their experimental finding that the diffusion coefficient of the monosulphonated dyes reached a maximum value at a dye concentration in the fibre that was near to the stoichiometric AEG content of the nylon 6 film employed. The $D_L{}^0$ and $D_P{}^0$ terms in equation (2.22) represent the the contributions of the respective species to the apparent diffusion coefficient ($D(c)$).

$$D(c) = RT\left[D_L{}^0 \frac{\alpha(1-\theta)}{\alpha(1-\theta)^2 + 1} + D_P{}^0 \frac{1}{\alpha(1-\theta)^2 + 1}\right] \tag{2.22}$$

Figure 2.11 shows the results of the application of equation (2.22) to the diffusion of CI Acid Orange 7 in nylon 6 film, from which it is evident that the diffusion coefficient ascends slowly at first and then steeply with

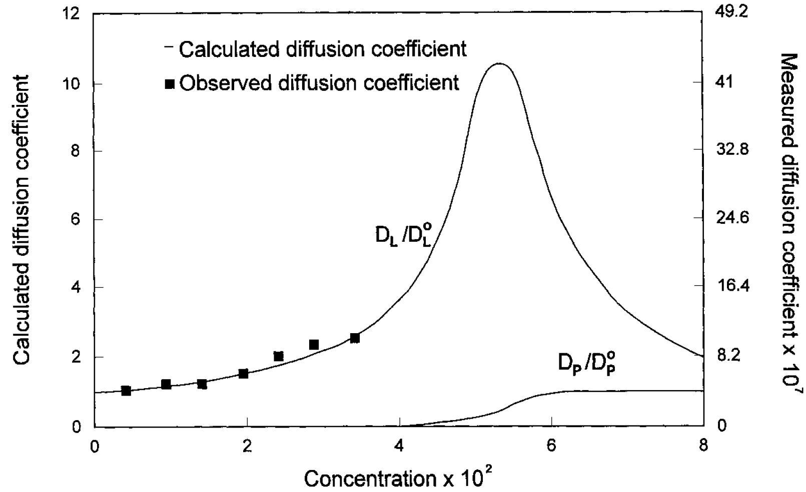


Figure 2.11 Relative diffusivity versus dye concentration for CI Acid Orange 7 in nylon 6 film of AEG content 4.447 × 10^{-5} eq. g^{-1} [205]

(Reproduced with permission from T. Iijima. Copyright © 1974 John Wiley & Sons, Inc. Reprinted by permission) increasing saturation of the amino end groups, reaching a maximum that is in approximate accordance with the stoichiometric AEG content. The diffusivity of the adsorbed species, L, is of primary significance in determining this concentration–dependence of diffusion coefficient. However, at saturation values in excess of the AEG content, the diffusivity of the dissolved species becomes substantial.

This particular approach has been further developed and applied to describe the diffusion of disulphonated direct dyes [235] as well as that of a series of mono-, di- and trisulphonated non-metallised acid dyes [206] in nylon 6. In the latter study [206], Tak *et al.* showed that the apparent diffusion coefficient of the three monoazo dyes used, decreased with increasing degree of sulphonation, this being attributed to the corresponding increase in both the molecular volume of the dye and the extent of ion–ion interaction operating between the dye and the protonated amine groups in the fibre that accompanied an increase in degree of sulphonation. Also, for each of the three dyes, a plot of diffusion coefficient as a function of dye concentration revealed that the diffusion coefficient increased with increasing dye concentration, reaching a maximum value which was almost in accordance with the AEG content of the substrate [206]. As Table 2.5 shows, in the context of the dual sorption and diffusion model, it was shown that, as might be expected, the (Nernst) partition coefficient, K_P, decreased whilst the Langmuir type sorption constant, K_L, increased with increasing degree of sulphonation (i.e. increasing z) [206].

In later work [207] it was demonstrated that the sorption and diffusion behaviour of the trisulphonated monoazo dye previously studied [206] in the presence of NaCl was adequately described using the bimodal model.

Sada *et al.* [227] considered that the concentration-dependence of acid dye diffusion in nylon could be satisfactorily interpreted by a mechanism of parallel transport, namely that the dye molecules diffuse, in a parallel manner, within and along the pores, this being accompanied by simultaneous multimodal Langmuir adsorption. By utilising existing experimental data for the diffusion of various acid dyes in nylon [231, 236, 237] these workers [227] concluded that the concentration-dependence of acid dyes on nylon could be explained in terms of the proposed parallel transport,

Table 2.5 Parameters for polybasic acid dye diffusion in nylon 6 film [206]

Dye	z	K_L ($l\ mol^{-1}$)	K_P ($l\ g^{-1}$)	S (eq. g^{-1})	α
CI Acid Orange 7	1	6.4×10^5	0.160	3.72×10^{-5}	150
CI Food Yellow 3	2	1.1×10^5	0.024	3.61×10^{-5}	1650
Sulphanilic acid ∞ R acid	3	2.0×10^5	0.013	3.71×10^{-5}	5700

(Reproduced with permission from T. Ijima and the Society of Fiber Science and Technology of Japan) accompanied by bimodal Langmuir adsorption, the latter taking into account one type of dye site being physically more active than the other type. In other work [238], these authors sought to interpret the concentration-dependent diffusion of CI Acid Blue 182 in nylon 6 film in terms of surface diffusion (along the pores) incorporating one Nernst-type and two Langmuir-type adsorption mechanisms; whilst the particular diffusion model satisfactorily described the concentration-dependence at low dye concentrations, it was not satisfactory at high concentrations. Subsequently, it was shown [239] that at high dye concentrations, true adsorption equilibrium was not instantaneously established throughout the nylon 6 film, but rather, that under the dyeing conditions used (80°C; pH 2.1), although a quasi-equilibrium was attained after some 2 hours, true equilibrium was established only after 30 hours or more. From this, it was concluded that the substrate comprised two regions, one region being available for rapid dye penetration and the other region, which is connected to the first and formed by the slow relaxation of the polymer, being of poor penetration. In the latter context, these authors subsequently argued [240] that when dye molecules penetrate the film, the substrate must undergo structural rearrangement to accommodate the adsorbed dye molecules. As, during this process, the polymer segments must move, not only because of the presence of the dye molecules but also because of the movement of adjacent polymer segments, this structural rearrangement cannot be simultaneous and must therefore be gradual. Evidence was presented which showed that such relaxation of the polymer structure increased only the amount of dye adsorbed by the Nernst mechanism and did not alter that due to the bimodal Langmuir adsorption. Consequently, it was proposed that, at high dye concentrations, the concentration-dependent diffusion of CI Acid Blue 182 in nylon 6 film can be described in terms of surface diffusion incorporating two Langmuir-type adsorption mechanisms and one pseudo-Nernst-type mechanism [240].

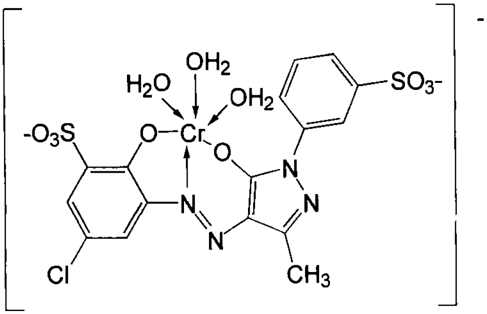
The proposal of Sada *et al.* [239, 240] that the substrate comprised two regions, one available for rapid dye penetration and the other connected region which is formed by the slow relaxation of the polymer and of poor penetration, may be of relevance to the previously discussed radial non-uniformity of nylon fibres. Indeed, in their review of this particular topic, Duscheva *et al.* [67] propose that the rate of dyeing of nylon fibres with acid dyes is not controlled solely by dye diffusion but, instead, is determined by sorption in a specific stage of the dyeing process and by diffusion in another stage.

2.2.2.2. Pre-metallised acid dyes. This type of dye, which was commercially introduced in 1919, was developed to overcome the disadvantages associated with the use of mordant dyes on wool [77]. As the chemistry of this dye type has been comprehensively discussed by several workers

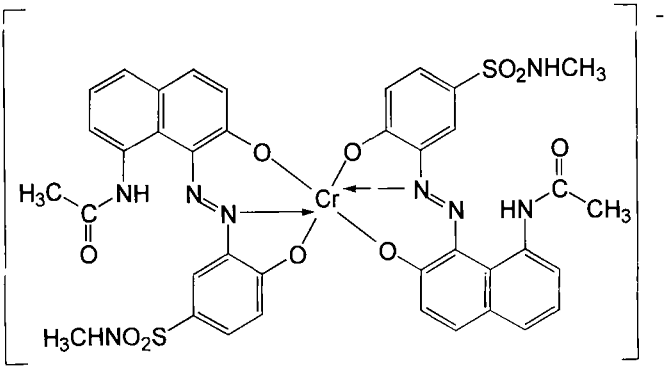
[77, 241–244] the following serves only as a brief account. As their name implies, such *metal-complex* dyes comprise one metal atom (usually chromium although cobalt is also employed) which is complexed with either one or two molecules of a dye ligand. Thus, both 1:1 (CI Acid Red 183 (IV)) and 1:2 (CI Acid Black 60 (V) and CI Acid Orange 148 (VI)) pre-metallised acid dyes are available; three types of 1:2 dyes are marketed, namely *weakly polar* (V), *disulphonated strongly polar* (VI) and *monosulphonated strongly polar* [77]. Commonly, tridentate, bicyclically metallisable monoazo dye ligands are used in such dyes [57] although other dye ligands have been described [241, 242, 244, 245]; whilst many transition-metals ions form complexes with such metallisable dye ligands, Co^{3+} and especially Cr^{3+} are most widely employed owing to the superior stability of the ensuing complexes [77].

GENERAL APPLICATION PROPERTIES. Only selected 1:1 pre-metallised acid dyes are employed on nylon owing to the generally low saturation values achieved [96]; also, the dyes exhibit only low to moderate coverage of fibre irregularities and poor compatibility in admixture [24]. The low pH (≈ 2) which can be used for the application of these types of dye to wool [72] cannot be employed for nylon owing to the fibre's marked acid sensitivity and thus higher pH values (4–6) are used in conjunction with a, typically, weakly cationic levelling agent [24]. Generally, selected dyes provide a wide range of moderately bright shades of good wet fastness and very good light fastness. No aftertreatment with syntans or the full backtan is given so as not to impair the brightness of the dyeings [24]. Dyeing is commonly carried out at 98°C although elevated temperatures (105–110°C) can be employed [246].

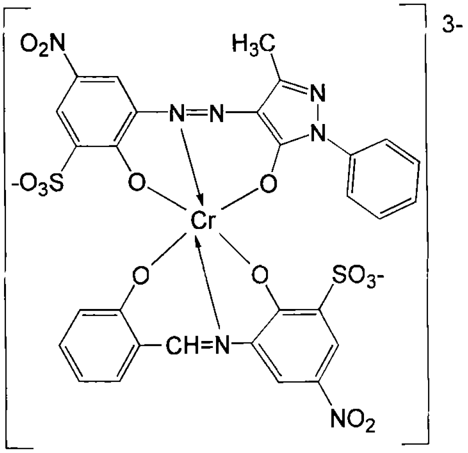
In contrast to their 1:1 pre-metallised acid counterparts, 1:2 metal-complex dyes display high build-up on nylon and excellent compatibility in admixture. They yield rather dull dyeings of very good light and wet fastness on polyamide fibres but, owing to their large M_r and high substantivity, tend to accentuate physical irregularities in the substrate, although this latter aspect varies according to the type of 1:2 dye used [24] and can be minimised by recourse to elevated temperatures and the use of dyeing auxiliaries. Typically, unsulphonated types are applied at pH 6–8 using $(NH_4)_2SO_4$ in the presence of a weakly cationic levelling agent at temperatures, depending on the substrate, of up to 130°C; pretreatment prior to dyeing with an anionic blocking agent can be employed to expedite coverage of barré. Monosulphonated dyes are applied, typically, at pH 5 to 6.5 (the lower pH value being for pale shades and the latter value for deep shades) using NH_4COOCH_3/CH_3COOH at temperatures of between 95 and 120°C in the presence of a weakly cationic levelling agent. An aftertreatment, with a syntan or the full backtan, can be used to improve the wet fastness properties of the dyeings on nylon [24, 96].


-
H_2O
OH_2
OH_2
SO_3^-
^-O_3S
O
Cr
O
N
N
N
N
Cl
CH_3

IV


-
SO_2NHCH_3
O
O
O
Cr
H_3C
C
NH
N
N
N
N
HN
C
CH_3
O
O
O
H_3CHNO_2S

V

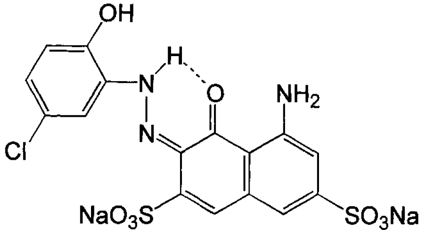

3-
O_2N
H_3C
N=N
N
N
^-O_3S
O
O
Cr
O
O
SO_3^-
CH=N
NO_2

VI

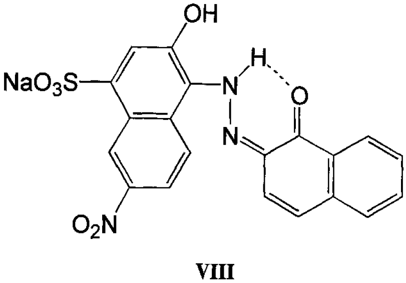
DYE ADSORPTION. Relatively few publications have attended the dyeing of nylon with pre-metallised acid dyes; Back and Zollinger [247] found that the equilibrium uptake of an unsulphonated 1:2 Cr complex onto nylon 6 at pH 7 was in excess of the AEG content of the fibre and also that the dye was adsorbed on to nylon 6 which had been acetylated from which it was concluded that the dye was adsorbed by means of both a Langmuir (electrostatic) and a 'solution' mechanism. In later work [248], using 1:2 metal-complex dyes of varying hydrophobicity, these workers proposed that the hydrophilic dyes were adsorbed on to nylon 6.6 by virtue of interaction with the amino end groups of the substrate whereas the more hydrophobic dyes were adsorbed by a solution mechanism. Hauss [249] observed that the adsorption of monosulphonated 1 : 2 dyes on nylon was pH dependent in that dye uptake increased with decreasing pH and dye exhaustion was greatest in the range pH 4–7 with pH 5 being the optimum pH for application.

2.2.3. *Mordant dyes*

The practice of pretreating textiles with mordants (salts of various metals or tannins) so as to secure dyeings of increased depth of shade and/or improved colour fastness or different hues was reported by Pliny in the first century AD [250]. In the *Colour Index* [71], the term *mordant dye* applies specifically to those dyes which are applied in conjunction with a metallic mordant. In this context, the term *mordant dye* does not apply to



VII



VIII

(a) basic dyes which are applied in conjunction with a tannin to cellulosic fibres, (b) dyes (usually direct dyes) which are applied to cellulosic fibres and are aftertreated with a metallic salt, or (c) to dyes which, although containing metallisable groups, are not metallised *in situ* on the substrate. Nowadays, chromium salts are predominantly employed as mordants, as a consequence of which, the term *chrome dye* is often incorrectly used.

In essence, the majority of mordant dyes resemble non-metallised acid dyes in that they carry sulphonate and/or carboxylic acid groups and are therefore anionic. However, mordant dyes contain ligands (e.g., OH, NH_2, COOH) which enables them to form a stable, coordination complex with the chromium ion *in situ* within the fibre, the formation of which is usually accompanied by a marked increase in the wet and light fastness of the dyeing and an often dramatic change in the hue of the dyeing [72, 77]. On wool, for which the dyes were developed, three methods can be used for their application, namely *pre-chrome*, *metachrome* and *afterchrome*, depending on whether the mordant (commonly $Na_2Cr_2O_7$ or $K_2Cr_2O_7$ although $NaCrO_4$ and $KCrO_4$ are also used) is applied *before*, *during* or *after* the dye. In the case of nylon, the *afterchrome* dyeing method is predominantly used. The generally very low fastness properties of unmordanted dyeings negates the use of mordant dyes as acid dyes *per se* [72]. Of the various chemical classes of mordant dye available [72], anthraquinone [251] and azo [252] (mostly monoazo) types predominate, as exemplified, for use on nylon [253], by CI Mordant Blue 13 (VII) and CI Mordant Black 11 (VIII), respectively. The dyes yield mostly dull shades of very good fastness to light and wet treatments and, whilst the dyes cover physical irregularities in the substrate well, they are sensitive to chemical variations.

DYE ADSORPTION. The dyeing of nylon with mordant dyes was investigated shortly after the introduction of the fibre [73, 74]. White [73] observed that both the pre-chrome and metachrome dyeing methods were unsuitable for the application of mordant dyes to nylon 6.6 owing to inadequate dye–chromium complex formation whilst the afterchrome method yielded dyeings of good fastness although the quantity of potassium dichromate required was greater than that employed for the application of the dyes to wool. Stott [74] confirmed White's observation that greater amounts of dichromate were needed for nylon 6.6 and that the duration of the chroming stage was longer than that used for the afterchrome dyeing of wool; Grundy [254] considered that the duration of the chroming stage was more important than the amount of dichromate employed. Stott [74] found that lower pH values than were used for wool were needed to promote adequate dye exhaustion and also that the attainment of deep shades was problematic owing to the low saturation value of the dyes on the substrate. In a study of the dyeing of nylon 6.6, Boulton [255] found that the metachrome and afterchrome dyeing methods yielded dyeings of similar wash fastness, that the light fastness of mordant dyes on nylon 6.6 was lower than comparable dyeings on wool and that the mordant dyes used accelerated the photodegradation of the fibre. Hadfield and Sharing [256], in an investigation of the dyeing of nylon 6.6 with mordant dyes by the pre-chrome, metachrome and afterchrome dyeing methods, concluded that the pre-chrome method was unsuitable as dichromate caused a loss in strength of the substrate (tenderisation) and insufficient dye–Cr complex formation occurred; also, the metachrome method was found to be unsuitable as, under the pH conditions employed, neither the dyes nor the dichromate possessed adequate substantivity towards the substrate. These workers [256] observed that the afterchrome dyeing method was most suitable, but suffered several disadvantages, namely that high concentrations of dichromate and low pH values were required, that complete dye–chromium complex formation was not achieved with all of the dyes studied and residual $K_2Cr_2O_7$, if not completely removed after the chroming stage, tenderised the fabric. It was found [256] that at pH 2.8 to 3, the equilibrium uptake of dichromate on to undyed nylon 6.6 corresponded to the AEG content of the fibre; the role of the amino end groups in uptake of the dichromate anions was further demonstrated by the finding that virtually no dichromate was adsorbed on to acetylated nylon 6.6. The uptake of dichromate onto nylon which had been dyed with 1% and also with 6% o.m.f. of three different mordant dyes revealed that the presence of the dyes reduced the rate of adsorption of dichromate but the extent of uptake of dichromate was greater than that on to undyed nylon 6.6; both the rate and extent of uptake of dichromate on to dyed nylon increased with increasing temperature. The finding, that uptake of dichromate on to dyed nylon was in excess of the AEG content of the fibre, was attributed [256] to the fact that as adsorption of the anionic Cr^{VI} occurred, simultaneous reduction of the adsorbed hexavalent anions to the cationic Cr^{III} form occurred within the fibre. As the Cr^{III} cations possess no affinity for the protonated terminal amino groups, they would be displaced by Cr_2O_7 anions, this exchange process being responsible for the observed uptake of dichromate ions in excess of the AEG content of the fibre. Hadfield and Sharing [256] concluded that, when compared with wool, the problems associated with the dyeing of nylon with mordant dyes were the lower number of sites within nylon for both dye anions and dichromate anions together with the fact that, unlike wool, nylon could not reduce Cr^{VI} to Cr^{III}. Thus, several reducing agents, namely sodium thiosulphate, sodium hyrosulphite as well as sodium sulphide were added to the chroming bath in order to achieve this necessary reduction of dichromate, as a result of which, dyeings of improved fastness were obtained [256] (Figure 2.12).

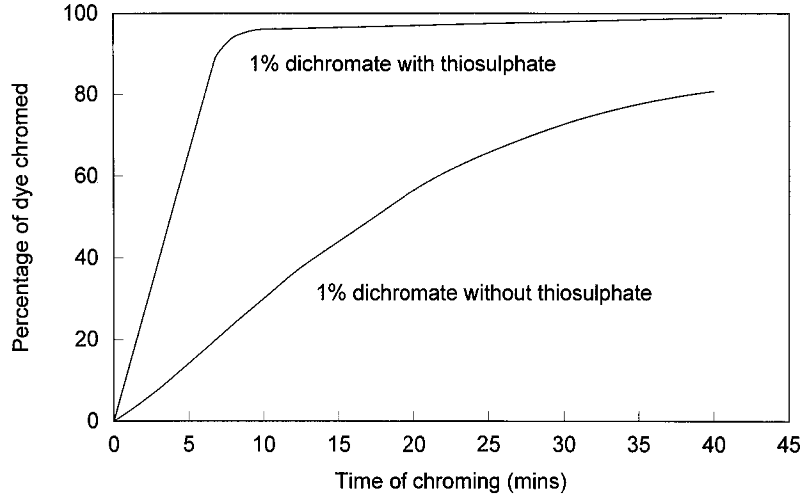


Figure 2.12 Effect of addition of sodium thiosulphate on the rate of chroming of CI Mordant Violet 8 on nylon 6.6 [256]
(Reproduced with permission from H.R. Hadfield and the Society of Dyers and Colourists)

As mentioned previously, whilst mordant dyes cover physical irregularities in the substrate well, they are sensitive to chemical variations. Hadfield and Seaman [257], in a study of the effect of temperature on the levelling of mordant dyes on nylon 6.6 when applied by the afterchrome dyeing method, showed that selected mordant dyes could be classified into three groups according to their suitability for use at 95 and 130°C. These workers [257] found that the dyes could be divided into those:

- suitable for application at both 95 and 130°C;
- suitable for application at 95°C only owing to dye decomposition at 130°C;
- suitable for application at 130°C only owing to incomplete dye–chromium complex formation.

Hadfield and Seaman [257] also observed that the rate of chroming at 130°C was faster than that at 95°C and that the addition of a reducing agent to the metallising bath was not required when afterchroming was carried out at 130°C. These workers [257] noted that although they had only used 130°C for both dyeing and afterchroming stages, lower temperatures, such as 110°C, might show advantages over 95°C.

Douglas [258] reported that copper complexes of mordant dyes, obtained using $NaCuCl_2$, exhibited higher light fastness but lower wet fastness on nylon 6.6 than their chromium complex counterparts and that cobalt complexes of the dyes displayed lower light fastness than the corresponding chromium complexes.

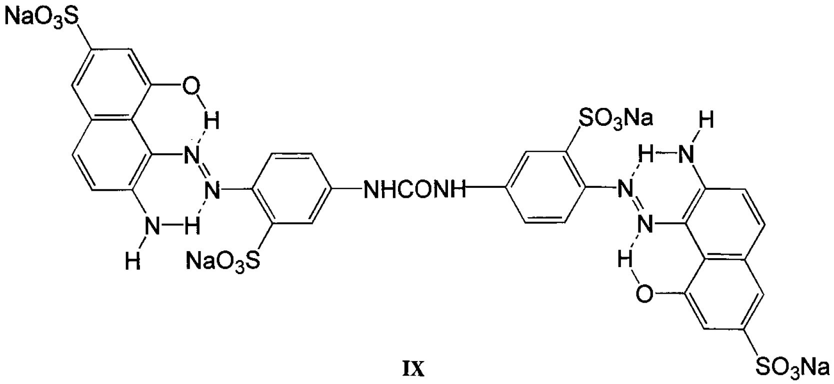
Several of the observations made by Hadfield and his coworkers [256, 257] are utilised in the current mordant dyeing of nylon; the afterchrome dyeing method is mostly used although the metachrome method is also employed [246], it is important to remove residual dichromate from the dyed material so as to avoid skin irritation [258] and to achieve high sublimation fastness of the dyeings [246], a reducing agent, sodium thiosulphate (at a concentration of four times that of dichromate) is included in the chroming bath and afterchroming is commonly carried out at between 95 and 110°C [24]. However, mordant dyed polyamide exhibits a harsh handle owing to oxidative degradation of the fibre and unlevel dyeings cannot easily be overcome [246]; also, the shade of some mordant dyes is affected by traces of other metals, such as Fe and Cu in the dyebath.

Owing to environmental concerns that attend the use of chromium salts together with the difficulties inherent in colour matching afterchrome dyeings, the use of this dye class on nylon is nowadays mainly restricted to the production of black shades and other specific end uses.

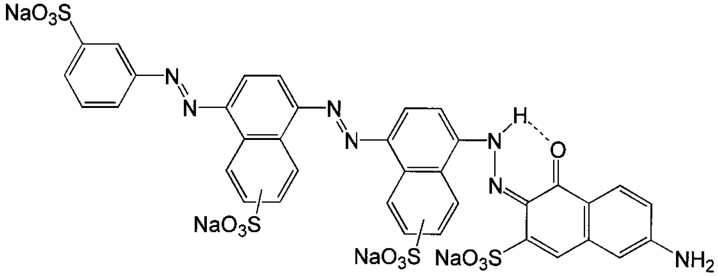
2.2.4. Direct dyes

Direct dyes, the first commercial example of which (CI Direct Red 28) was introduced in 1884 [72], are the second most popular class of dye used on cellulosic fibres. Chemically, the dyes belong to several classes [72], the most important being azo, the majority of which are of the disazo, trisazo and polyazo types although there are some monoazo representatives [252, 259]. The forces of interaction that operate between this class of dye and cellulosic fibres are predominantly van der Waals, resulting from the highly conjugated, linear and coplanar structure of the dyes; this particular structure of the dyes also results in the dyes exhibiting marked aggregation tendencies both in solution and within the substrate. In the case of the dyeing of cellulosic fibres, the dyes are divided into three classes, A, B and C, according to their sensitivity to salt (NaCl) [71, 260] which is necessary to promote dye–fibre substantivity [72, 79, 85].

In the case of nylon, only a small number of selected direct dyes are employed, such as CI Direct Red 75 (IX) and CI Direct Blue 74 (X), owing to their tendency to highlight physical irregularities and their sensitivity to chemical variations in the substrate as well as their generally low migration character on nylon fibres. The dyes are applied to nylon, often individually or in conjunction with a small proportion of shading acid dyes, under weakly acidic conditions (pH ≈ 5) [24], their dyeing behaviour closely resembling that of acid dyes. Using data obtained by Morita *et al.* [261] for the diffusion coefficients of direct dyes within nylon 6 when



IX



X

applied at pH 4.5, Komiyama *et al.* [235] demonstrated that the diffusional behaviour of the dyes was identical to that of acid dyes. The dyes yield economically attractive deep shades of good wet fastness and moderate to good light fastness; however, the wet fastness of the dyeings cannot be improved using the methods employed for the aftertreatment of the dyes on cellulosic fibres [96] although some improvement can be achieved by the use of an aftertreatment with a syntan or the full backtan.

DYE ADSORPTION. White [73] found that the substantivity of direct dyes towards nylon 6.6 varied from zero to high and that dyeings of adequate light and wash fastness could be achieved using selected dyes; however, diazotised and developed direct dyes were unsuitable for application to the fibre owing to only partial development being achievable. Stott [74] also found that the number of direct dyes that were suitable for nylon 6.6 was low and observed that acidic conditions increased the substantivity of the dyes towards the substrate. This latter observation was confirmed by both Whittaker [260] and Boulton [255], the latter worker also demonstrating that both the rate and extent of dye exhaustion were dependent on pH (Figure 2.13).

Whittaker [260] showed that the exhaustion of some direct dyes on nylon 6.6 was enhanced by treatment with various organic compounds,

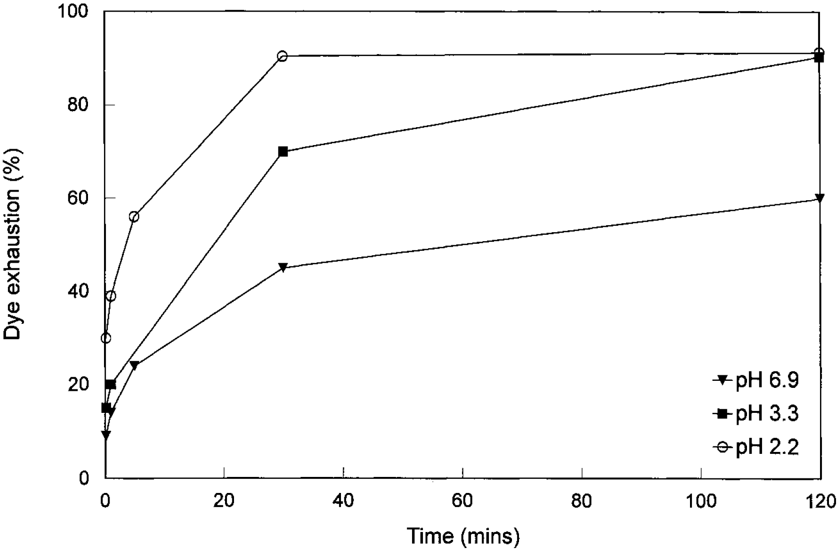


Figure 2.13 Effect of pH (potassium hydrogen phthalate – HCl/NaOH buffer) on uptake of 1% o.m.f. CI Direct Orange 23 on nylon 6.6 yarn [255]
(Reproduced with permission from J. Boulton and the Society of Dyers and Colourists)

notably 2-naphthol, the latter compound being effective when applied either as a pretreatment of the substrate prior to dyeing or when applied conjointly with the dye. Abdou and Bendak [262] observed that in the dyeing of nylon 6 with direct dyes, the addition of benzyl chloride to the dyebath increased both the colour yield of the dyeings and the rate of dye uptake, this being attributed to the benzyl chloride having plasticised the fibre. Whittaker found that pretreatment of nylon 6.6 with steam increased dye exhaustion as also did pretreatment with various metallic salts [260]. Boulton [255] showed that an increase in dyeing temperature increased the rate of dye uptake but reduced equilibrium dye uptake, and that both the rate and extent of dye uptake were increased or decreased by the addition of NaCl to the dyebath when dyeing was carried out under neutral or acidic pH conditions, respectively. Furthermore, some direct dyes were found to tenderise the fibre whereas others appeared to impart a protective effect towards photodegradation [255].

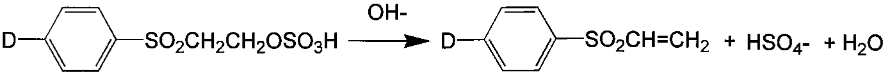
Grundy [263] observed that the levelling of direct dyes on nylon 6.6 was enhanced by the presence of soap in the dyebath. From the observation that cationic surfactants displayed high substantivity towards nylon fibres [264], MacGregor and Pugh [103] found that the presence of low concentrations of such agents (of at least C8) increased the rate of uptake of direct dyes on to nylon 6.6. Ryu *et al.* [265] reported that the colour yield of CI Direct Black 155 on nylon 6 fabric was enhanced by sputter etching the substrate using low-temperature argon plasma, this being attributed to a reduction in the reflection of incident light upon the fabric caused by the formation of microcraters within the substrate.

2.2.5. Reactive dyes

With regards the use of this dye type on nylon, a distinction can be made between *anionic* and *disperse* reactive dyes; this section is concerned with the former dye type.

Reactive dyes differ from all other classes of dye insofar as they can become covalently bound to nucleophiles in appropriate substrates. Although the first commercial reactive dye (CI Acid Orange 30) was introduced in 1932 for use on wool, the reactivity of the labile chlorine atom in the chloroacetylamino substituent of the dye and, thus, the ability of the dye to react with wool, was not at the time recognised [266]. Following the recognition that dyes could be covalently bound to wool [267] further developments resulted in the commercial launch of reactive dye ranges for wool in 1952 and 1954 and for cellulosic fibres in 1956 [268]. Thus far, whilst many ranges of reactive dye have been developed, each range differing from another in terms of the reactive group(s) employed, only one type of reactive dye, namely the *Procinyl* (ICI) range of disperse reactive dyes, discussed in section 2.4.1.3, has been marketed specifically for application to nylon fibres; all other reactive dye ranges have been developed for use on either wool or cellulosic fibres. On the latter two fibre types, reactive dyes have enjoyed much success and furnish a wide range of shades of very good to excellent wet and light fastness; in contrast, reactive dyes have not been successful on nylon fibres.

With very few exceptions, which includes non-ionic, disperse reactive dyes discussed below, reactive dyes are water-soluble and anionic, these characteristics being provided by the presence of one or more sulphonate groups in the chromogen. Although the vast majority of anionic reactive dyes are intended for use on wool and cellulosic fibres, some can also be applied to nylon. Typically, anionic reactive dyes are applied to nylon at 95°C in the presence of a weakly cationic levelling agent under acidic (pH 4–6) conditions [24, 269], this being necessary to achieve adequate substantivity of the anionic dyes for the protonated amino end groups in the fibre. However, such dyes are very sensitive to chemical and also physical variations in the substrate and, owing to their very low migrating power, careful control of dye exhaustion, usually by means of temperature, must be exercised [269]. A further major drawback to the use of anionic reactive dyes on nylon is that only pale to moderate depths of shade are obtained on regular nylon, although deeper shades are attainable on nylons of higher AEG content. Both monofunctional and bifunctional dyes can be used on nylon [245, 269], the latter type generally yielding higher depth dyeings [24]. The low depth of shade obtained on regular nylon can be attributed to two causes; firstly, the relatively low AEG content of the substrate and, secondly, the pH at which dyeing is carried out. As Lewis points out [33], when dyeing at 95°C, as the pK_a of the amine conjugate acid $(-CH_2-)_6$-$^+NH_3$ will be about 8 and since the unprotonated amino end groups are the nucleophiles with which the dyes react, the acidic conditions commonly employed for the application of the dyes to nylon are inefficient insofar as many of the terminal amino groups will be protonated and thus such acidic application conditions are inefficient in terms of achieving a high degree of dye–fibre fixation. This situation was addressed in 1960 in the case of anionic vinyl sulphone reactive dyes [270–272] insofar as the sulphatoethyl derivative (XI) was converted into the reactive vinyl form (XII) prior to application to the substrate by treatment with alkali, this procedure resulting in high saturation values [96].



XI XII

Anionic reactive dyes, when applied at low to moderate depths of shade on regular nylon, exhibit excellent wet fastness on the substrate. Although deep shades can be secured, in such full depths, the dye is present mainly as unfixed dye that exhibits the characteristically poor to moderate wet fastness of acid dyes. High wet fastness is achievable by recourse to an aftertreatment with a syntan in the case of monofunctional dyes or a clearing process that removes unfixed dye in the case of bifunctional dyes [24].

2.3. Cationic dyes

The presence of carboxylic acid terminal groups in nylon fibres accords substantivity towards cationic dyes. The main use of this type of dye is in the dyeing of cationic-dyeable nylon which is principally used in differential-dyeing fibres. In the context of regular (unmodified) polyamide fibres, although it was recognised soon after the introduction of the fibres that cationic dyes displayed substantivity towards regular nylon fibres under neutral dyebath conditions [73, 74] and that uptake of the dyes was dependent upon both pH and carboxylic acid content [40], it was generally concluded that the wet- and light-fastness properties of the dyeings were inadequate. Since this time, very few studies have addressed the application of cationic dyes to unmodified nylons. However, as Lewis [33] comments, the cationic dyes available when commercial methods for dyeing nylon were being sought were mainly those containing delocalised cationic charges and the application of cationic dyes to nylon may be worthy of reconsideration. In this context, Lockhande *et al.* [273] demonstrated that the exhaustion of basic dyes on nylon 6 when applied at 95°C was enhanced by the addition to the dyebath of various inorganic salts, namely the chlorides of Na, Mg, Cu, Co and Zn, this being attributed to the Cl^- ions having been adsorbed on to the protonated amino end groups of the fibre and thereby having lowered the repulsive effects operating between the cationic dye and the protonated amino end groups in the fibre; of the various chlorides examined, $ZnCl_2$ was the most effective owing to the additional swelling action imparted to the substrate. These workers [274] further showed that the addition of NaCl, $MgCl_2$ as well as monochloroacetic acid and trichloroacetic acid to the dyebath enabled nylon 6 to be dyed with cationic dyes at 50°C and also [275] that the increase in cationic dye uptake achieved using trichloroacetic acid was due to the solvent having plasticised the fibre (i.e. having reduced T_g) whilst enhanced cationic dye uptake secured using monochloroacetic acid was due to fibre swelling.

2.4. Non-ionic dyes

This section concerns the dyeing of nylon with three classes of dye, namely *disperse*, *azoic colorants* and *vat*, which, at the end of dyeing, are present in the fibre as non-ionic species. However, whilst each of these three types of dye is non-ionic, only disperse dyes are non-ionic when adsorbed on to the substrate, whereas both vat dyes and azoic colourants (or rather the naphtholate in the latter case) are adsorbed as anions.

2.4.1. Disperse dyes

Details of the development of this dye class as well as the characteristics of disperse dyes are given in Chapter 1 in which it is discussed that the earlier, low M_r, types of disperse dye that were developed for the dyeing of cellulose diacetate fibres (the so called 'acetate dyes') were subsequently followed by disperse dyes of higher M_r and greater hydrophobicity than were developed for application to the more hydrophobic cellulose triacetate and, more importantly, polyester substrates. Ginns and Silkstone [24] propose that disperse dyes for nylon can be divided into two groups, namely dyes of low M_r and dyes of high M_r, in terms of their general application and fastness properties.

Soon after the commercial launch of nylon fibres, the 'acetate dyes' were found to exhibit good build-up, good migration power and excellent coverage of physical irregularities when applied to the substrate under conditions very similar to those used for applicationto cellulose diacetate fibres (80–85°C in the presence of a dispersing agent) [73–75, 263, 276–278] although the shade of the dyeings on nylon differed to that attained on diacetate fibres [263, 278]. In a study of the adsorption of 22 different 'acetate dyes' on nylon 6.6, Vickerstaff [279] demonstrated that the dyes varied in their rates of uptake at different temperatures, as a result of which, the dyes were differentiated into three types, namely Classes A, B and C, these representing slow, intermediate and rapid dyeing types, respectively, this classification system gaining commercial usage [280]. Although in pale and medium depths, the build-up of the 'acetate' disperse dyes was very similar to that obtained on diacetate fibres, at heavy depths the dye's build-up on nylon was less than that on diacetate [280], this being manifest [279] by the lower saturation values of the dyes on nylon than on diacetate. Whilst the wash fastness of such low M_r dyes on nylon was similar to that of the dyes on diacetate at temperatures of less than 70°C, at higher temperatures the fastness of the nylon dyeings was inferior to that of the dyeings on cellulose diacetate [278]. Furthermore, the light fastness of the dyes on nylon was slightly lower than on diacetate [278] whereas, in contrast, the fastness of dyeings on nylon to gas fumes was higher than on diacetate [152, 278]. The use of low M_r disperse dyes, which display generally high migration characteristics and thus good coverage of physical irregularities, low fastness to wet treatments and sublimation, is nowadays confined to those end-uses that do not neccessitate high wet fastness. Owing to their lower diffusional power and higher substantivity towards nylon, higher M_r disperse dyes generally exhibit higher fastness to wet treatments and sublimation but poorer coverage of physical variations in the substrate than their lower M_r counterparts. However, whilst the light fastness of the dyes on nylon is similar to that of the lower M_r dyes [24] the wet fastness of higher M_r dyes on nylon leave much to be desired. Thus, all types of disperse dye display only moderate to good fastness to wet treatments on nylon [281], as a consequence of which, their use is limited to outlets for which such fastness is adequate. Some improvement of wet fastness can be achieved by means of an aftertreatment with a syntan although this improvement disappears after only one laundering [24]. Furthermore, whilst disperse dyes are not sensitive to chemical variations in the fibre and, in general exhibit very good coverage of physical irregularities, the dyes vary widely in their sensitivity to such physical structural variations [282].

Although virtually any commercial disperse dye can be used to dye nylon, commonly, many dye makers recommend only a range of selected dyes. Typically, disperse dyes are applied to nylon at a temperature of 98°C, although elevated temperatures (up to 110 or 120°C for nylon 6 and 6.6, respectively can be used [24]), at pH 6 to 7. Anionic dispersing agents are most commonly employed for the application of disperse dyes to polyamide fibres as non-ionic types tend to reduce the rate of dyeing owing to their pronounced solubilising effect on the dye [283]. Sequestering agents are often used as many dyes are sensitive to trace metals, although an excess of sequesterant can reduce the light fastness of dyeings [283]. Some disperse dyes, especially blues, exhibit the tendency of ozone fading, this being more pronounced under humid conditions [87, 283]

The dyeing of nylon 6.6 with nitrodiphenylamine and azo [284] as well as anthraquinone and quinophthalone [285] dyes in the presence of various radical initiators (glucose, ammonium persulphate, potassium periodate and thiourea dioxide) has recently been carried out, in which it was observed that some of the radical initiators enhanced the colour yield and wash fastness of some of the dyes. However, these effects were often accompanied by a marked change in the shade of the dyeings. The enhanced fastness and colour yields obtained were attributed to the radical initiators having brought about dye polymerisation and/or dye–fibre covalent fixation, whilst the observed shade changes were considered to be due to the formation of reductive or oxidative products of the dyes [284, 285].

2.4.1.1. Thermodynamics of dyeing. Although the mechanism of dyeing nylon with disperse dyes has received relatively little attention, it is generally accepted that it is identical to that recounted in Chapter 1 for the dyeing of polyester fibres (and all other hydrophobic fibres) with this class of dye. In this context, dye–nylon substantivity can be considered to arise by virtue of a combination of hydrogen bonding, dispersion forces as well as possibly dipole–dipole and dipole–induced dipole forces of interaction. Suganuma [286] considers that disperse dyes are adsorbed on to the chain amide groups by hydrogen bonding, dipole–dipole and dispersion forces and Brody [210] considered that the dyes were adsorbed within voids caused primarily by chain folding. Blacker and Patterson [287] determined the dichroic orientation factors for several adsorbed disperse dyes on nylon 6.6 which revealed that the orientation of the dye increased as the concentration of dye in the substrate increased during dyeing, and concluded that the dye molecules initially occupy the least orientated regions in the fibre and only when these are occupied are the more orientated regions (in which the spacing of the polymer chains approaches that of a crystalline region) occupied.

If the assumption that disperse dye adsorption on nylon mirrors that on polyester, the uptake of the dyes on nylon fibres should follow a linear (Nernst) mechanism. Evidence for this latter proposal has been proposed by the findings that constant partitions were observed between an aqueous solution of *o*-nitroaniline [168] and also phenol [288] and nylon 6.6, that the uptake of disperse dyes are virtually unaffected by pH [263], AEG content and also acetylation [40]. Furthermore, linear isotherms have been obtained for the adsorption of commercial disperse dyes on nylon 6.6 [179, 289, 290], on nylon 6.6 and 6T [210] and in the case of a

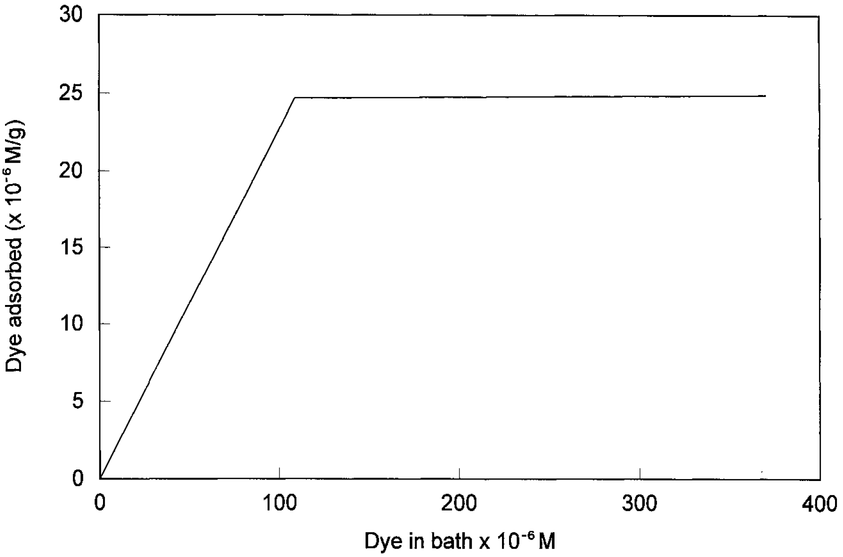


Figure 2.14 Adsorption isotherm of CI Disperse Red 13 on nylon 6.6 at 90°C [289]
(Reproduced with permission from A. Johnson and the Society of Dyers and Colourists)

disperse dye transferred from a starch film to a nylon 6.6 film [291] (Figure 2.14). Brody [210] found that the saturation values of several disperse dyes on nylon 6.6 increased with increasing aqueous solubility of the dyes and that identical saturation values were obtained for the same dye on three different types of nylon. This author [210] also considered that the dyes were adsorbed by means of a Langmuir mechanism, although some doubts attend this particular proposal [179].

2.4.1.2. Kinetics of dyeing. The diffusion of disperse dyes within nylon fibres is Fickian in that measured diffusion coefficients are concentration-independent [292] (Figure 2.15). The rate of dyeing is considered [168, 293] to be governed by rate of dye diffusion in the fibre; $t^{\frac{1}{2}}$ values of several commercial disperse dyes were shown to vary over a wide range [168, 279], as a result of which, the dyes were differentiated into Classes A, B and C, these representing slow, intermediate and rapid dyeing types, respectively. The $t^{\frac{1}{2}}$ of 1,4-diaminoanthraquinone in nylon 6 was found to increase with increasing temperature over the range 100 to 150°C when the dye was applied in the absence of water [294]. McGregor *et al.* [292] observed that the diffusion coefficient of CI Disperse Red 15 in nylon 6.6 film when applied from water was higher than when applied from water-saturated iso-octane and, also, that the presence of water lowered the

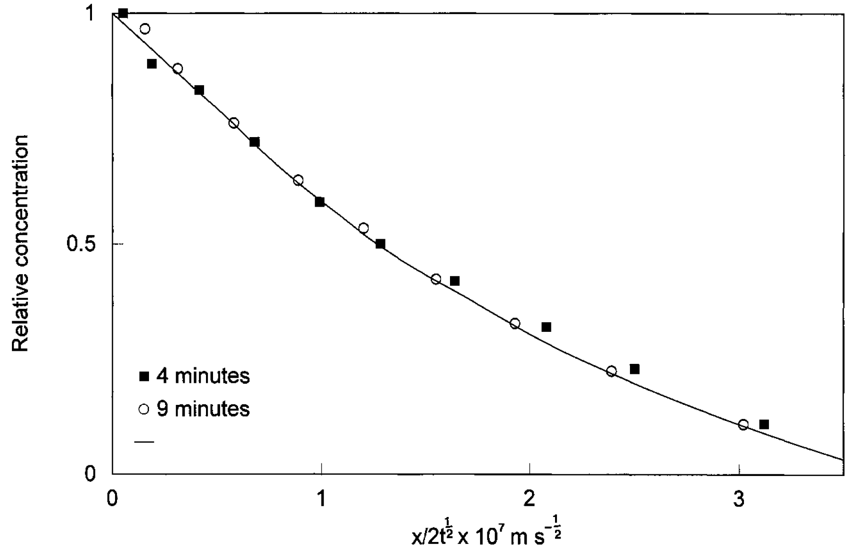


Figure 2.15 Concentration–distance profile for CI Disperse Red 15 in nylon 6.6 at 55°C [225]
(Reproduced with permission from the Society of Dyers and Colourists)

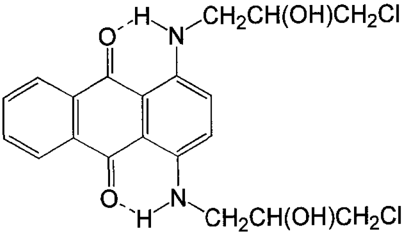
activation energy of diffusion of the dye, which these workers [292] attributed to the water having plasticised the fibre. The diffusion coefficient of several monoazo disperse dyes in nylon 6.6 was found to decrease with increasing M_r of the dyes whereas no such correlation was observed for a series of AQ disperse dyes [279]. Hori *et al.* [295] studied the temperature-dependence of the diffusion of several disperse dyes in nylon 6 film using a theoretical treatment that combined both porous matrix and free volume models of dye diffusion via equation (2.23), which was previously described by Hori *et al.* [296], wherein D_M is the apparent diffusion coefficient, Φ_0 the frequency of diffusional jumps, δ the jumping distance, Θ the fractional volume of the swollen amorphous region, τ the tortuosity factor, K the partition coefficient of the dye between the polymer and the dyebath, ΔH_H the enthalpy change required to form a 'hole' for the diffusional jumps, T_g the glass transition temperature and A and B are intrinsic constants for the treatment of the segmental motion of the polymer.

$$\ln D_M = \overset{\text{A}}{\frac{\ln \Phi_0\delta^2}{6}} + \frac{\ln \Theta}{\tau} \overset{\text{B}}{-\ln K} - \frac{\Delta H_H}{T} - \overset{\text{C}}{\frac{AB}{B + (T - T_g)}} \qquad (2.23)$$

These workers [295] observed that the diffusion coefficient of the dyes was independent of concentration and, using equation (2.23), estimated the contributions that dye diffusion in the pore liquid (A), dye affinty (B) and segmental motion (C) made towards the diffusion of disperse dyes in nylon 6 film, these being 20–35%, 33–41% and 39–42%, respectively, which, when compared with values secured for the diffusion of disperse dyes within polyester (A, 13–17%; B, 28–38%; C, 49–55%), revealed that for the less hydrophobic nylon fibres, the contributions from dye diffusion in the pore liquid and from segmental motion were higher and lower, respectively, than those for the diffusion of the dyes within polyester, thus demonstrating that for nylon, the porous matrix model of diffusion is more pertinent than the free volume model.

2.4.2. *Disperse reactive dyes*

In view of the problems associated with the use of anionic reactive dyes on nylon (i.e. coverage of fibre irregularities as recounted earlier), ICI introduced the *Procinyl* range of disperse reactive dyes in 1958; the range, which comprised five dyes, was withdrawn in the 1980s. The dyes were disperse dyes that carried reactive groups and, in essence, were intended to combine the favourable characteristics of disperse and reactive dyes on nylon, namely excellent coverage of substrate irregularities and high wet fastness, respectively. Although the structures of the dyes were not disclosed, patent literature suggests that several different reactive groups were used, including chlorohydrin, chlorotriazine and chloroethylaminosulphone; the structure of CI Reactive Blue 6 is XIII.

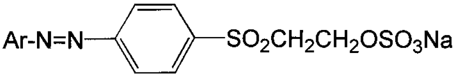


XIII

The dyes were applied to nylon in a two-stage process; initial dye application was carried out at pH 4 under which conditions they did not react with the fibre and behaved as conventional disperse dyes in their adsorption and diffusional behaviour [297]. After dye exhaustion had been achieved, covalent reaction of the dye with the amino end groups in the fibre was then affected by an increase in pH of the dyebath to 10.5; both the exhaustion and fixation stages were carried out at 95°C for 60 minutes [297]. Evidence for dye–fibre fixation accrued from the observation that the dyes could not be completely stripped from the dyed fibre using solvents, such as chlorobenzene, which completely stripped conventional disperse dyes from the substrate. Also, when nylon which had been dyed with Procinyl Scarlet G was dissolved in *o*-chlorophenol and the ensuing solution precipitated in propanol, the supernatant liquor was uncoloured and the precipitated nylon coloured, this differing to the situation achieved using the non-reactive homologue of Procinyl Scarlet G, for which the supernatant was coloured and the precipitated nylon uncoloured [297].

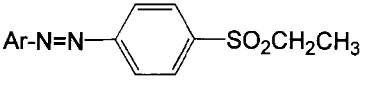
Scott and Vickerstaff [297] demonstrated, using two Procinyl dyes, that the quantity of dye fixed to nylon 6.6 increased with increasing concentration of dye applied and reached a value that was in excess of the AEG content of the fibre. As, theoretically, only one dye molecule should react with each terminal amino group, these workers attributed the observed *over-fixation* of the dyes to reaction with the chain amide groups [297]. However, as was pointed out by Peters in a discussion of the findings of Scott and Vickerstaff [297], two other explanations may be offered for the over-fixation namely, that the dye may react with itself forming dimers, trimers, etc., or that the dye can react twice with each amino end group, firstly with the primary amine and secondly with the resulting secondary amine. Both of these alternative explanations appear feasible.

The approach adopted by ICI with their Procinyl dyes to overcome the problem of anionic reactive dyes highlighting fibre irregularities, namely that the reactive disperse dyes combine the favourable properties of both disperse dyes (excellent coverage of fibre irregularities) and reactive dyes (excellent wet fastness) on nylon, has been pursued by other workers [298–300, 304–311].



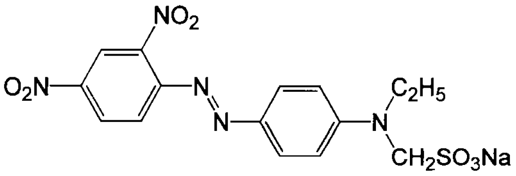
XIV

In a study of the dyeing properties of four monoazo reactive disperse dyes of general structure (XIV) on conventional decitex nylon 6.6 fabric, Lo [298] found that dye exhaustion increased with increasing pH of application in the range pH 5–10 and with increase in temperature over the range 40–95°C; maximum dye fixation occurred at pH 8. These findings concurred with those of Dohmyou *et al.* [299] who observed that maximum fixation of a dye of type (XIV) on both polyester and nylon 6 occurred at pH 8 and that both the exhaustion and fixation of the dye on nylon 6 increased with increasing temperature of application. Burkinshaw and Collins [300] extended the study made by Lo [298] by examining the dyeing and wash fastness characteristics of three reactive disperse dyes of structure (XIV) and one monoazo disperse dye (of general structure (XV)) on both conventional and microfibre nylon 6.6.



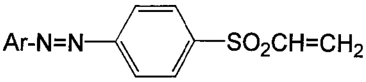
XV

In addition to combining the excellent coverage of fibre irregularities and high wet fastness through the use of reactive disperse dyes, this work [300] had two further aims: firstly, to determine whether the wash fastness of the reactive disperse dyes on microfibre (85f92; 0.9 dtexpf) nylon 6.6 fibres was similar to that on their conventional (78f46; 1.7 dtexpf) decitex counterparts (each type of fibre was of the same AEG content (66.4 g-eq. g × 10 ^{6})); and, secondly, to determine the feasibility of using disperse dyes on nylon which did not require milling. In the latter context, the immediate precursors of disperse dyes were developed by Gardner and Saunders for secondary cellulose acetate fibres and marketed by BDC in the early 1920s [301, 302].



XVI

These 'temporarily solubilised' methyl sulphonate dyes, such as Ionamine Red KA (XVI), hydrolysed in the dyebath to yield the corresponding low water-solubility, non-ionic derivative, which were adsorbed on to the hydrophobic cellulose acetate fibre. Practical difficulties associated with varying rates of hydrolysis of the dyes [303] led to the Ionamine range being supplanted by non-hydrolysable, low aqueous water-solubility dyes applied from fine aqueous dispersion (i.e. disperse dyes). The three reactive disperse dyes employed by Burkinshaw and Collins [300] resemble the Ionamine dyes in that the use of aminophenyl-4-(β-sulphatoethyl sulphone) as diazo component in structure (XIV) conferred 'temporary solubility' upon the three reactive disperse dyes insofar as the sulphuric acid ester group imparted sufficient water-solubility to the dyes to facilitate dissolution of the dyes in water, thereby obviating the need to mill the dyes in the presence of a dispersing agent, as is required for conventional disperse dyes; β-elimination of the sulphuric acid ester group during the course of dyeing then yields the non-ionic, sparingly water-soluble, vinyl sulphone form of the dye (XVII).



XVII

Indeed, it was found that dissolution of the three reactive disperse dyes was readily achieved in cold (room temperature) water without recourse to the aid of a dispersing agent and, at the end of dyeing, residual dye was present in the dyebath as a fine dispersion [300]. However, as was recorded by Lo [298], Burkinshaw and Collins [300] found that the levelness of the dyeings achieved with the reactive disperse dyes was improved by the presence of a small concentration of an anionic levelling agent in the dyebath.

Of various pH values (pH 7–9) and temperatures (80–95°C) used to apply the three reactive disperse dyes to the two types of nylon 6.6 fabric [300], highest colour strength, for both conventional and microfibre nylon 6.6, was achieved when the dyes had been applied at pH 8 at 95°C (Figure 2.16), these findings concurring with those of Lo [298] and also Dohmyou *et al.* [299]. The observation that colour strength increased with increasing temperature, reaching a maximum value for application at 95°C, was attributed to a corresponding increase in diffusion rate of the dyes that accompanied an increase in temperature, whilst the finding that

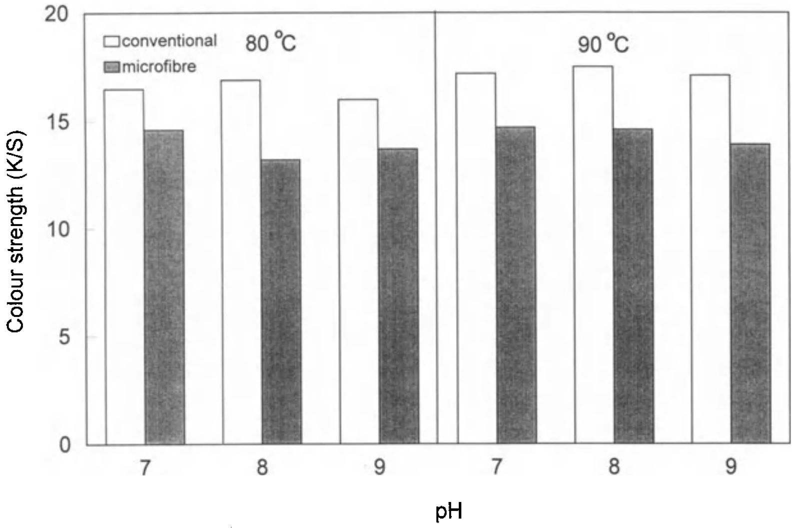
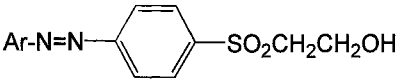


Figure 2.16 Effects of pH and temperature on uptake of dye A on conventional (78f46) and microfibre (85f92) nylon 6.6 [300]

(Reprinted from *Dyes and Pigments*, Vol. 25, S.M. Burkinshaw and G. Collins, The Dyeing of Conventional and Microfibre Nylon 66 with reactive disperse dyes, pp. 31–48, copyright 1994, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington, OX5, 1GB, UK) maximum colour strength was achieved at pH 8 was explained in terms of the hydrolysis of the reactive dyes that occurred during dyeing [300]. It was argued that in the early stages of dyeing at pH 7, 8 and 9, there would be little, if any, electrostatic interaction operating between the anionic, sulphatoethyly sulphone dye and the fibre, as the amino end groups in the substrate will be non-protonated; indeed, at such pH values the fibre could be considered to possess an overall negative potential owing to ionisation of the carboxyl end groups. Thus, in the early stages of dyeing at pH 7, 8 and 9, dye–fibre substantivity was assumed to arise by means of, for instance, ion-dipole, ion–induced dipole and dipole–dipole interactions. As β-elimination of the sulphuric acid ester group ($-OSO_3^-$) of the dye would occur as dyeing proceeds to give the non-ionic, vinyl sulphone derivative of the dye (XVII) and, as this elimination reaction, which is base-catalysed, is considered to commence at a temperature of between 40 and 50°C, it was considered that in the later stages, and perhaps for the greater proportion of the dyeing cycle, the dye would be present in the dyebath, at each of the three pH values studied, in the non-ionic, vinyl sulphone form (XVII), the adsorption of which should be pH-independent. However, as it was observed that colour strength was pH-dependent, insofar as, maximum colour strength was acheived at pH 8, consideration was made of the competitive nature of the dye–fibre and dye hydrolysis reactions occurring during dyeing [300]. As a consequence of the rate of β-elimination of the sulphuric acid ester group of the dye being base-catalysed, it was reasoned that the rate of formation of the reactive, vinyl sulphone derivative (XVII) was also base-catalysed; thus, both the rate and extent of fixation of the dye to the substrate could be expected to increase with increasing pH of application. Hence, the extent of dye fixation, expressed in terms of colour strength of the dyeings, should have been greatest when dyeing had been carried out at pH 9; the finding that this was not so was attributed to the rate of hydrolysis of the vinyl form of the dye in the dyebath also being base-catalysed, with the result that the rate of formation of the hydrolysed (XVIII) form of the dye in the dyebath increased with increasing pH.



XVIII

Thus, it was concluded that the colour strength obtained at pH 9 was lower than that achieved at pH 8 because of a higher rate and extent of dye hydrolysis at the higher application pH value.

These workers [300] also observed, for each of the three dyes used, that the colour strength obtained for the dyeings on conventional fabric was higher than that secured for the dyeings on microfibre nylon 6.6 (Figure

2.16), this being attributed to the greater extent of surface reflection inherent with the dyed microfibre. The difference in colour strength between dyeings on the two types of fibre was further illustrated by the lower build-up profiles obtained for each of the three dyes on microfibre as well as the higher concentration of each of the three dyes required to achieve a 1/1 standard depth on microfibre; in the latter context, it was shown that between 20 and 25% more dye was required to achieve this standard depth on microfibre. As the polymer used in the microfibre was the same as that employed in the conventional fibre, these observed differences in colour strength of dyeings obtained on conventional and microfibre nylon 6.6 were attributed to the greater surface reflection of the dyed microfibre.

The three reactive disperse dyes were shown to exhibit excellent wash fastness on both conventional and microfibre nylon 6.6 at 1/1 standard depth, the level of fastness achieved being identical on both types of fibre, even though, as mentioned above, 20–25% more dye had been applied to the microfibre to achieve the same visual (1/1 standard) depth on both fibre types [300]. The excellent build-up profiles obtained for the three reactive disperse dyes was in sharp contrast to the very poor build-up profile secured for the disperse dye on both substrates. This finding, which is illustrated in Figure 2.17, was attributed to covalent reaction of

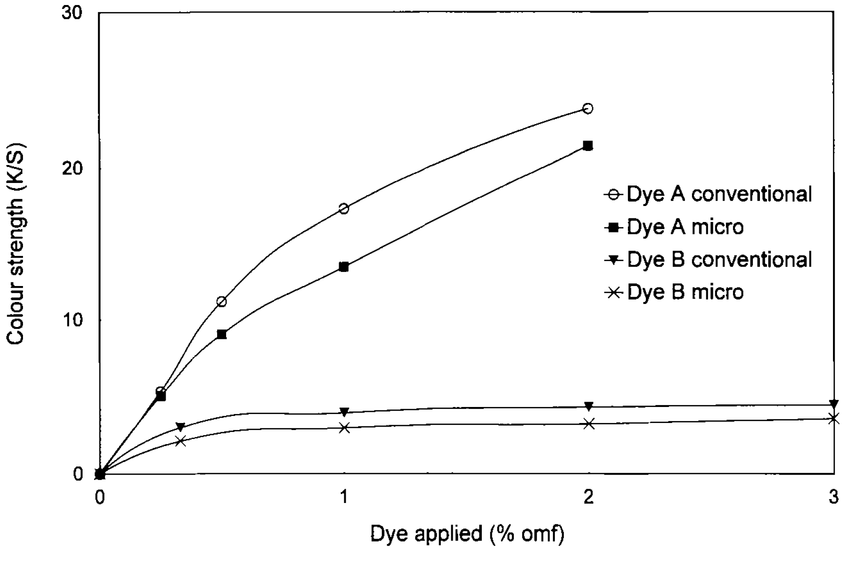
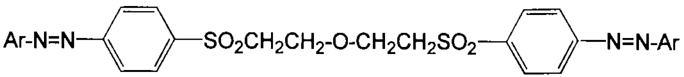


Figure 2.17 Build-up profiles of reactive disperse dye A (95°C, pH 8) and disperse dye B (95°C, pH 6.5) on conventional (78f46) and microfibre (85f92) nylon 6.6 [300]

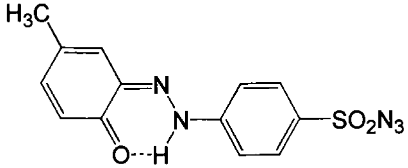
(Reprinted from *Dyes and Pigments*, Vol. 25, S.M. Burkinshaw and G. Collins, The Dyeing of Conventional and Microfibre Nylon 66 with reactive disperse dyes, pp. 31–48, copyright 1994, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington, OX5, 1GB, UK) the reactive disperse dyes having promoted dye uptake [300]. The finding that the shape of the build-up curves were similar on both conventional and microfibre nylon 6.6 for each dye was attributed to both types of fibre having been comprised the same polymer [300].

Evidence has been obtained [298, 304] that the extent of fixation of reactive dyes of type (XIV) was in excess of the AEG content of the nylon 6.6 fabrics used. This can be explained in terms of the comments made by Peters in a discussion of the findings of Scott and Vickerstaff [297], that such dyes may react with themselves to form dimers, trimers, etc. (XIX) or that the dyes can react twice with each amino end group in the substrate, firstly with the primary amine and secondly with the resulting secondary amine.



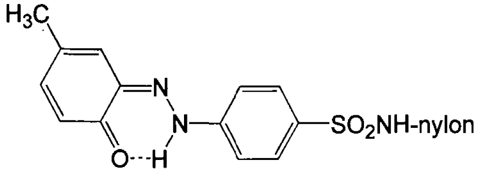
XIX

Griffiths and McDarmaid [305] demonstrated that sulphonazide disperse dyes were covalently bound to nylon 6 film.



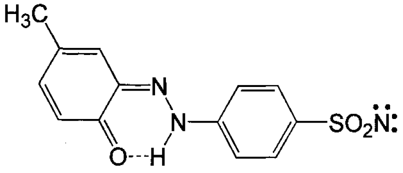
XX

Using 2-hydroxy-5-methyl-4′-sulphonazideobenzene (XX), these workers showed that when applied under aqueous conditions at 100°C and 120°C, the dye became attached to the amino end groups in the polymer by means of a nucleophilic substitution reaction in which the nucleophilic terminal amino group in nylon attacked the sulphonazide group and displaced the azide ion (N_3^-) resulting in a sulphonamide linkage between the dye and the fibre (XXI).



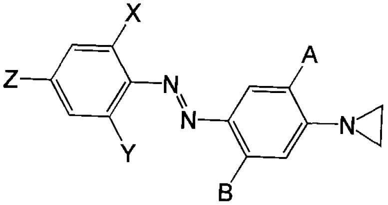
XXI

These workers [305] also showed that when the samples of nylon 6.6 film which had been dyed at 100 and 120°C were subsequently dry heated at 170°C, the amount of dye covalently attached was in excess of the AEG content of the film by a factor of three; the observed dye fixation in excess of the AEG content was ascribed to the formation, at 170°C under anhydrous conditions, of the nitrene derivative of the dye (XXII) which inserted into the C—H bonds of the polymer.

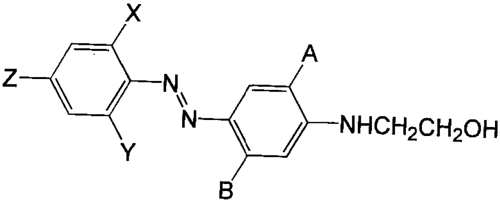


XXII

Monoazo disperse dyes that contained an aziridinyl terminal group in the conjugated system [306, 307], of general formula XXIII, were found to yield dyeings of higher wash fastness than conventional disperse dyes of similar structure and M_r when applied to nylon 6.6 at the same standard depth of shade (1/1) from aqueous dyebaths [307].



XXIII



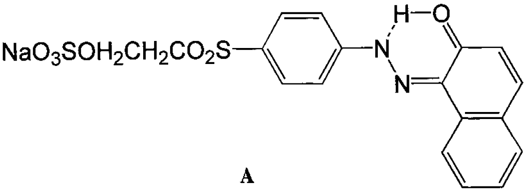
XXIV

From the observation that the hydrolysed form of the dye (XXIV) exhibited lower wash fastness on the fibre than its reactive counterpart (XXIII), it was concluded that the observed high wash fastness of the dyes on nylon 6.6 was attributable to dye polymerisation and/or covalent insertion of the dyes into a methylene group of the chain amide in the substrate, the latter process occurring by means of a one-electron transfer, free radical mechanism [307].

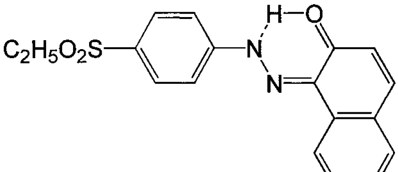
De Giorgi *et al.* investigated the dyeing of nylon 6 with monochlorotriazinyl [308–311] and trichloropyrimidinyl disperse reactive dyes and observed that the two types of dye exhibited very similar dyeing characteristics, dye exhaustion being achieved under acidic pH conditions and dye fixation secured using alkaline pH values.

2.4.3. *Azoic colourants*

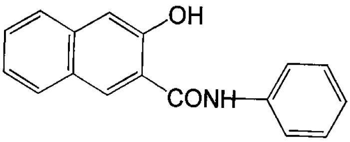
In 1880, Read Holliday commercially introduced the process of, firstly, impregnating cotton with a solution of sodium-2-naphtholate and subsequently treating the naphtholated fibre with a solution of diazotised 2-naphthylamine which resulted in the formation, *in situ*, of the azo dye *Vacanceine Red* (Colour Index, 1st edn, No. 93). The replacement of 2-naphthylamine with *p*-nitroaniline yielded the more commercially important *Para Red* (CI Pigment Red 1) in 1889 and other 'ice colours', obtained using 2-naphthol, were developed. In 1912, *Naphthol AS* (XXV) was introduced by the Greishem Elektron Co. as a replacement for 2-naphthol and the term *azoic* was recommended to describe the products formed between such arylamides of 2,3-hydroxynaphthoic acid and diazotised aromatic amines [72].



A



B



XXV

Currently, a wide range of both CI Coupling Components (Napthols, or naphthols as they are known generically) and CI Diazo Components (aromatic amines) are widely employed on cellulosic fibres. Azoic colorants also enjoy limited use, mostly for the production of black shades on both polyester and acetate fibres.

In the case of nylon, the conventional method of applying this type of colorant to cellulosic fibres, namely the application of the naphtholate (the sodium salt of the CI Coupling Component or *naphthol*) followed by the subsequent application of the diazotised aromatic amine (CI Diazo Component) and coupling *in situ* [72], cannot be used owing to the low extent of penetration of the diazotised amine within the naphtholated fibre [280]. Rather, as proposed by Whittaker [260], the naphtholate and the free aromatic base, the latter in either dispersion or solution [280], are simultaneously applied to the substrate at between 80 and 85°C, and, after impregnation, diazotisation is effected *in situ* at 15–20°C. In this application method, the impregnation temperature of 80–85°C is necessary in order to achieve adequate uptake of the naphtholate; the amine, in effect, being adsorbed as a disperse dye. Generally, the shades obtained on nylon are duller than comparative shades on cellulosic fibres, this dullness increasing with increasing depth of shade [280]. Although azoic colorants exhibit good coverage of both physical and chemical variations in nylon substrates and yield dyeings of very good light and wet fastness, their use is mostly restricted to the production of black shades [24], often by recourse to the use of diazotised and developed disperse dyes [152]. However, Saville [312] proposed that this one-bath application method yielded ring-dyeings and that a two-bath application method, in which the naphtholate was applied at 80°C prior to the acidified aromatic amine at 80°C, gave better dye penetration. This author [312] also suggested that the dullness of azoic colorants on nylon was due to the presence, within the dyed fibre, of uncoupled amine.

2.4.4. *Vat dyes*

These dyes contain at least two conjugated carbonyl groups which enables them to be converted, by reduction under alkaline conditions, into the corresponding water-soluble, anionic leuco compound, in which form the dye is applied to the substrate. The vat-dyeing of cellulosic fibres and also, to a lesser extent wool, has been practised for many centuries using vat dyes of natural origin (Indigo, woad), the vat-dyeing process having gained considerably from the commercial introduction of the reducing agent sodium hydrosulphite (dithionite) which was discovered by Schutenberger in 1871 [72]. Considerable research has resulted in the current wide range of synthetic vat dyes, of which, Indigoid and Anthraquinoid are the most important chemical classes [72, 251, 313–315].

The use of vat dyes is nowadays mostly confined to cellulosic fibres on which they exhibit excellent light- and wet-fastness properties. The dyes are little used on nylon fibres, their main usage in this context being in the dyeing of cotton/nylon blends [316]. In 1939 Stott [74] reported that vat dyes exhibited low substantivity towards the substrate when applied using conditions employed for the dyeing of cellulosic fibres, this having been attributed to the low diffusional behaviour of the leuco dye anions within the substrate [96]. Stott [74] also observed that the light fastness of the dyes on nylon was lower than that on cellulosic fibres and silk, this being confirmed by Whittaker [260] and has been attributed to the low extent of penetration of the oxidised form of the dye within the substrate [312] as well as the lack of aggregation of the oxidised dye particles within the fibre [96]; furthermore, the light fastness of vat dyes on nylon is very low, especially when the nylon is delustred with TiO_2 and vat dyes of low light fastness on nylon often are sensitisers of photodegradation of the fibre [174]. However, some vat dyes exhibit excellent light fastness on nylon fibres [24, 79, 96]; also, the light fastness of some dyes on nylon can be improved by steaming the oxidised dyeing [312] or treating the oxidised dyeing with phenolic compounds [317] or, in the case of solubilised vat dyes, by oxidising the dyeing in the presence of salicylic acid. Each of these treatments is considered to swell the fibre and enhance dye aggregation [96]. Whittaker [260] observed that deep shades were achievable on nylon fibres by applying the dyes at temperatures [90–95°C) that were higher than those (typically 60°C) used to apply the dyes to cellulosic fibres, the latter finding being confirmed by Saville [312] and Douglas [318]. The uptake of both the leuco derivative and the unreduced vat dye is not dependent on the AEG content of the fibre [40] and, whilst the dyes therefore cover chemical variations in the fibre well, they are relatively sensitive to physical irregularities in the substrate.

Whittaker [152] has attributed the relatively unimportant role of vat dyes in the dyeing of nylon fibres to the difficulties involved in their application and their generally low light fastness on the substrate.

References

1. E Clayton, *JSDC*, **55** (1939) 32.
2. R E Putscher, in *Kirk Othmer Encyclopedia of Chemical Technology*, 3rd edn, Vol. 18, J Wiley, New York, 1982, p. 328.
3. M I Kohan, in *Ullmans Encyclopedia of Industrial Chemistry*, Vol. A21, VCH, Basel, 1992, p. 179.
4. J Zimmermann, in *Encyclopedia of Polymer Science and Engineering*, Vol. 11, J Wiley, New York, 1988, p. 315.
5. H K Reimschussel, in *Handbook of Fibre Science and Technology* Vol. IV, (ed. M Lewin and E M Pearce), Marcel Dekker, New York, 1985.
6. M I Kohan, in *High Performance Polymers: Their Origin and Development*, (ed. R B Seymour and G S Kirshenbaum), Elsevier, New York, 1986.
7. J H Saunders, in *Kirk Othmer Encyclopedia of Chemical Technology*, 3rd edn, Vol. 18, J Wiley, New York, 1982, p. 372.
8. J H Saunders, in *Encyclopedia of Polymer Science and Engineering*, Vol. 11, J Wiley, New York, 1988, p. 410.
9. S M Burkinshaw and H Skelton, *Dyes and Pigments*, **26** (1994) 15.

10. H Hoff, in *Man made Fibres: Science and Technology*, (ed. H F Mark, S M Atlas and E Cernia), Vol. 2, Wiley, New York.
11. K Miyasaka and K Makishima, *J. Poly. Sci.*, A-1, **5** (1967) 3017.
12. K Miyasaka and K Ishikawa, *J. Poly. Sci.*, A-2, **6** (1968) 1317.
13. H Arimotto, *Kobunski kagaku*, **19** (1962) 204, 212.
14. D J Marfell, Du Pont Fibres (UK), personal communication.
15. J B Speakman and A K Saville, *J Text. Inst.*, **37** (1946) 271.
16. *Fibres from Synthetic Polymers* (ed. R Hill), Elsevier, Amsterdam, 1954.
17. W E Morton and J W S Hearle, *Physical Properties of Textile Fibres*, Text. Inst., Manchester, 1962.
18. J A Brydson, *Plastics Materials*, Van Nostrand, London, 1966.
19. D J Marfell, PhD Thesis, Leeds University, 1971.
20. K E Kyllo and C M Ladisch, *Proc. AATCC Int. Conf.* (1983) 361.
21. M Tsurata and A Koshimo, *J. Appl Poly. Sci.*, **9** (1965) 11.
22. H W Peters and T R White, *JSDC*, **77** (1961) 603.
23. H J Palmer, *J Text. Inst.*, **49** (1958) T33.
24. P Ginns and K Silkstone, in *The Dyeing of Synthetic-polymer and Acetate Fibres* (ed. D M Nunn), Dyers Co. Pub. Trust, Bradford, 1979.
25. C H Do and H K Reimschussel, *J. Poly. Sci., A, Poly. Chem.*, **25** (1987) 2301.
26. M Igarashi, PhD Thesis, Utah University, Utah, 1982.
27. C H Do, E M Pearce and B J Bulkin, *J. Poly. Sci., A, Poly. Chem.*, **25** (1987) 2409.
28. C T Graves and M G Overoyd, *Polymer*, **4** (1963) 81.
29. M Kashiwagi, *J. Poly. Sci.*, **1** (1963) 189.
30. D Campbell and A Peterlin, *J. Poly. Sci., A*, **6** (1968) 481.
31. H M Leuvel and K V Lind, *J. Poly Sci., A-2*, **8** (1970) 401.
32. T C Chiang and J P Sibilia, *J. Poly. Sci., A-1*, **10** (1972) 605.
33. D M Lewis, in *Synthetic Fibre Materials*, (ed. H Brody), Longman, Harlow, 1994.
34. H Berg, *Mell. Text.*, **52** (1971) 448.
35. D Dierkes and E Lux, *Text. Prax.*, **22** (1967) 650.
36. A Liddiard, *Rev. Prog. Col.*, **1** (1969) 64.
37. W de Winter and A Decorte, *Text. Res. J.*, **41** (1971) 726.
38. M D Chantler, G A Partlett and J A B Whiteside, *JSDC*, **85** (1971) 621.
39. A R Munden and H J Palmer, *Text. Res. J*, **41** (1950) 609.
40. H J Palmer, *JSDC*, **67** (1951) 609.
41. H W Peters and J C Turner, *JSDC*, **74** (1958) 252.
42. S Blackburn and T L Dawson, *JSDC*, **87** (1971) 473.
43. W T Holfeld and M S Shepard, *Can. Text. J.*, **94** (8) (1977) 65.
44. K Silkstone, *Rev. Prog. Col.*, **12** (1982) 22.
45. H T Pratt, in *Knit Barré: Causes and Cures*, AATCC, 1972.
46. W T Holfeld and D P Hallada, *Can. Text. J.*, **92** (11) (1975) 48.
47. K Greider, *JSDC*, **91** (1974) 435.
48. G Thomas and W T Holfeld, *Text. Chem. Col.*, **4** (1972) 216.
49. D P Hallada and W T Holfeld, in *Knit Barré: Causes and Cures*, AATCC, 1972.
50. J Shore and J Park, *Rev. Prog. Col.*, **12** (1982) 43.
51. W T Holfeld and M S Shepard, *Can. Text. J.*, **94** (4) (1977) 80.
52. A W Etchells, *Amer. Dyest. Rep.*, **35** (1946) 38.
53. A W Etchells, *Amer. Dyest. Rep.*, **40** (1951) 598.
54. M Tsurata and A Koshimo, *J. Appl. Poly Sci.*, **9** (1965) 3; **9** (1965) 11.
55. A Koshimo, *J. Appl. Poly. Sci.*, **9** (1965) 81.
56. J O Warwicker, *J. Appl. Poly. Sci.*, **19** (1975) 1147.
57. A Koshimo and T Kakisita, *J. Appl. Poly. Sci.*, **9** (1965) 91
58. W T Holfeld and D P Hallada, *Proc. 1972 AATCC Conference*, 33, 39.
59. W Taubert and J H Rau, *Text. Prax.*, **28** (1973) 92.
60. W T Holfeld and M S Shepard, *Can. Text. J.*, **94** (5) (1977) 72.
61. H Wilsing, *Mell. Text.*, **52** (1971) 459.
62. G T Davis and H S Taylor, *Text. Res. J.*, **35** (1965) 405.
63. H Morizane, Y Suda and F Nakajima, *Colourage*, (1970) 26.
64. Y Takagi and H Hattori, *J. Appl. Poly. Sci.*, **9** (1965) 2167, 2177.
65. R McGregor and R H Peters, *JSDC*, **84** (1968) 267.

66. M E Hopper, R H Peters and R McGregor, *JSDC*, **86** (1970) 117.
67. M Duscheva, M Itcherenska and E Gavriola, *Mell. Text.*, **70** (1989) 360.
68. G Heidemann, *Chemifasern*, **20** (3) (1970) 1.
69. L C Garasimova, K B Andrianova and L A Gordeeva, *Chimitscheskie wolonka*, **14** (1975) 62.
70. J A Coates, V Ellard and I D Rattee, *JSDC*, **96** (1980) 14.
71. W T Holfeld and R H Pike, *Text. Chem. Col.*, **17** (1985) 231.
72. S M Burkinshaw, in *The Chemistry and Application of Dyes* (ed. D Waring and G Hallas), Plenum Pub., New York, 1990.
73. G S J White, *JSDC*, **55** (1939) 409.
74. P H Stott, *Amer. Dyest. Rep.*, **28** (1939) 582.
75. P H Stott, *Amer. Dyest. Rep.*, **29** (1940) 646.
76. *Colour Index*, revised 3rd edn, Soc. Dyers and Colourists, Bradford, 1987.
77. S M Burkinshaw, in *Wool Dyeing*, (ed. D M Lewis), Society of Dyers and Colourists, 1992.
78. J E Rowe, *Amer. Dyest. Rep.*, **75** (6) (1986) 43.
79. C B Stevens, in *The Dyeing of Synthetic Polymer and Acetate Fibres* (ed. D M Nunn), Dyers Co. Pub. Trust, Bradford, 1979.
80. T L Dawson and B P Roberts, *JSDC*, **95** (1979) 47.
81. R Nahta, *Amer. Dyest. Rep.*, **68** (3) (1979) 32.
82. B C Burdett, *Rev. Prog. Col.*, **13** (1983) 41.
83. *Nylosan Dyes*, Technical Information, Sandoz, Basle, 1986.
84. B Evans and W T Holfeld, *Proc. AATCC Int. Conf.*, (1977) 158.
85. J Shore, in *Colorants and Auxiliaries* (ed. J Shore), Vol. 1, Society of Dyers and Colourists, Bradford, 1990.
86. F M Rowe and W G Dangerfield, *JSDC*, **52** (1936) 48.
87. R A F Moore, S B Reutsch and H-D Weigmann, *Proc. AATCC Int. Conf.*, (1984), 143.
88. M A Heriant, *Amer. Dyest. Rep.*, **75** (9) (1986) 38.
89. R H Bost, P F McLawhorn and J L Rush, *Proc. AATCC Int. Conf.*, (1981) 125.
90. T L Dawson, *Text. J. Austr.*, **42** (1967) 45.
91. S Blackburn and T L Dawson, *JSDC*, **87** (1971) 473.
92. J A Bittles, J A Brooks, J J Iannarone and H P Landerl, *Amer. Dyest. Rep.*, **47** (1958) 183.
93. Anon, *Du Pont Tech. Bull.*, (10) (1954) 32.
94. Anon, *Du Pont Tech. Bull.*, (11) (1955) 133.
95. J A Brookes and J E Reith, *Amer. Dyest. Rep.*, (1955) 698.
96. H U Schmidlin, *Preparation and Dyeing of Synthetic Fibres*, Chapman and Hall, London, 1963.
97. W Beckmann, *Practical Dyeing Problems – Analysis and Solutions*, AATCC International Symposium, Washington, 1977.
98. J A Hughes, H H Sumner and B Taylor, *JSDC* **87** (1971) 463.
99. T J Reardon, *AATCC Dyeing Symposium*, (1980) 15.
100. T C Hemling, H Stitzel and J R Aspland, *Proc. 1989 AATCC International Conference and Exhibition*, 80.
101. *ICI Product Data Sheets CAFT 4(R)*, ICI Surfactants, Bolton, 1988.
102. Courtaulds, USP 2,871,536 (1945).
103. J H MacGregor and C Pugh, *JSDC*, **61** (1945) 122.
104. W H Hindle, *Amer. Dyest. Rep.*, **45** (1956) 972.
105. E I Valko, *Osterr. Chem Ztg.*, **40** (1939) 173.
106. E I Valko, *JSDC*, **55** (1939) 759.
107. G R Turner, W E Newby and S B Speck, *Amer. Dyest. Rep.*, **56** (1967) 998.
108. A Datyner, *Rev. Prog. Col.*, **23** (1993) 40.
109. T M Baldwinson, in *Colorants and Auxiliaries*, Vol. 2, (ed. J Shore), SDC, 1990.
110. W Langmann, *Mell. Textil.*, **54** (1973) 654.
111. Y Nemoto, K Mase and H Funahashi, *Proc. 6th Int. Con. Surf. Act.*, **3** (1972) 363.
112. Y Nemoto and H Funahashi, *J. Coll. Int. Sci.*, **79** (1981) 313.
113. E I Valko, *Rev. Prog. Col.*, **3** (1972) 50.
114. S Craven and A Datyner, *JSDC*, **77** (1961) 304.
115. S Craven and A Datyner, *JSDC*, **83** (1967) 545.

116. W Langmann, *Tenside*, **7** (1970) 198.
117. Y Nemoto and H Funahashi, *Ind. Eng. Chem. Prod. Res. Dev.*, **19** (1980) 136
118. A Datyner and M J Delayney, *JSDC*, **87** (1971) 263.
119. A Datyner, M J Delayney and F Iijima, *Text. Res. J*, **43** (1973) 48.
120. *Telon S Process*, Bayer Tech Manual 481e, Part 1.
121. *The Chemistry and Technology of Leather*, (ed. F O'Flaherty, W T Roddy, and R M Lollar), Vol. 1, Reinhold, New York, 1956.
122. M Nierenstein, *The Natural Organic Tannins*, Churchill, London, 1934.
123. K Freudenberg, *Z. Physiol. Chem.*, **116** (1921) 277.
124. E Knecht, C Rawson and R Lowenthal, *A Manual of Dyeing*, 6th edn, Vol. I, Griffin, London, 1920.
125. C C Cook, *Rev. Prog. Col.*, **12** (1982) 73.
126. F Rowe, *JSDC*, **54** (1938) 98.
127. A S Travis, *The Rainbow Makers*, Lehigh University Press, Bethlehem, 1993.
128. O Witt, *JSDC*, **1** (1885) 92.
129. J S Kelson amd L A Holt, *JSDC*, **108** (1992) 327.
130. USP 840,264 (1907).
131. USP 1,238,307 (1917).
132. J Shore, *JSDC*, **87** (1971) 3.
133. C Calin, *Text. Prax.*, **20** (1965) 835.
134. D F Scott, *Dyer*, **136** (1966) 365.
135. R J Janas, *JSDC*, **86** (1970) 73.
136. S Yoshikawa and E Doi, *Sen-i Gakkaishi*, **31** (1975) 491.
137. K Ogasawara, Y Kato and T Kuoiwa, *Sen-i Gakkaishi*, **32** (1976) 121.
138. T L Dawson and J C Todd, *JSDC*, **95** (1979) 417.
139. J Shore, *JSDC*, **87** (1971) 37.
140. J L Ashworth and D Blackburn, *JSDC*, **81** (1965) 369.
141. N J Christie, *Amer. Dyest. Rep.*, (9) (1978) 27.
142. BP 4648 (1911).
143. BP 8511 (1912); BP 8512 (1912); BP 24,216 (1912).
144. BP 24,982 (1912); BP 8028 (1914); BP 18,259 (1913); BP 17,172 (1914); BP 17,172 (1914); USP 1,232,620 (1917); USP 1,344,950 (1920); BP 331,216 (1920); BP 362,797 (1931); BP 494,871 (1939)
145. *The Manufacture and Practical Applications of German Synthetic Tanning Agents and Related Substances*, BIOS Final Report No 762, 2089607C.
146. P S Chen, *Syntans and Newer Methods of Tanning*, The Chemical Elements, Mass., 1950.
147. H G Turley, *J. Leath. Chem. Ass.*, **40** (1945) 58.
148. *Synthetic Tanning Agents and Leather Auxiliary Products of the IG Farbenindustrie*, BIOS Final Report No. 240, 2089607C.
149. BP 375,160 (1932); BP 425,527 (1935); BP 493,999 (1939); BP 494,042 (1939); BP 576,562 (1946); BP 610,038 (1948); BP 615,190 (1949); BP 768,762 (1957).
150. BP 148,139 (1921); BP 173,313 (1922); BP 218,316 (1924); BP 211,118 (1924); USP 1,564,002 (1926); BP 297,830 (1929); BP 353,872 (1931).
151. BP 305,013 (1928)
152. C M Whittaker, *Dyeing with Coal Tar Dyestuffs*, 2nd edn, Balliere, Tindall and Cox, London, 1926.
153. USP 1,450,463 (1923); BP 244,104 (1927).
154. BP 360,378 (1931); USP 1,928,257 (1933).
155. M Tomita and M Tokitataki, *JSDC*, **96** (1980) 297.
156. USP 4,619,853 (1986).
157. USP 4,680,212 (1987).
158. T F Cook, *Stain Blockers for Nylon Carpets*, Text. Res. Inst., New Jersey, 1991.
159. J K Aspland, *Amer. Dyest. Rep.*, **25** (4) 1993 153.
160. S M Burkinshaw, *Colourage*, **37** (1991) 51.
161. S M Burkinshaw, K D Maseka, R Gordon and D Marfell, *Proceedings of the 1994 AATCC Int. Conf.*, 1994.
162. S M Burkinshaw, and N F Nikolaides, *Proc. 8th Int. Wool Textile Res. Conf.*, Vol. IV, WRONZ, Christchurch, 1990, p. 137.
163. S M Burkinshaw, and N F Nikolaides, *Dyes and Pigments*, **15** (1991) 225.

164. S M Burkinshaw, and N F Nikolaides, *Dyes and Pigments*, **16** (1991) 299.
165. C C Cook, and J Guthrie, *Polymer*, **22** (1981) 1439.
166. USP 5 350 422 (1994).
167. E Elöd and F Schachowsky, *Mell. Text.*, **23** (1942) 437.
168. T Vickerstaff, *The Physical Chemistry of Dyeing*, Oliver and Boyd, London, 1950.
169. P W Carlene, A S Fern and T Vickerstaff, *JSDC*, **63** (1947) 388.
170. V A Myagkov and A B Pakshever, *J. App. Chem. (USSR)*, **29** (1956) 839TP, 1341TP.
171. F T Wall and A Beresniewicz, *J. Phys. Chem.*, **60** (1956) 692.
172. A R Mathieson, C S Whewell and P E Williams, *J. Appl. Poly. Sci.*, **8** (1964) 2009.
173. J Marshall, *J. Poly. Sci.*, **6** (A-1), (1968) 1583.
174. J Boulton, *JSDC*, **62** (1946) 65
175. F T Wall and T J Swoboda, *J. Phys. Chem.*, **56** (1952) 50.
176. R H Peters, *JSDC*, **61** (1945) 95.
177. G A Gilbert and E K Rideal, *Proc. Roy. Soc.*, **A182** (1944) 335.
178. L Peters and J B Speakman, *JSDC*, **65** (1949) 63.
179. R H Peters, *Textile Chemistry*, Vol. III, Elsevier, Amsterdam, 1975.
180. H H Sumner, in *The Theory of the Coloration of Textile Fibres*, (ed. A Johnson), Dyers Co. Pub. Trust, Bradford, 1989.
181. I D Rattee and M M Breuer, *The Physical Chemistry of Dye Adsorption*, Academic Press, London, 1974
182. S R Sivaraja Iyer, in *The Chemistry of Synthetic Dyes*, Vol. VII, (ed. K Venkataraman), Academic, New York, 1974.
183. J Steinhardt and M Harris, *J. Res. Nat. Bur. Stands.*, **24** (1940) 335.
184. G Chantry, The self-diffusion of acids in nylon, PhD Thesis, Leeds University, 1971.
185. F T Wall and P M Saxton, *J. Phys. Chem.*, **57** (1953) 370.
186. F G Donnan and E A Guggenheim, *K. Physik. Chem.*, **162A**, (1932) 348.
187. W R Remington and E K Gladding, *J. Amer. Chem. Soc.*, **72** (1950) 2553.
188. L Peters, *J. Text. Inst.*, **51** (1960) T1290.
189. A R Mathieson and C S Whewell, *J. Appl. Poly. Sci.*, **8** (1964) 2029.
190. F C McGrew and A K Shneider, *J. Amer. Chem. Soc.*, **72** (1950) 2547.
191. H Zollinger, *Chimia*, **13** (1959) 100.
192. E H Daruwalla, *Colourage Annual*, (1970) 59.
193. M Karasawa, H Msekido and T Iijima, *J. Soc. Fiber Sci. Technol. Japan*, **21** (1965) 327.
194. B G Ferrini and H Zollinger, *Helv. Chim. Acta*, **50** (1967) 897.
195. E Atherton, D A Downey and R H Peters, *Text. Res. J.*, **25** (1955) 977.
196. E Elod and H G Frolich, *Mell. Text.*, **30** (1949) 103.
197. H Takasawa, N Kuroki and A Katayama, *Sen-i-Gakkaishi*, **24** (1965) 185.
198. M Mituishi, T Kichila, T Takaoka and T Ishiwateri, *Sen-i Gakkaishi*, **42** (1986) T-374.
199. M A White, PhD Thesis, Leeds University, 1968.
200. B Milicevic, *Mell Text.*, **54** (1973) 1071.
201. G Back and H Zollinger, *Helv. Chim. Acta*, **41** (1958) 2242; **42** (1959) 1526.
202. H Brody, *Text. Res. J*, **35** (1965) 844.
203. H Zollinger, G Back, B Milicevic and A N Roseira, *Mell. Text.*, **42** (1961)
204. M Greenhalgh, A Johnson and R H Peters, *JSDC*, **78** (1962) 315.
205. J Komiyama and T Iijima, *J. Poly. Sci.; Poly. Phys.*, **12** (1974) 1464.
206. T Tak, J Komiyama and T Iijima, *Sen-i Gakkaishi*, **35** (1979) T486.
207. Y Kawana, J Komiyama, J H Petropoulos and T Iijima, *J. Poly. Sci.; Poly. Phys.*, **23** (1985) 181.
208. R McGregor and P Harris, *J. Appl. Poly. Sci.*, **14** (1970) 513.
209. H E Ulery, *JSDC*, **90** (1974) 401.
210. H Brody, *Text. Res. J.*, (1965) 895.
211. G Valk, G Stein and A El Bendak, *Mell. Text.*, **57** (1976) 166.
212. G Valk and G Stein, *Mell. Text.*, **59** (1978) 593.
213. C D O'Briain and R H Peters, *JSDC*, **69** (1953) 435.
214. G Valk, G Stein and A El Bendak, *Mell. Text.*, **60** (1979) 580.
215. N J Bhatt and E H Daruwalla, *Text. Res. J.*, **34** (1964) 435.
216. I D Rattee, *Chem. Soc. Rev.*, **2** (1972) 145.
217. I D Rattee, *Colourage (Annual)*, (1970) 23.
218. J Komiyama, J H Petropoulos and T Iijima, *JSDC*, **93** (1977) 217.

219. A Datyner, M J Delaney and F Iijima, *Text Res. J*, (1973) 48.
220. J Kraska and K Blus, *JSDC*, **106** (1990) 110.
221. R H Peters and J H Petropoulos, *Bull. Inst. Text. Fr.*, **84** (1959) 59.
222. R McGregor, R H Peters and J H Petropoulos, *JSDC*, **77** (1961) 704.
223. J P Bell, *Text. Res. J*, **38** (1968) 984.
224. J P Bell, *J. Appl. Poly. Sci.*, **12** (1968) 627.
225. F Jones, in *The Theory of Coloration of Textiles*, 2nd edn, (ed A Johnson), Dyers Co. Pub. Trust, Bradford, 1989.
226. H Weisz, *Trans. Far. Soc.*, **60** (1967) 1801.
227. E Sada, H Kumazawa and T Ando, *JSDC*, **99** (1983) 92.
228. R M Barrer, *Symp. Fibrous Proteins*, SDC, Bradford, 1946.
229. E Atherton and R H Peters, *Text. Res. J*, **26** (1956) 497.
230. E Atherton, D A Downey and R H Peters, *JSDC*, **74** (1958) 242.
231. M Sekido, T Iijima and A Takahashi, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, **68** (1965) 524.
232. H Morizane, Y Suda and K Nakajima, *Sen-i Gakkaishi*, **27** (1971) 113.
233. K Kanno and T Iijima, *Sen-i Gakkaishi*, **26** (1970) 117.
234. M Kimura, J Yoshie and T Shimizu, *Sen-i Gakkaishi*, **28** (1972) 265.
235. J Komiyama, J H Petropoulos and T Iijima, *JSDC*, **93** (1977) 217.
236. H Morizane, Y Suda and J Shirota, *Sen-i Gakkasihi*, **27** (1971) 113.
237. R McGregor, R H Peters and J H Petropoulos, *Trans. Far. Soc.*, **58** (1962) 1054.
238. E Sada, H Kumazawa and T Ando, *J. Appl. Poly. Sci.*, **28** (1983) 3817.
239. E Sada, H Kumazawa and T Ando, *JSDC*, **100** (1984) 97.
240. E Sada, H Kumazawa and T Ando, *JSDC*, **102** (1986) 105.
241. R Price, in *The Chemistry of Synthetic Dyes*, Vol. III, (ed. K Venkataraman), Academic Press, New York, 1970.
242. F Beffa and E Steiner, *Rev. Prog. Col.*, **4** (1973) 60.
243. N A Evans and I Stapleton, in *The Chemistry of Synthetic Dyes*, Vol. VIII, (ed. K Venkataraman), Academic Press, New York, 1978.
244. F Beffa and G Back, *Rev. Prog. Col.*, **14** (1984) 33.
245. F Jones, in *Colorants and Auxiliaries*, Vol. 1, (ed. J Shore), Soc. Dyers and Col., Bradford, 1990.
246. *Dyeing and Finishing of Polyamide Fibres and their Blends with Other Fibres*, BASF Manual B 358e, BASF (1972).
247. G Back and H Zollinger, *Helv. Chim. Acta*, **41** (1958) 2242.
248. G Back and H Zollinger, *Helv. Chim. Acta*, **42** (1959) 1526.
249. J Hauss, *Mell. Text.*, **57** (1976) 925.
250. R Meldola, *JSDC*, **26** (1910) 103.
251. G Hallas, in *Colorants and Auxiliaries*, Vol. 1, (ed. J Shore), Soc. Dyers and Col., Bradford, 1990.
252. C V Stead, in *Colorants and Auxiliaries*, Vol. 1, (ed. J Shore), Soc. Dyers and Col., Bradford, 1990.
253. F Walker, in *The Chemistry and Application of Dyes*, (ed. D Waring and G Hallas), Plenum, New York, 1990.
254. J G Grundy, *JSDC*, **60** (1944) 205.
255. J Boulton, *JSDC*, **62** (1946) 65.
256. H R Hadfield and D N Sharing, *JSDC*, **64** (1948) 381.
257. H R Hadfield and H Seaman, *JSDC*, **74** (1958) 392.
258. G T Douglas, *JSDC*, **67** (1951) 133.
259. D R Waring, in *The Chemistry and Application of Dyes*, (ed. D Waring and G Hallas), Plenum, New York, 1990.
260. C M Whittaker, *JSDC*, **59** (1943) 69.
261. M Morita, T Iijima, M Yoshida and M Sekido, *J. Chem. Soc. Japan Ind. Chem. Sec.*, **70** (1967) 180.
262. L A Abdou and A Bendak, *Amer. Dyest. Rep.*, **71** (11) (1982) 35.
263. J G Grundy, *JSDC*, **60** (1944) 205.
264. Courtaulds: BP 533, 872 (1943).
265. J Ryu, J Dai, K Koo and T Wakida, *Amer. Dyest. Rep.*, (1992) 278.
266. W F Beech, *Fibre Reactive Dyes*, Logos, London, 1970.

267. GP 721,231 (1937).
268. P Rhys and H Zollinger, in *The Theory of the Coloration of Textile Fibres*, 2nd edn, (ed. A Johnson), Dyers Co. Pub. Trust, Bradford, 1989.
269. R L Denyer, D A Garrett and D R Lemin, in *Procion Dyestuffs in Textile Dyeing*, ICI, Manchester, 1962.
270. H Luettringhaus, *Amer. Dyest. Rep.*, (1961) 30.
271. E Ungermann and W Hacker, *SVF-Fachorgan*, **15** (2) (1960) 111.
272. R Buagmann, *SVF-Fachorgan*, **15** (2) (1960) 97.
273. H T Lockhande, A N Saligram and S R Shukla, *Amer. Dyest. Rep.*, **80** (3) (1991) 54.
274. H T Lockhande, A N Saligram and S R Shukla, *Amer. Dyest. Rep.*, **80** (5) (1991) 48.
275. H T Lockhande, A N Saligram and S R Shukla, *Amer. Dyest. Rep.*, **81** (2) (1992) 40.
276. G S J White, *JSDC*, **30** (1941) 710.
277. V Taurey, *Amer Dyest. Rep.*, (1940) 541.
278. E B Abbot, *JSDC*, **60** (1944) 58.
279. T Vickerstaff, *JSDC*, **59** (1943) 92.
280. *The Dyeing of Nylon Fibres*, ICI, Manchester, 1958.
281. I R Haynes, *Amer. Dyest. Rep.*, (3) (1980) 19.
282. H W Peters and J C Turner, *JSDC*, **74** (1958) 252.
283. K J Rowe, *Amer. Dyest. Rep.*, (6) (1981) 15.
284. S M Burkinshaw and J G Lu, *Dyes and Pigments*, **22** (1993) 131.
285. S M Burkinshaw and J G Lu, *Dyes and Pigments*, **22** (1993) 207.
286. K Suganuma, *Text. Res. J.*, (1979) 536.
287. J G Blacker and D Patterson, *JSDC*, (1969) 598.
288. A Munden and H Palmer, *J. Text. Inst.*, **41** (1941) 609P.
289. A Johnson, R H Peters and A S Ramadan, *JSDC*, (1964) 129.
290. J Wegmann, *Can. Text J*, (11) (1962) 37.
291. E H Daruwalla and H A Turner, *JSDC*, **69** (1953) 440.
292. R McGregor, R H Peters and C R Ramachandran, *JSDC*, **85** (1969) 6.
293. C L Bird and D F Scott, *JSDC*, **72** (1956) 56.
294. P Gruner and J Janousek, *JSDC*, **85** (1969) 3.
295. T Hori, I Fujita and T Schmizu, *JSDC*, **102** (1986) 181.
296. T Hori, Y Sato and T Shimizu, *JSDC*, **97** (1981) 6.
297. D F Scott and T Vickerstaff, *JSDC*, **76** (1960) 104.
298. Lo S S, The dyeing of nylon 6.6 with reactive disperse dyes, MSc Thesis, Leeds University, 1991.
299. M Dohmyou, Y Shimizu, and M Kimura, *JSDC*, **106** (1990), 395.
300. S M Burkinshaw and G Collins, *Dyes and Pigments*, **25** (1994) 31.
301. W M Gardner, *JSDC*, **38** 171 (1922).
302. A G Green and K H Saunders, *JSDC*, **39** 10 (1923); **40** 138 (1924).
303. R K Fourness, *JSDC*, **69** 513 (1956).
304. S M Burkinshaw and G Collins, unpublished work.
305. J Griffiths and R I McDarmaid, *JSDC*, **93** (1977) 455.
306. G Hallas, J F Dawson and S M Burkinshaw, *BP 2 221 693B* (1991).
307. S M Burkinshaw and G Hallas, *JSDC* **109** (1993) 78.
308. M R de Giorgi and A Cerniani, *Text. Res. J.*, **57** (1987) 563.
309. M R de Giorgi and A Cerniani, *Ann. Chim.*, **74** (1984) 159.
310. M R de Giorgi, A Cerniani and M G Pinna, *Ann. Chim.*, **76** (1986) 293.
311. M R de Giorgi, A Cerniani and A Pisano, *Mell. Text.*, **69** (1988) 567.
312. A K Saville, *Amer. Dyest. Rep.*, (1946) 51.
313. K Venkataraman, *The Chemistry of Synthetic Dyes*, Vol. II, Academic Press, London, 1952.
314. *The Chemistry of Synthetic Dyes and Pigments*, (ed. H A Lubs), Reinhold, New York, 1956.
315. U Baumgarte, in *The Dyeing of Cellulosic Fibres*, (ed. C Preston), Dyers Co. Pub. Trust, Bradford, 1986.
316. J Shore, in *The Dyeing of Synthetic Polymer and Acetate Fibres*, (ed. D M Nunn), Dyers Co. Pub. Trust, Bradford, 1979.
317. F Butterworth and G Crossland, BP 632,083.
318. G T Douglas, *Amer. Dyest. Rep.*, (1951) 122.

3 Acrylic

3.1. Introduction

Owing to the wide range of both chemical modifications (using comonomers, incorporation of additives and also polymer mixtures) and physical modifications (carried out at the polymerisation, dope preparation and spinning stages) employed in the preparation of polyacrylonitrile (PAN) fibres, the physical properties and dyeing characteristics of the fibres vary markedly between commercial varieties.

Unmodified polyacrylonitrile is extremely difficult to dye owing to the homopolymer's compact structure and high glass transition temperature, T_g (in the region of 105°C in air [1]). Copolymerisation [2–4] of acrylonitrile with one or more comonomers increases the thermoplasticity of the homopolymer and also reduces both the heat- and solvent-resistance, by reducing the structural regularity of the homopolymer; this, in turn, substantially improves the processability and also the dyeability of the fibre. Neutral comonomers, such as methyl acrylate or methacrylate, modify the crystalline structure of PAN; the ensuing, reduced compactness of the the fibre increases the permeability of the the fibre towards dyes. Polar, non-ionisable comonomers (e.g. ketones, ethers and alcohols) increase dye adsorption by virtue of enhanced non-ionic interactions with dyes. The addition polymerisation of polyacrylonitrile is commonly achieved using a potassium persulphate–sodium bisulphite redox initiator system, as a consequence of which, chain terminal sulphate and sulphonate groups are introduced into the polymer [5–9] which imparts to the fibre substantivity for basic (cationic) dyes. However, since, in the case of a fibre derived almost entirely from acrylonitrile, the number of such strongly anionic groups is limited (of the order 30–35 m-eq. kg^{-1} [10, 11]) and thus precludes dyeing to heavy depths, the use of acidic comonomers containing, for example, sulphonic, phosphoric or carboxylic acid groups, together with that of alternative polymerisation catalysts [1], increases the number and also determines the nature of anionic groups present within the fibre which, in turn, influence both the rate and extent of uptake of cationic dyes. However, since many different copolymer compositions are employed [2, 12], the nature and number of anionic groups differs between commercial fibres; values in the range 50 to 150 m-eq. kg^{-1} have been reported [13]. The use of basic comonomers, such as 2-vinyl pyridine, that contain pyridine or amino groups, imparts to the fibre substantivity for anionic dyes; thus, differential-dyeing fibre variants are available.

Acrylic fibres contain between 5 and 15% of one or more comonomer while fibres that contain more than 15% comonomer are termed modacrylic. As an example, the acrylic fibre Courtelle S (Courtaulds) is a polymer comprising 92.9% acrylonitrile, 6% methyl acrylate and 1.1% 2-methyl acrylamido propane sulphonic acid (AMPS) whilst the modacrylic fibre Teklan (Courtaulds) comprises approximately 49.5% acrylonitrile, 49.5% vinylidene chloride and 1% itaconic acid [14]. Modacrylic fibres enjoy much less textile usage than their acrylic counterparts, the majority of commercially important examples possessing reduced flammability [4, 15]. Although the nature of the acidic dye sites within such fibres is similar to that of acrylic fibres [16], the strike rate of basic dyes is greater at lower temperatures than on acrylic fibres and the denser structure of modacrylic polymers results in lower dye diffusion, which can lead to problems in achieving level dyeing [17].

Although PAN fibres can be either wet or dry spun, the former method, employing aqueous solutions, is preferred [1, 2, 16, 18, 19] as it provides a more accessible microstructure and thus superior dyeability that results from the large internal surface area (of the order 200–300 m^2 g^{-1} [20]) provided by the production of microvoids during the coagulation process; the internal surface area of dry spun fibres is less than 1 m^2 g^{-1} [20].

The reader is directed elsewhere for further details of the variety of both chemical and physical modifications employed in PAN fibre production and the coloration of the fibres in relation to new fibre developments [2–4, 12, 16, 18, 19, 21–24].

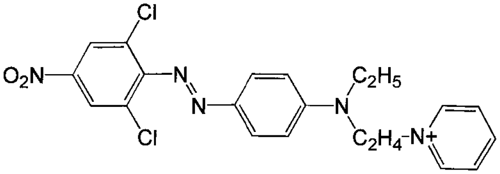
PAN fibres are characterised by a combination of desirable, all-round properties, especially their high resistance to outdoor exposure and high degree of chemical resistance. Their properties will, however, vary according to the presence, nature and manner of incorporation of comonomer and also the spinning method employed. From the viewpoint of dyeing, the more important properties of PAN fibres are their hydrophobic nature, which is mainly responsible for the characteristic high light fastness of basic dyes on the fibres, their high chemical resistance under typical dyeing and finishing conditions and the tendency to soften at temperatures above their T_g. The latter parameter, T_g, is of major significance in relation to dyeing since it is responsible not only for the characteristic excellent wet-fastness properties of resultant dyeings but also, especially in the case of cationic dyes, for the very high sensitivity of the dye–polyacrylonitrile fibre system which, in turn, imposes high levels of dyebath control upon the dyer.

Although, as discussed above, both basic- and acid-dyeable PAN fibres are available, the former type of fibre predominates; consequently, basic dyes are most widely employed in dyeing whilst disperse dyes, which are applicable to both fibre types, are used to a much lower extent and anionic dyes enjoy very small usage.

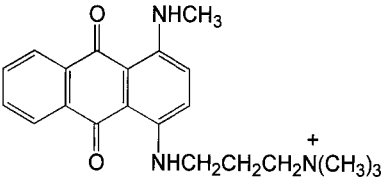
3.2. Cationic dyes

The chemistry of cationic dyes has been comprehensively discussed by several authors [25–29]. The dyes dissolve in water yielding coloured cations of, characteristically, high tinctorial strength and brilliance. Although some of the earliest chemical classes of basic dye, such as triphenylmethane and oxazine types, are still used to dye PAN fibres, they have mainly been supplanted by new classes of dye (e.g. anthraquinone, aza-, diaza- and triazacarbocyanines, hemi- and diazahemicyanines and naphtholactams) which were specifically developed for dyeing PAN fibres and exhibit excellent, all-round fastness properties on the substrate. Two types of basic dye are available for dyeing PAN fibres, namely *conventional* and *migrating* cationic dyes of which the former type, as exemplified by the Yoracryl (YCL), Basacryl (BASF), Maxilon (Ciba-Geigy) and Astrazon (Bayer) ranges, predominates. As is later discussed, *conventional* cationic dyes generally exhibit low migrating power on PAN fibres which results in problems of achieving level dyeing; to overcome this, hydrophilic, *migrating* cationic dyes, typified by the Basacryl MX (BASF), Remacryl E (Hoechst) and Maxilon M and BM (Ciba-Geigy) ranges, have relatively recently been introduced.

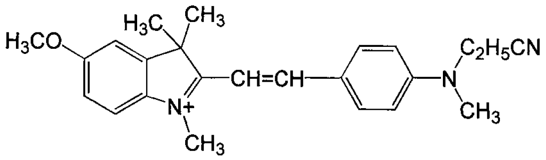
All cationic dyes used for dyeing PAN fibres can be divided into two chemical types, namely delocalised (pendant) dyes, in which the positive charge is localised on one, usually a nitrogen, atom (e.g. CI Basic Orange



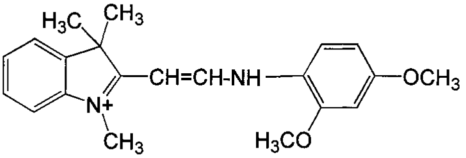
I



II



III



IV

30:1 (I) and CI Basic Blue 119 (II)) and delocalised dyes, as exemplified by CI Basic Red 14 (III) and CI Basic Yellow 11 (IV), in which the positive charge is delocalised over the entire dye molecule.

Generally, both conventional and migrating cationic dyes furnish a wide range of, typically, brilliant hues of excellent fastness to washing and wet treatments and light on PAN fibres.

3.2.1. Thermodynamics of dye adsorption

The uptake of cationic dyes on basic-dyeable PAN fibres follows a Langmuir adsorption mechanism [30] which clearly demonstrates that adsorption occurs primarily by means of ion–ion interaction operating between the cationic dye and the anionic (e.g. SO_3^-, OSO_3^- and COO^-) groups within the substrate. The Langmuir adsorption mechanism denotes that PAN fibres possess a saturation value for dye uptake which is of significance in the practical dyeing of PAN fibres with basic dyes (Figure 3.1).

Although the dyeing of PAN fibres with basic dyes was discussed shortly after the introduction of the fibre [31–34], detailed investigations of the mechanism of the dye–fibre interaction did not appear [35] until the development of high light fastness dyes, when several workers [36–38] proposed that the cationic dyes were bound, as salts, to acid groups in the fibre. Laucius *et al.* [37], in a study of the dyeing of Orlon (Du Pont), first reported the presence of a saturation value for the adsorption of cationic dyes. Glenz and Beckmann [10] observed that several basic dyes yielded a saturation value of 37 mmol kg^{-1} on Dralon (Bayer) at equilibrium at 80–100°C, which was in good agreement with titration values obtained for the polymer dissolved in DMF (namely 32 and 37 mmol kg^{-1} using ammonia and sodium hydroxide respectively) and, from the

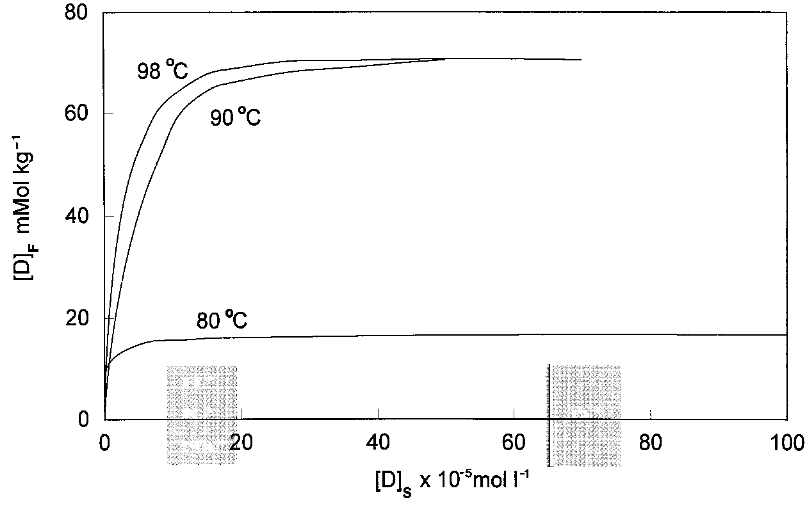
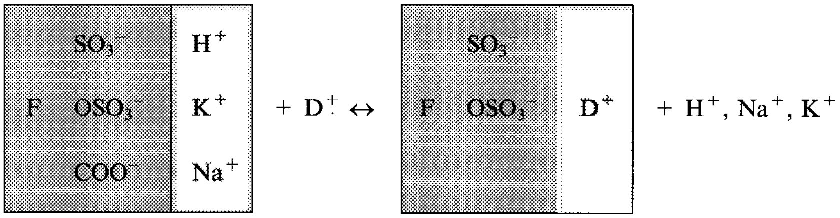


Figure 3.1 Adsorption isotherm for CI Basic Blue 3 on Courtelle S (Courtaulds) tow at pH 4.5 [197]
(Reproduced with the permission of D. Aitken)

shape of the equilibrium isotherms obtained, suggested that dye adsorption occurred at specific acid sites within the substrate. Langmuir plots of the adsorption of cationic dyes on PAN were subsequently obtained by several workers [13, 39, 40]; Vogel *et al.* [39] observed that the maximum extent of dye uptake corresponded to the sulphur content of the fibre and proposed that dye uptake occurred on sulphonate and sulphate groups that were present either within or at the chain ends of the polymer.



Scheme 3.1

Remington and Schroeder [41] suggested that in Orlon fibres the acidic sulphonate sites in the undyed fibre were neutralised by colourless cations which were subsequently displaced by dye cations during dyeing. This ion-exchange mechanism (Scheme 3.1, wherein D^+ is the cationic dye and F the fibre), in which the fibre exchanges the cations (e.g. sodium, potassium or hydrogen) associated with its component sulphate, sulphonic or carboxyl groups with the dye cation, has been confirmed by many other workers [1, 13, 40, 41–45]. Removal of the colourless cations within the fibre, which are usually sodium ions [1], yields values for acidic group contents that are equivalent to those obtained using Langmuir saturation values [13]. In the context of this ion-exchange mechanism, Cegarra [1] concluded that the number of available dye sites is determined by the number of dissociated acidic groups which are accessible for dye–fibre interaction to occur, that the dye must be dissociated in order for interaction to occur and that factors influencing ionisation of both fibre and dye will affect dye uptake.

Various workers [10, 40, 42, 46] observed ‘overdyeing’ namely, that the quantity of cationic dye adsorbed by PAN fibres could be slightly greater than that expected from the number of acidic groups present in the substrate. This anomaly has been explained by assuming that a small amount of the dye dissolved in the fibre by means of a simple partition mechanism [10, 35, 40, 46–48] or that dye aggregation occurred within the fibre [40, 46]. Forces of interaction other than ion–ion may contribute to adsorption [35, 49]. Owing to the structural characteristics of both dye and fibre, such as the highly polar nature of cyano groups in the substrate and substituents in cationic dyes, forces of interaction such as ion–dipole, dipole–dipole and dipole–induced dipole, together with hydrophobic interaction can be considered to contribute to dye–fibre substantivity.

According to the ion-exchange mechanism (Scheme 3.1), dyeing equilibrium can be described in terms of exchange of the dye cation (D^+) with the cation associated with the fibre, which, for simplicity, will be considered to be a proton (H^+). In the presence of additional, competing cations such as Na^+, the ion-exchange process is subject to the condition that the saturation value of the fibre (S) is given by equation (3.1).

$$S = [D^+] + [H^+] + [Na^+] \tag{3.1}$$

The resulting Langmuir isotherms are given by equations (3.2) to (3.5), from which, using equations (3.3) and (3.5), a plot of $[D^+]_f/[D^+]_s$ versus $(D^+)_s$ at either constant $[Na^+]_s$ or constant $[H^+]_s$, should give a straight line of slope $K^D{}_H/[H^+]_s$ or $K^D{}_{Na}/[Na^+]_s$ respectively, with an intercept of S on the abscissa.

$$\frac{[D^+]_f}{(S - [Na^+]_f - [D^+]_f)} = \frac{K^D{}_H}{[H^+]_s}\,[(D^+]_s \tag{3.2}$$

$$\frac{[D^+]_f}{[D^+]_s} = \frac{K^D{}_H}{[H^+]_s}\,(S - [Na^+]_f - [D^+]_f) \tag{3.3}$$

$$\frac{[\mathrm{D}^+]_\mathrm{f}}{(S - [\mathrm{H}^+]_\mathrm{f} - [\mathrm{D}^+]_\mathrm{f})} = \frac{K^\mathrm{D}{}_\mathrm{Na}}{[\mathrm{Na}^+]_\mathrm{s}}[\mathrm{D}^+]_\mathrm{s} \tag{3.4}$$

$$\frac{[\mathrm{D}^+]_\mathrm{f}}{[\mathrm{D}^+]_\mathrm{s}} = \frac{K^\mathrm{D}{}_\mathrm{Na}}{[\mathrm{Na}^+]_\mathrm{s}}(S - [\mathrm{H}^+]_\mathrm{f} - [\mathrm{D}^+]_\mathrm{f}) \tag{3.5}$$

where the suffices ‘f’ and ‘s’ represent fibre and solution respectively.

Rosenbaum [40], using an experimental PAN polymer, observed deviation from the predictions of equations (3.3) and (3.5) which were attributed to the weakly acidic nature of the anionic groups in the substrate. Harwood *et al.* [42], using five basic dyes on a PAN film, found that extrapolation of plots of $[\mathrm{D}^+]_\mathrm{f}/[\mathrm{D}^+]_\mathrm{s}$ versus $[\mathrm{D}^+]_\mathrm{s}$ in the absence of Na^+ ions (i.e. using equation (3.3)) yielded an apparent saturation value (S_1) that was consistent in magnitude (26–28 m-eq. kg^{-1}) for each dye used and approximately 80% of the total acid group content (35.1 m-eq. kg^{-1}) of the substrate as determined by titration. Furthermore, these workers [42] demonstrated that dye uptake in excess of S_1 could occur, which, in some cases, was equal in amount to the total of strongly acidic groups (S_1 + S_2) in the PAN film and proposed that dyeing may be associated with two kinds of anionic site, namely, the sulphonate end groups which corresponded to the apparent saturation value (S_1) and the sulphate groups which corresponded to the quantity S_2. Since equation (3.3) was obeyed only over 80% of the dye concentration range employed, and because the observed isotherms did not always exhibit uptake eqivalent to the quantity S_1 + S_2, the authors [42] proposed that the sulphate groups were either inaccessible or hydrolysed to non-substantive hydroxyl groups under the conditions encountered during equilibrium dyeing. Harwood *et al.* [42] also suggested that additional dye uptake (S_2) in excess of the apparent saturation value could be attributed to a solution mechanism for dyes of low substantivity. Guion and McGregor [50] concluded that the equilibrium adsorption of CI Basic Blue 22 on PAN fibres was not adequately described by equation (3.5), since the value of $K^\mathrm{D}{}_\mathrm{Na}$ varied with dye concentration. These workers [50] also found that at high electrolyte concentrations, chloride ions were adsorbed to a small, but nevertheless significant, extent and concluded that in addition to exchange of the sodium ions in the substrate associated with strongly acidic ($\mathrm{SO_3}^-$ and $\mathrm{OSO_3}^-$) groups, weakly acidic sites also participated in dye adsorption, the dye cations inducing dissociation of these weak groups. McGregor and Harris [51] proposed a general method for ion sorption in fibres containing ionisable groups; this model has been applied to the sorption of basic dyes on PAN fibres by several workers [42, 50, 52–60] and employs a Donnan approach to equilibrium sorption in which it is assumed that, provided the fibre is electrically neutral, the concentration of all ions on the fibre is related through a distribution constant to their concentration in the internal solution phase and that their concentration in the internal aqueous phase is related through a Donnan coefficient to their concentration in the external solution. According to this model, the distribution equation (equation (3.6)) is applied to all ions present, such as D^+, Na^+, H^+ and Cl^- ions (equations (3.7) to (3.10), wherein X represents the ion, i the internal phase, s the external solution, z the charge on the ion, K the distribution coefficient of the ion and λ the Donnan coefficient).

$$[X]_i = \lambda^z K [X]_s \tag{3.6}$$

$$[D^+]_i = \lambda K_D [D^+]_s \tag{3.7}$$

$$[Na^+]_i = \lambda K_{Na} [Na^+]_s \tag{3.8}$$

$$[H^+]_i = \lambda K_H [H^+]_s \tag{3.9}$$

$$[Cl^-]_i = (1/\lambda) K_{Cl} [Cl^-]_s \tag{3.10}$$

The distribution equations ((3.7) to (3.10)) can be combined, for example as equation (3.11), the ensuing exchange coefficient ($K^D{}_H$) not necessarily assuming that an ion-exchange mechanism operates:

$$\frac{K_D}{K_H} = K^D{}_H = \frac{[D^+]_f\,[H^+]_s}{[D^+]_s\,[H^+]_f} \tag{3.11}$$

Since for electrical neutrality equation (3.12) applies, the resulting sorption isotherm for hydrogen ion exchange is given by equation (3.13), which shows that the $[Cl^-]_f$ virtually increases the saturation value and can therefore give rise to overdyeing:

$$[D^+]_f + [H^+]_f + [Na^+]_f = S + [Cl^-]_f \tag{3.12}$$

$$\frac{[D^+]_f}{(S + [Cl^-]_f) - [Na^+]_f - [D^+]_f} = K^D{}_H \frac{[D^+]_s}{[H^+]_s} \tag{3.13}$$

The Donnan approach has been used to describe the dyeing mechanism of PAN fibres with basic dyes in a form that contains all the parameters involved, namely all ions (Na^+, H^+, Cl^- and D^+) and two types (S_1 and S_2) of dye site [57–59, 61].

The high substantivity of cationic dyes towards PAN fibres acrues primarily from the large negative zeta potential (of the order −44 mV [62]) established at the surface of the fibres in water; however, as discussed above, forces of interaction other than ion–ion may also contribute to substantivity. This negative zeta potential is gradually reduced and becomes slightly positive owing to accumulation of dye cations at the fibre surface, even at relatively low dye concentrations [10, 63]. Subsequent diffusion of this surface-adsorbed dye within the fibre re-establishes the negative surface potential and the adsorption-diffusion process is repeated. Glenz and Beckmann [10] showed that dye concentrations greater than that required to neutralise the zeta potential did not significantly change the potential, indicating that in most cases dyeing occurs from an almost constant, saturated concentration of dye at the fibre surface [27, 43, 45, 64, 65].

3.2.2. Kinetics of dye adsorption

The diffusional behaviour of cationic dyes in PAN fibres has received relatively little attention owing to difficulties encountered in accurately determining the diffusion coefficient [1]. Ring dyeing is easily obtained [10, 39] as a result of the characteristically very high substantivity of the basic dye–PAN fibre system. Rosenbaum [11, 45, 66] found that the apparent diffusion coefficient, D_a, increased with increase in sulphonate end group content of the fibre and was also independent of dye concentration. Although it has been suggested that the rate of dyeing is almost independent of liquor ratio [27], Cegarra [1] demonstrated that the dyeing rate constant k $(M_t/t^{1/2})$ increases rapidly in the initial stages of dyeing before remaining nearly constant with further increase in concentration. This author [1] thus concluded that the well-known phenomenon observed in the dyeing of PAN fibres with basic dyes, namely that level dyeing is promoted at high dye concentration, is due to the lower rate of dye adsorption at high dyebath concentrations. Sand [67] observed that the value of D_a increased with increasing concentration, and Cegarra [1] proposed that the rate of dyeing could be described by the exponential equation (3.14), the velocity constant, k, obtained increasing with increase in dye concentration in the dyebath.

$$M_t = M_\alpha(1-e^{-kT})^{1/2} \tag{3.14}$$

Subsequently, Cegarra *et al.* [196] demonstrated that the rate of dyeing at equilibrium was described by equation (3.15), wherein M_t and M_α represent the amount of dye adsorbed by the fibre at time t and equilibrium, respectively, and k is the rate constant at temperature T of the isotherm.

$$k_T = -\log\left(\frac{1-(M_t^2 / M_\alpha^2)}{t}\right) \tag{3.15}$$

These authors [196] showed that values of k obtained for three cationic dyes, each at the same concentration, increased with increasing temperature on three different PAN fibres, and that for each dye, at each temperature used, the values of k differed. From determinations of the acidic group content and the T_g of the three fibres studied, these workers concluded that k depended more on T_g than on the number of anionic groups present in the fibre, although the latter had some effect [196]. Chen *et al.* [68], in a study of the effects of fibre porosity and dye size on the diffusional behaviour of several cationic dyes in PAN fibres, obtained

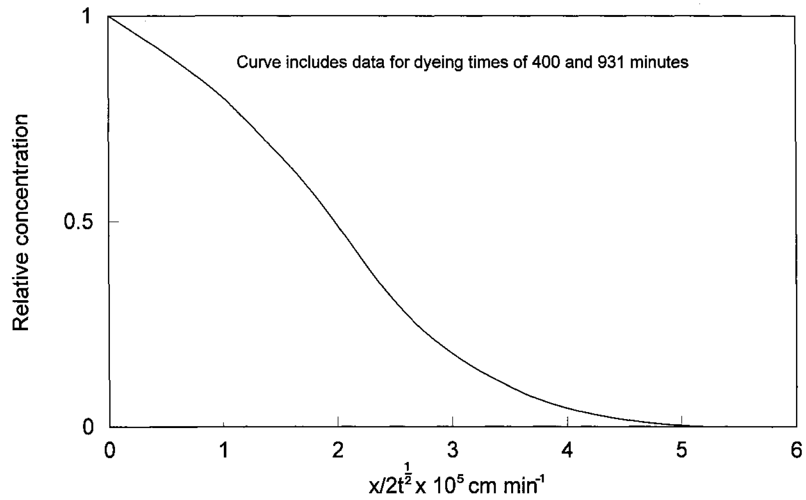


Figure 3.2 Concentration–distance profile for 1 gl^{-1} CI Basic Blue 22 at 95.6°C [70]
(Reproduced with permission from R.H. Peters and the Society of Dyers and Colourists)

no correlation between fibre porosity and D_a and obtained a non-linear relationship between D_a and cation molecular mass.

The non-Fickian diffusional behaviour of basic dyes within PAN fibres, which is very similar to that found for anionic dyes on nylon fibres, can be attributed to the very high substantivity of the dyes for the limited sites within the substrate. The pronounced concentration-dependence of diffusion coefficient is clearly demonstrated by the sigmoidal concentration–distance profiles obtained [69, 70] as shown in Figure 3.2. It is suggested [43, 71] that initially, the dye rapidly saturates the dye sites at the fibre surface followed by diffusion from this surface.

The observed concentration–dependence of cationic dye diffusion (Figure 3.3) can be explained in terms of the nature of the interaction between the cationic dye and the anionic groups in the substrate.

At the start of dyeing, because there are many available dye sites within the substrate and the dye concentration gradient across the substrate is very high, dye uptake on to the surface of the substrate will be rapid. For subsequent dye adsorption to occur, either adsorbed dye molecules must desorb from their original position and become re-adsorbed on to other dye sites further within the fibre, or new dye molecules must penetrate the dyed surface to become adsorbed at sites further within the substrate. Such a process will depend on the affinity of the dye, the concentration gradient across the substrate, the availability/accessibility of dye sites within the substrate as well as the number of adsorbed dye molecules. In the early stages of dyeing, because the dye concentration

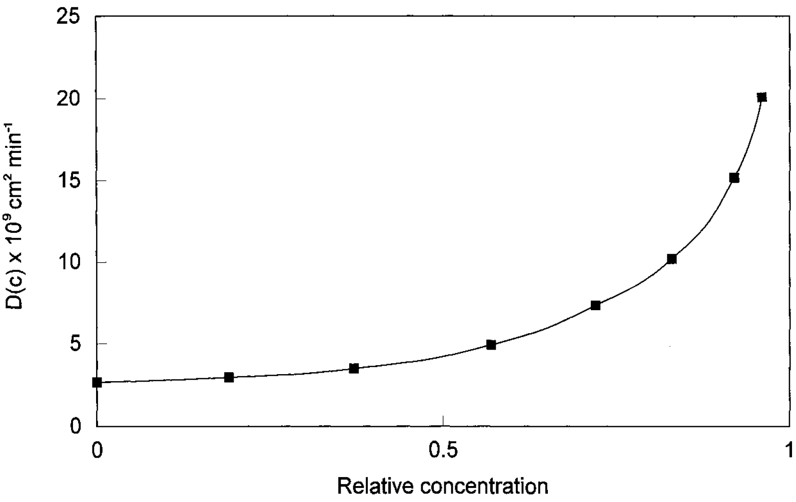


Figure 3.3 Concentration–dependence of the diffusion coefficient of CI Basic Yellow 13 at 99.8°C [70]
(Reproduced with permission from R.H. Peters and the Society of Dyers and Colourists)

gradient across the substrate is high and the number of available dye sites within the substrate is also high, a large proportion of the diffusing dye molecules will become readily adsorbed and therefore immobile so that the rate of dye diffusion and thus the diffusion coefficient will be low; this situation is reflected in the well-known high strike exhibited by many cationic dyes on PAN fibres. As dyeing proceeds, whilst the dye concentration gradient falls, as does the number of available dye sites in the substrate, the proportion of the diffusing molecules that are immobile decreases, with the effect that, in the later stages of dyeing, as saturation of the substrate is approached, the diffusion coefficient increases markedly, as observed [70].

Although Sivaraja Iyer [72] concludes that the cationic dye diffusion in PAN fibres is based on a site-to-site mechanism, an explanation of the concentration-dependence of cationic dye diffusion within PAN fibres has been given in terms of the ionic transfer of hydrogen (or sodium) ions for dye [70, 73].

3.2.3. Effect of pH on dye adsorption

Balmforth *et al.* [13] demonstrated that equilibrium uptake increased with increase in pH of application. The finding that this effect was more pronounced for fibres that contained weakly acidic groups than for fibres that contained only strongly acid groups led these workers [13] to conclude that whilst the dissociation of strongly acidic (e.g. SO_{3-}) groups is not significantly affected by pH, that of weakly acidic (e.g. COOH) groups is highly dependent on pH. Rosenbaum [40] demonstrated that equilibrium dye exhaustion decreased with decrease in pH as a result of a decrease in the ionisation of sulphonate groups in the fibre. The effect of pH on dye uptake has also been explained in terms of the change in zeta potential of the fibre [74] and also [1] competition between protons and dye cations on neutralisation of the negative zeta potential; thus, the rate of dyeing decreases with increasing pH, this effect being most noticeable for fibres that contain only weakly acidic groups [1]. Many PAN fibres exhibit a 10–20% increase in fibre saturation value (section 3.2.8) and rate of dyeing for a one unit increase in pH within the range pH 3.5 to 6 [27]. Commonly, basic dyes are applied to PAN fibres under acidic conditions in the range pH 3.5 to 6 (the range of highest stability for both fibre and dye [27, 73, 75]) and preferably between pH 4.5 and 5.5. Carlini and Paffoni [76] showed that four benzothiazolylazo cationic dyes decomposed during dyeing in the pH range 6.6 to 7, the stability of the dyes in aqueous solution depending on the nature of the quaternary groups present. A buffer system (commonly sodium acetate/acetic acid) is usually employed to avoid any increase in pH that may arise by evaporation of acid during dyeing; it has been suggested that control of dyebath pH to 0.5 units is preferred [77].

3.2.4. Effect of electroyte on dye adsorption

Electrolytes, such as sodium sulphate, reduce the equilibrium uptake of cationic dyes [13, 78] (Figure 3.4); the mobile sodium ions compete with the dye cation for acidic sites within the fibre [13, 35] and also displace the ion-exchange equilibrium (Scheme 3.1) to the left [1]. The rate of uptake of cationic dyes is also reduced by the addition of electrolytes to the dyebath [10, 13, 35, 75, 79, 80] since electrolyte decreases the equilibrium uptake of the dye and diffusion coefficient is concentration–dependent. Zimmerman and Cate [81] showed that the migration power of CI Basic Blue 54 increased markedly with increasing concentration of Na_2SO_4 up to 40% o.w.f. and thereafter increased at a slower rate. In a detailed study [82] using eleven electrolytes, retardation of dye uptake was found to depend on the ionic volume and electronegativity of the cation, the retarding action decreasing in the order $K^+ > Na^+ > Li^+ > Al^{3+}$. Anions had little effect on retardation of dye uptake and their nature was of little significance, the retarding effect decreasing in the order $SO_4^- > Cl^- > PO_4^{3-} > SCN^-$ and I^-. Support for these findings was obtained by Longo *et al.* [83] who demonstrated that adsorption of CI Basic Red 29 on to PAN fibre was markedly affected by the nature and size of the electrolyte cation, dye uptake decreasing with increasing cation size; electro-

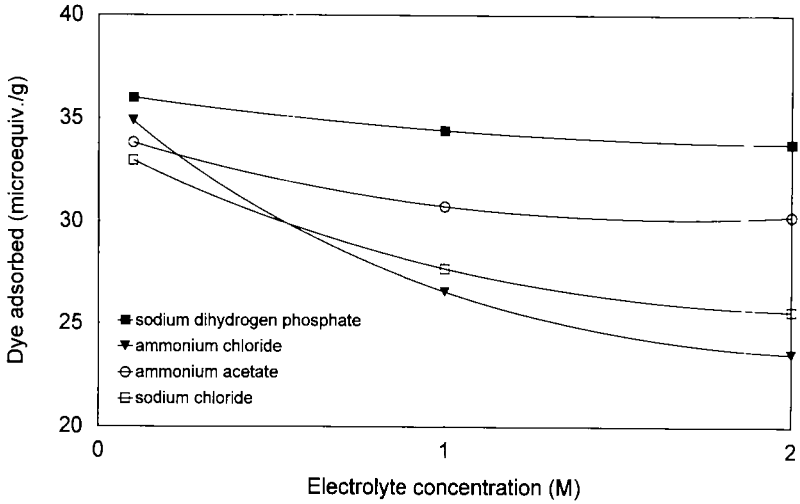


Figure 3.4 Effect of electrolytes on equilibrium cationic dye uptake [13] (Reproduced with permission from D. Balmforth and the Society of Dyers and Colourists)

lyte anions exerted little influence on dye uptake. Alberti *et al.* [84] showed that retardation of cationic dye uptake increased in the order $Li^+ < Na^+ < K^+$ and that the nature of the anion had little effect. In later work [85] these authors showed that retardation of dye uptake and saturation uptake of dye increased linearly with increase in radius of the hydrated electrolyte cation, results which were later confirmed by other workers [86]. Electrolytes also reduce the zeta potential of the fibre [11, 35]; this effect has been shown to depend upon the valency of the electrolyte cation [87]. In practice, electrolyte (NaCl or, preferably, Na_2SO_4) is often used to weakly retard dye uptake and thus promote level dyeing, the retarding effect of electrolytes being greatest for basic dyes of high *K*-value.

3.2.5. *Effect of temperature on dye adsorption*

As previously mentioned, the T_g of PAN fibres is of major significance in relation to dyeing; temperature has a most dramatic effect on both the rate and, to a lesser degree, the extent of dye uptake. Rosenbaum [43, 45, 88] proposed a free volume model to describe the marked temperature-dependence of dye diffusion within PAN fibres. At temperatures below T_g, amorphous polymers, such as PAN, behave as rigid solids or glasses in which the segmental mobility of the constituent polymer chains is effectively zero. An increase in temperature increases the segmental motion of the macromolecular chains; the limited regions of free volume begin to coalesce, forming larger voids in the polymer that permit increased segmental motion. This change in segmental mobility occurs over a very narrow temperature range and results in a dramatic increase in free volume. T_g denotes the temperature at which the changes take place and, in passing through T_g, the properties of the polymer change to those of a highly viscous, rubbery liquid. The transition from glassy to rubbery behaviour is attended by marked changes in the electrical, mechanical and thermodynamic properties of the polymer.

Thus, at temperatures below the T_g, little, if any dye uptake occurs owing to the highly compact, glassy structure of the polymer. At or about the T_g of the fibre, the rate of dye uptake increases owing to the onset of segmental mobility; further increase in temperature causes an exponential increase in the free volume within the polymer which, in turn, results in an equally dramatic increase in both the accessibility of anionic dye sites and the rate of dye diffusion. This situation is illustrated by the results shown in Figure 3.5. As discussed in detail in section 3.2.6 below, water is a plasticiser of acrylic fibres in that it reduces the T_g of the substrate. In the case of the Courtelle S tow employed in this particular study [106, 197], it was found that water decreased the T_g of the fibre from 92°C in air to 72°C. Thus, in Figure 3.5 it is evident that dye uptake only occurred at temperatures in excess of the 'wet' T_g, namely 72°C.

Peters and Wang [89] demonstrated that the accessibility of Acrilan for

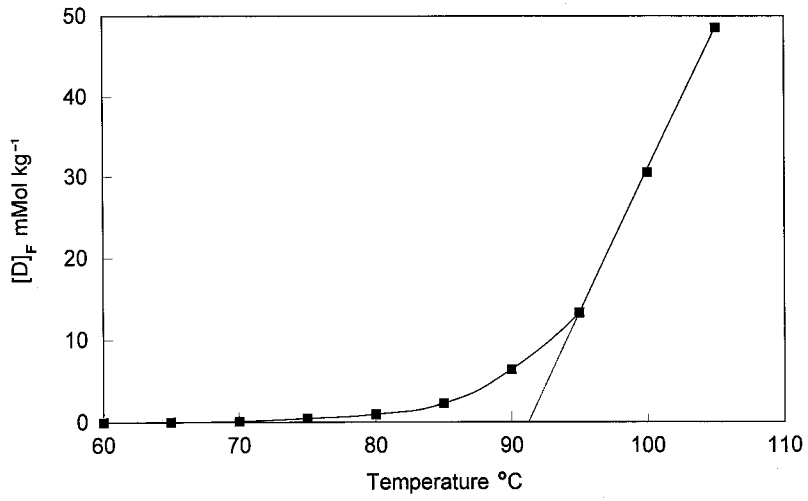


Figure 3.5 Effect of temperature on the adsorption of CI Basic Blue 3 (1.4×10^{-3} mol l^{-1}) on to Courtelle S tow at pH 4.5 [197]
(Reproduced with the permission of D Aitken)

CI Basic Green 4 was related to the fraction of the polymer segments that are mobile. The marked increase in dyeing rate above T_g occurs over a relatively small temperature range and saturation of the anionic dye sites is rapidly achieved; it is proposed that, within this region, a temperature change of 1°C increases the rate of dyeing by 30% [73]. The marked increases in dye diffusion that occurs at or about T_g is often referred to as the dyeing transition temperature, T_d, whose value is slightly greater than the T_g of the fibre as measured by some physical method. That Td is greater than T_g can be attributed to the fact that whilst T_g denotes the temperature at which segmental mobility commences, T_d denotes the particular temperature at which sufficient free volume becomes available for dye diffusion to occur. In Figure 3.5, the intercept of the dotted line on the x axis denotes the T_d for the particular dye used (CI Basic Blue 3), namely 91.3°C [197], this being some 19.3°C greater than the 'wet' T_g of the wet Courtelle S tow employed [106, 197].

It has been demonstrated for disperse dyes on PET [90] that values of T_d vary between dyes on the same fibre. It seems reasonable to assume that a similar situation will exist for basic dyes on PAN fibres; thus, for a given PAN fibre under given dyeing conditions, the value of T_d for several cationic dyes may vary according to the diffusional character of each dye. Temperature does not significantly affect the saturation value of PAN fibres [27], as evidenced by the work of Asquith *et al.* [91, 92] who demonstrated that although the number of accessible dye sites varies with temperature, the number is reasonably constant at temperatures greater than the T_g of the fibre whilst the number of accessible sites decreases rapidly at temperatures below T_g. Thus, at temperatures above T_g (85°C), virtually all anionic sites in Acrilan (Monsanto) were found to be accessible to cationic dye molecules whereas at temperatures below T_g they were not [91, 92]; consequently values of D_a obtained at temperatures above T_g do not relate to those secured at temperatures below T_g. Hossain *et al.* [93] propose that the availability of dye sites increases with increasing segmental mobility of the fibrous polymer chains.

$$\log D_a = \log D_0 - \frac{E^*}{\mathrm{R}T} \tag{3.16}$$

According to the Arrhenius equation (equation (3.16)) a plot of log D_a versus $1/T$ should be linear of slope E^*/R; however, Rosenbaum [88] obtained a sigmoidal relationship for the diffusion of CI Basic Green 4 into an experimental PAN fibre. The apparent diffusion coefficient increased with increasing temperature; below T_g, the plot of D_a against $1/T$ approached linearity but at temperatures greater that T_g, curvature was obtained (Figure 3.6).

Determination of the activation energy of diffusion, E^*, by plotting tangents to the curve at different points showed that at temperatures

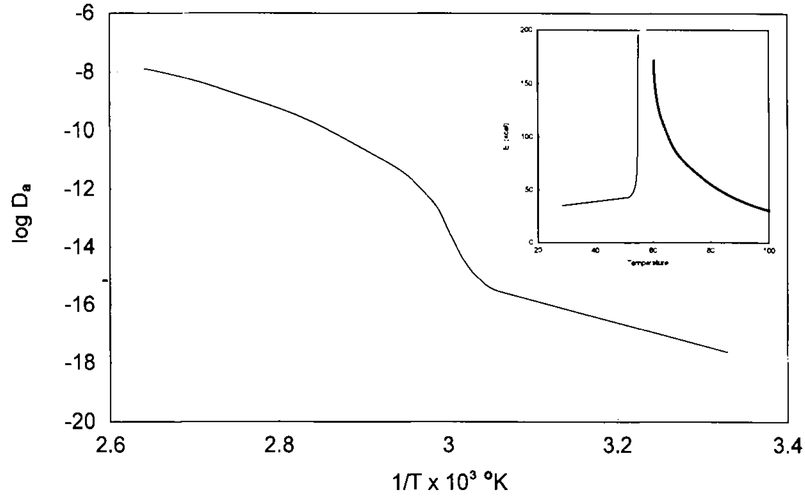


Figure 3.6 Variation of D_a with $1/T$ for CI Basic Green 4 [88]
(Copyright © 1965 John Wiley & Sons, Inc. Reprinted with permission)

below the T_g of the fibre, E^* was essentially constant until, with the advent of T_g, E^* increased dramatically; above T_g, E^* decreased exponentially with increasing temperature [88] (Figure 3.6). These results clearly demonstrate that the T_g of the fibre presents the major barrier towards dye uptake. Rosenbaum [88] correlated the temperature-dependence of both cationic dye diffusion and change in physical properties of PAN fibres using the WLF [94] equation expressed in the form of equation (3.17) wherein A and B are constants, D_T and D_{T_g} are diffusion coefficients at ambient temperature T and at T_g and log a_T is the shift factor.

$$\log \frac{D_T}{D_{Tg}} = \log a_T = \frac{A(T - T_g)}{B + (T - T_g)} \qquad (3.17)$$

The adherence of the diffusion data to equation (3.17) [88] confirmed that dye diffusion is governed by the segmental mobility of the polymer chains. Several workers [95–97] have proposed that both free volume and porous matrix models operate, the relative contribution made by each model depending on the structure of the particular fibre employed.

The T_g of PAN homopolymer has been shown to vary over a wide range; values of 52–180°C have been reported [92, 98, 99]. In a similar manner, considerable work has been carried out on the determination of the T_g of PAN copolymers and, in general, owing to the diverse variety of different copolymer compositions employed together with the range of processing variables used, a wide range of values for T_g have been reported.

3.2.6. *Effect of water on PAN fibres*

Since the dyeing of PAN fibres is normally carried out from aqueous dyebaths, the T_g of wet PAN fibre is of great importance in relation to dyeing. However, although several methods have been employed [100], relatively little work has been carried out in this area owing to practical difficulties which attend the determination of the T_g of wet fibre. Although PAN fibres are often regarded as being hydrophobic in nature, they nevertheless are sufficiently hydrophilic to enable them to be readily dyed with hydrophilic, cationic dyes, for which substantial water adsorption by the fibre is a necessity. The adsorption of water molecules by PAN fibres can be considered to occur by virtue of various forces of interaction, such as hydrogen bonding with the cyano and methylene groups in the fibre, dipole–dipole interactions with the highly polar cyano groups in the substrate, as well as ion–dipole forces operating between the various ionic groups present in the polymer and the water molecules.

Water, in addition to acting as a solvent for the dye and dyebath additives, reduces the T_g of PAN fibres; this reduction entails plasticisation and has been demonstrated by many workers. Bryant and Walker [101], in a study of the stiffness and resiliency of several types of fibre, observed that the T_g of PAN fibre in water was in the range 60–80°C and Beevers and Heap [102] concluded, during a study of the temperature-dependence of elastic recovery of Courtelle, that the fibre's T_g in water was approximately 60°C. Rosenbaum [103], using extension at break, observed that water reduced the T_g of PAN fibre by between 30 and 35°C; Gur–Arieh and Ingamells [104] related the extension in length of Acrilan filament to T_g reduction and demonstrated that the T_g of the filaments was reduced from 90°C in air to 57°C in water. Hori *et al.* [97], using Differential Scanning Calorimetry (DSC), showed that the T_g of both porous and conventional PAN fibres decreased with increasing water content and approached an almost constant value for each of the four fibre types examined. Asquith *et al.* [92], using Dynamic Mechanical Analysis (DMA), found that the T_g of Acrilan in water was 56°C; Bell and Murayama [105] employed DMA to show that the T_g of an acrylonitrile–vinyl acetate copolymer was reduced from 128°C in air to 80°C at 100% relative humidity and Aitken *et al.* [106], also using DMA, demonstrated that distilled water reduced the T_g of Courtelle S (Courtaulds) from 92°C in air, a value which closely agreed with those obtained for the fibre using both DSC and Thermo Mechanical Analysis (TMA) under comparable conditions, to 72°C. Although water is known to swell hydrophilic (natural) fibres, PAN fibres characteristically possess low water absorption (typically 1–3% at 20°C and 95% RH [107]) and swell only slightly in water [107, 108] at temperatures below T_g. The solubility parameter concept (section 1.2.2), which has been used to explain the mechanisms of both carrier dyeing and solvent-assisted dyeing, gives a quantitative measure of polymer swelling. Essentially, according to this concept, the ease of mixing of two substances (e.g. polymer and solvent) will be greatest when the solubility parameters (δ) of each substance are of equal magnitude. The solubility parameter of water is 96.2 $J^{0.5}$ $cm^{-1.5}$ [108], a value which differs markedly to that of many fibres, including those of PAN, for which values of δ have been reported as 53.6 $J^{0.5}$ $cm^{-1.5}$ [109] and 64.7 $J^{0.5}$ $cm^{-1.5}$ [110]. The large difference in the values of δ for water and PAN fibres confirms that the two materials are immiscible, the water having little, if any, solvating (i.e. swelling) power for the fibre, which, of course is observed in practice. Indeed, Gur–Arieh and Ingamells [111] report that reduction in T_g of Acrilan due to water occurs with no change in filament diameter and Fuzek [100] concludes that plasticisation due to water cannot be predicted on the basis of the moisture regain, contact angle or water imbibition of the fibre. Thus, fibre swelling cannot be considered to contribute to the observed plasticising action of water on PAN fibres.

Since a plasticiser functions as a diluent of polymeric substrates, its presence disturbing the regular structure of the polymer and thereby increasing thermoplasticity by a reduction of the magnitude of interchain bonding, then, in order to operate, the plasticiser must be adsorbed by the polymer and, in general, the extent of plasticisation will increase with increasing concentration of plasticiser in the polymer. In a study of the effect of water on the T_g and Young's modulus of nylon 6, Reimschussel [112] found that T_g decreased to a finite value with increasing water content. This author [112] proposed that the plasticising action of water (T_g reduction) on nylon 6 entailed the reversible replacement of intercaternary hydrogen bonds and that the limiting value for T_g was approached when the water content of the polymer approached that required for complete interaction with all accessible amide groups; this mechanism was also found to be applicable to other polymers including nylon 6.6. Aitken *et al.* [106] clearly demonstrated that the plasticisation of PAN fibre by water is reversible, in that the T_g of dry Courtelle S (Courtaulds) (90°C) was reduced to 72°C by immersion in water, the dry T_g (90°C) being restored when the water was subsequently removed from the wet fibre. The findings of Hori *et al.* [97], that the T_g of four PAN fibres decreased with increasing water content of the fibres, provides evidence that water acts as a diluent. Furthermore, these workers [97] also found that the T_g of each of the four types of commercial fibre used reached a finite value at different water contents, which concurs with the finding of Reimschussel for nylon 6 [112]. Thus, it can be proffered that the mechanism by which water reduces the T_g of PAN fibres may be similar to that proposed for nylon 6, namely that the water is reversibly bound (e.g. via hydrogen bonding) to appropriate (e.g. $-CN$) groups within the polymer. However, this phenomenon warrants further investigation.

3.2.7. Carrier dyeing

According to equation (3.17) the diffusion of basic dyes in PAN fibres is governed only by the term $(T - T_g)$ and, consequently, the rate of diffusion, and thus dyeing, can be increased either by increasing T or by reducing T_g, or both. Furthermore, since the T_g of the fibre constitutes the major barrier to dye diffusion, much work has attended methods of reducing this parameter in order to expedite dyeing; this particular approach concerns both carrier dyeing and solvent-assisted dyeing, which are applicable to fibres other than PAN. The commercial use of carriers is mostly confined to the dyeing of cellulose triacetate and polyester fibres using disperse dyes whilst solvent-assisted dyeing has not achieved widespread commercial utilisation. A detailed account of carrier dyeing is provided in section 1.2.11.

The plasticising action of many compounds and their effects on the dyeability of PAN fibres with basic dyes have been studied by several workers. Of the various compounds examined in this context, benzyl alcohol, which has been widely used in the solvent-assisted dyeing of wool [113–115], has been most extensively studied.

The isothermal uptakes of eleven carriers on Courtelle S were found to each follow a Nernst adsorption mechanism; the partition coefficient of the carriers increased with increasing hydrophobicity of the carriers [30]. Beal and Carbishley [116] described the enhanced uptake of basic dyes on Acrilan fibres furnished by solvent-assisted dyeing, the Irga-solvent (Ciba–Geigy) process being applicable to both printing and continuous dyeing methods. Rosenbaum [117] observed that while the effect of plasticisers on PAN fibres was not related to either the dielectric constant or solubility parameter of the plasticiser, some correlation existed between efficiency of plasticisation and dipole moment of the plasticiser. Ingamells *et al.* [118, 119] determined the effect of aqueous solutions of phenol and other carriers on reduction in T_g of Acrilan filaments, by measuring the elongation of the filaments at different temperatures and showed that the carriers reduced the T_g of the fibre. Gur-Arieh and Ingamells [111] measured the T_g of Acrilan filaments in water and in aqueous solutions of a range of organic compounds, using extension in filament length, and found no correlation between T_g reduction of wet Acrilan and fibre swelling. Although those compounds that reduced the T_g of the wet fibre tended to cause some swelling, the majority of T_g reduction was not proportional to the extent of swelling; indeed, some compounds increased

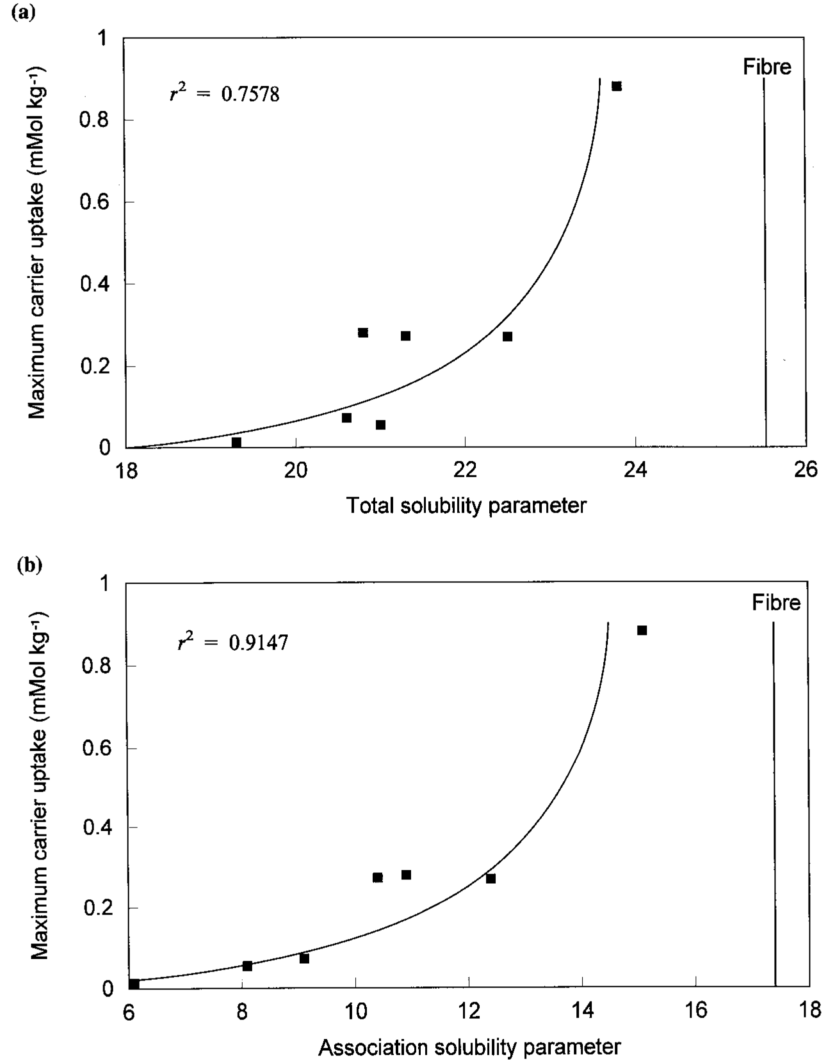
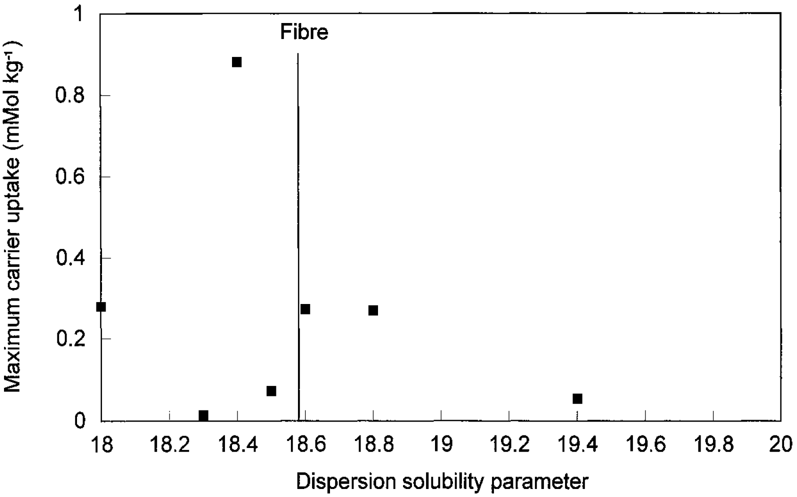


Figure 3.7 Relationship between maximum uptake of seven carriers at 80°C on acrylic tow and (a) δ_p (b) δ_a and (c) δ_d for the carriers. The vertical lines show the respective solubility parameter for the fibre [198]

(Reprinted from *Dyes and Pigments*, Vol. 23, S.M. Burkinshaw and D. Aitken, The effect of carriers on the dyeing of Courtelle S, pp. 225–242, Copyright 1993, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington, OX5 1GB, UK)

swelling but slightly increased T_g of the wet fibre [111]. In addition, these workers [111] found no correlation between total solubility parameter (δ_t) of the carrier and T_g reduction of Acrilan. In later work, Ingamells *et al.* [120] examined the effects of equimolar concentrations of several organic

(c)



compounds on T_g reduction of Acrilan filament; the extent of plasticisation (T_g reduction) was found to increase, non-linearly, as the total solubility parameter (δ_t) of the plasticiser approached that of the fibre. These workers [120] considered the relative contributions that the association (δ_a) and dispersion (δ_d) components of solubility parameter made towards T_g reduction, whereupon, it was observed, that whilst no relationship existed between plasticisation and values of δ_d for the fibre and plasticiser, a non-linear relationship was obtained between T_g reduction and δ_a for the plasticiser and fibre, maximum platicising action being secured when the δ_a of the fibre and plasticiser coincided. These authors [120] concluded that plasticization of Acrilan was controlled by polar forces only, dispersion forces playing no part in T_g reduction. The workers [120] also found that the extent of radial swelling of Acrilan filament imparted by an equimolar concentration of several plasticisers increased as the total (δ_t) and association (δ_a) solubility parameters of the plasticiser approached that of the fibre, with the effect that maximum T_g reduction occurred with least swelling. Although the correlation between δ_a and fibre swelling was low [120], this work confirms that plasticisation is not related to fibre swelling.

Confirmation of the proposal of Ingamells *et al.* [120] that carrier uptake is related to the association solubility parameter and, therefore, that polar forces are responsible for carrier–acrylic interaction, was obtained in a subsequent study [198] of the variation of maximum uptake of seven carriers on to Courtelle S (Courtaulds) with the δ_t, δ_a and δ_d solubility parameters, respectively. It was found (Figure 3.7) that whilst for each of the three solubility parameters considered, maximum carrier uptake increased as the respective solubility parameter of the carriers approached that of the fibre, the highest coincidence of all points to each of the three curves obtained (as given by the coefficient of determinations displayed in Figure 3.7) was observed for the plot of maximum carrier uptake versus δ_a values. However, the finding that, for each of the three solubility parameters considered, maximum carrier uptake increased as the respective solubility parameter of the carriers approached that of the fibre implies that other forces of interaction may also contribute to carrier–acrylic interaction.

Tokaoka [121] obtained a reduction in E^* of cationic dyes in PAN fibres in the presence of carriers such as phenol and nitrobenzene. The observed curvature of a plot of log D versus $1/T$ obtained by Ingamells [122] for CI Basic Green 4 on Acrilan filament demonstrated that E^* decreased with increasing temperature; the diffusion coefficient of the dye was found to be a function of $(T - T_g)$, showing that dye diffusion is governed by the segmental mobility of the polymer molecules. Asquith *et al.* [92], using DMA, demonstrated that *p*-nitrophenol reduced the transition temperature of dyeing for CI Basic Blue 22 on Acrilan from 83 to 57°C and reduced E^* from 62 to 39 kcal. A reduction of E^* for the uptake of basic dyes on PAN fibres has been reported for dyeing in the presence of benzyl alcohol [123] and other carriers [30]. Asquith *et al.* [92] also showed that fibre swelling played no part in T_g reduction and suggested that dis-aggregation of the dye in aqueous solution may also contribute to the enhanced dye uptake furnished by p-nitrophenol.

As discussed in section 1.2.11, several workers have suggested that carriers may have an effect on the dye. Accordingly, it is postulated [124] that the carrier adsorbed by the fibre increases the uptake of disperse dyes owing to the solubility of the dye in the carrier; Zimmerman *et al.* [125] argue that carriers increase the solubility of disperse dyes in the dyebath which results in enhanced rate of dyeing. Kim [30] measured the partition coefficient, K, of CI Basic Green 4 between water and eight different carriers and demonstrated that K was high for each carrier and the value of K varied considerably for each carrier. It was found that in aqueous solution, in the absence of PAN fibre, the dye was adsorbed by each carrier to an extent which increased with increase in the partition coefficient of the dye for the carrier. Kim [30] also showed that the partition coefficients of CI Basic Red 13 and CI Basic Blue 9 were lower than that of CI Basic Green 4 between water and the eight carriers and concluded that the solubility of cationic dyes in carriers depends on both the dye and carrier used. This author [30] also demonstrated that there was no correlation between the solubility of CI Basic Green 4 in a carrier and the effectiveness of that carrier in enhancing dye uptake, and thus concluded that solubilisation of the cationic dye contributes little towards carrier action.

Ingamells *et al.* [118, 119] showed that the extent of plasticisation of Acrilan filaments increased proportionally with increasing concentration of aqueous solutions of phenol and other carriers applied. Gur-Arieh and Ingamells [104] extended this approach to benzyl alcohol and found a linear relationship between the aqueous concentration of the alcohol applied and T_g of Acrilan filament. Gur-Arieh *et al.* [122] found that reduction in the dyeing transition temperature of CI Basic Green 4 on Acrilan filament was linearly related to the reduction in T_g of the fibre brought about by aqueous benzyl alcohol. Alberti *et al.* [123, 126–128] obtained a linear relationship between the dyeing transition temperature for CI Basic Green 4 on Velicren (SNIA) and concentration of benzyl alcohol in the dyebath, and also that the rate of dye uptake increased with increasing concentration of benzyl alcohol in the bath [126–128]. Kim [30] found that for various carriers, uptake of CI Basic Green 4 on to Courtelle S at different temperatures increased with increasing concentration of carrier in the dyebath up to a maximum concentration of carrier which corresponded to the solubility of the carrier. This worker [30] concluded that, at concentrations in excess of its aqueous solubility, the carrier was present in the dyebath as a third (liquid) phase for which the dye had greater affinity than either the fibre or water phases.

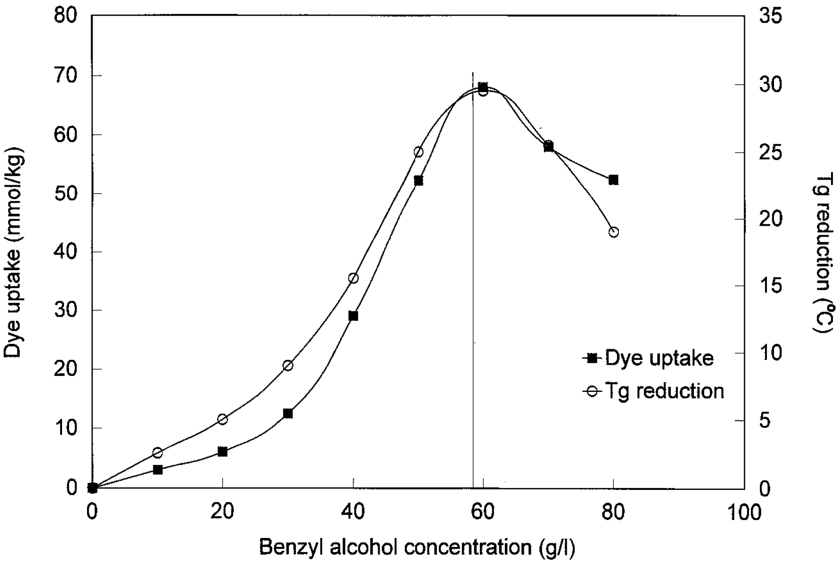


Figure 3.8 Effects of benzyl alcohol concentration on T_g and on uptake of CI Basic Blue 3 on Courtelle S tow at 80°C. The vertical line represents the aqueous solubility of the alcohol at 80°C [130]

(Reprinted from *Dyes and Pigments*, Vol. 18, D. Aitken, S.M. Burkinshaw and D. Price, The effect of Benzyl Alcohol on the T_g and dyeing behaviour of wet Courtelle S by means of DMA, pp. 23–34, 1992, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington, OX5 1GB, UK)

As Figure 3.8 shows, Aitken *et al.* [129, 130] obtained a non-linear relationship between T_g reduction of wet Courtelle S tow and concentration of benzyl alcohol adsorbed by the fibre; maximum plasticisation coincided with the maximum amount of plasticiser adsorbed by the substrate which, in turn, corresponded to the aqueous solubility of benzyl alcohol at the particular temperature employed (80°C). At concentrations in excess of the solubility of benzyl alcohol, the extent of plasticisation decreased, which was attributed to the plasticiser having greater affinity for the aqueous phase than for the fibre phase. These results [129, 130] confirm that benzyl alcohol functions as a true plasticiser of PAN fibre insofar as the extent of plasticisation (T_g reduction) increases with increasing concentration of benzyl alcohol adsorbed by the fibre. These workers [129, 130] also showed that the extent to which uptake of both CI Basic Blue 45 and CI Basic Blue 3 on to Courtelle S was enhanced, in the presence of benzyl alcohol, paralleled the extent to which the plasticiser reduced the T_g of the fibre (Figure 3.8). Dye uptake increased with increasing concentration of benzyl alcohol in the fibre, with maximum dye uptake coinciding with the maximum amount of plasticiser present in the substrate, which, in turn, corresponded to the aqueous solubility of benzyl alcohol; at concentrations in excess of the plasticiser's solubility, dye uptake decreased in accord with the decrease in amount of benzyl alcohol present in the fibre. These latter results clearly relate fibre plasticisation to enhancement of cationic dye uptake.

Kim [30], using several carriers, obtained a linear plot for the uptake of CI Basic Green 4 versus carrier concentration for Courtelle S, suggesting that each of the carriers used was of equal efficiency. According to the plasticisation theory of carrier action, in order for a carrier to function it must be adsorbed by the fibre and, therefore, the efficacy of a given carrier will depend upon the substantivity and diffusional characteristics of the carrier. If it is considered that solubility parameter concept represents, essentially, carrier–acrylic substantivity, then the molecular volume of a carrier can be considered as an approximate indication of the diffusional behaviour of the carrier within the substrate. In this context, Figure 3.9 shows that the maximum uptake of seven carriers on to acrylic tow was related to the molecular volume of the carrier [198].

Gur-Arieh *et al.* [122] showed that equilibrium uptake of CI Basic Green 4 on to Acrilan in the presence of benzyl alcohol, depended on $(T - T_g)$; this finding gained support in the work of Asquith *et al.* [92] for the uptake of CI Basic Blue 22 on to Acrilan in the presence of *p*-nitrophenol. The latter workers [92] also demonstrated that *p*-nitrophenol increased the accessibility of the dye sites within Acrilan. Peters and Wang [89] related the accessibility of Acrilan fibre to the loss tangent (tan δ) obtained using DMA by means of a structural parameter for the fibre that was related to the fraction of polymer segments that were mobile. From the finding that

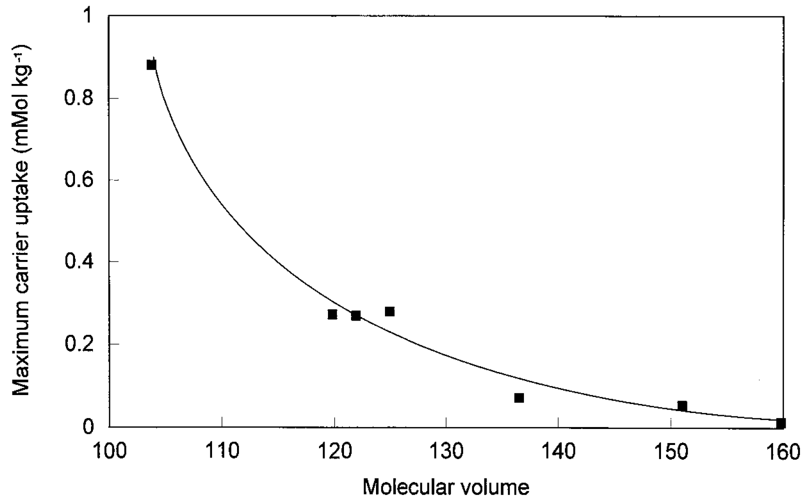


Figure 3.9 Relationship between maximum carrier uptake on to acrylic tow at 80°C and molecular volume for seven carriers [198]

(Reprinted from *Dyes and Pigments*, Vol. 23, S.M. Burkinshaw and D. Aitken, The effects of carriers on the dyeing of Courtelle S, pp. 225–242, Copyright 1993, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington, OX5 1GB, UK)

maximum uptake of CI Basic Green 4, in both the absence and presence of phenol and phenylphenol, was linearly related to the structural parameter, these workers [89] concluded that the accessibility of the fibre to the dye was related to the fraction of polymer segments that are mobile, which concurs with the suggestion made by Hossain *et al.* [93].

Dodd and Ingamells [131, 132] showed that perchlorethylene did not reduce the dry (in air) T_g of Acrilan 16, owing to the non-polar nature of the solvent and the dissimilarity in δ_a of the solvent and the fibre; furthermore, cationic dyes dissolve only slightly in the non-polar solvent. These workers [131, 132] examined the effect of several organic compounds on T_g reduction and dyeing of Acrilan 16 and employed benzyl alcohol as a cosolvent to facilitate dissolution of the organic compound and also cationic dyes. They found that the plasticising action of ethylene carbonate increased with decreasing concentration of benzyl alcohol in the cosolvent system and demonstrated that several commercial cationic dyes could be successfully applied to the fibre from an anhydrous perchlorethylene dyebath [131, 132].

3.2.8. Retarding agents

Characteristically, conventional cationic dyes exhibit very low migration power on PAN fibres as a result of their high substantivity and rapid uptake over a small (10–15°C) temperature range above the T_g of the fibre. Control of levelling by means of temperature control and electrolyte addition is inadequate; as a consequence, recourse is made to the use of commercial retarding agents, of which there are two types, namely cationic and anionic. Cationic retarders, which are principally used, are of two general types, namely conventional and polymeric.

3.2.8.1. Conventional cationic retarders. These [18, 19, 27, 35, 37, 44, 47, 64, 75, 82, 133–145] are, typically, water-soluble, colourless, quaternary ammonium compounds [18, 19, 27, 47, 133–136] of relative molecular mass (M_r) 300–500 [133], although other chemical types have been reported [18, 19, 47, 133], that function by competing with the dye cations for anionic sites at the surface and within the interior of the fibre. They reduce the rate of uptake by lowering the dye concentration gradient across the fibre and enhance dye migration by increasing the total number of cations in the dye–fibre system [27]. Zimmerman and Cate [134], using a titration-spectrophotometric method, demonstrated that cationic retarders are displaced by the cationic dye and that level dyeing is achieved by the dye and retarder retarding the uptake of each other during dyeing. Biedermann and Isichi [44] used atomic absorption to demonstrate that conventional cationic retarders are adsorbed on to PAN fibres by means of an ion-exchange mechanism. Since the number (and also nature) of anionic groups in PAN fibres vary, the quantity of conventional cationic retarder required to achieve optimum dye exhaustion and levelling varies between fibres, and also depends on the quantity of dye employed as well as the form of the substrate and dyeing machine used [133]. The amount of retarder used must be carefully chosen to prevent blocking [27, 137] of dye uptake and depends, in essence, on the dyeing characteristics of both the dyes and fibre used; the quantity of retarder required is calculated from information provided by the manufacturer. Cationic retarders are also ascribed K values [35, 82, 138, 141, 146] most commonly in the range 2 to 3.5 [146]; retarders with a K value slightly lower than that of the dyes with which it is employed gives optimum levelling and greatest cost-effectiveness [141, 146].

3.2.8.2. Polymeric cationic retarders. These retarders [27, 133, 145, 147–152] containing several hundred cationic groups per molecule, are mostly quaternised polyamines of M_r 1000–20 000 [133]. In contrast to their conventional cationic counterparts, polymeric retarders do not diffuse within the fibre but are adsorbed solely at the fibre surface and, consequently, do not enhance dye migration. This surface adsorption reduces the negative zeta potential of the fibre surface and also provides an electrical potential barrier which serve to reduce both the rate and extent of dyeing. Cegarra and Fiadeiro [150] determined the uptake of polyethoxylated amines by PAN fibres during dyeing with cationic dyes by measuring the total organic carbon content of the residual dyebath. In later work, Cegarra *et al.* [151, 152] showed that the retarding effect of polyethoxylated amines on the uptake of CI Basic Green 4 on PAN fibres increased with decreasing degree of ethoxylation and concluded that the retarding effect depended on the ease of penetration of the amine into the substrate and its solubility in the dyebath. Beckmann [27] reports that some polymeric cationic retarders can adversely affect the compatibility of dyes, particularly those of low affinity.

3.2.8.3. Anionic retarders. Beckmann [27] discusses the merits and demerits of anionic retarders [18, 19, 35, 133, 137, 139, 141, 145, 153–156] which enjoy considerably less usage than their cationic counterparts. These compounds interact with the cationic dye forming an anionic, thermally unstable dye–retarder complex that does not diffuse within the fibre [27, 156] and has low substantivity for the substrate. At low dyeing temperatures the complex is loosely bound to the fibre, facilitating dye migration, while at high temperatures the complex breaks down, releasing dye which can then be adsorbed on to the substrate. To prevent precipitation of the complex, a surplus of retarder is usually employed together with the addition to the dyebath of a non-ionic surfactant. Park [141] reports that anionic retarders do not lead to blocking problems but tend to be dye-specific in their action. Anionic retarders can also affect the compatibility behaviour of cationic dyes [146].

3.2.9. Dye–fibre characteristics

Since the uptake of basic dyes occurs on to a limited number of anionic sites within PAN fibres, then in order for a given mixture of dyes to yield the desired hue and depth of shade, the saturation characteristics of individual dyes and fibres must be known. A series of such saturation constants has been developed [10, 35, 157–159] the use of the three constants detailed below ensures that a given fibre is not over-saturated with dye, which, if allowed to occur, results in slow dyebath exhaustion and low fastness of the resulting dyeing to wet and rubbing treatments; methods for determining the following saturation characteristics have been devised by Bayer and later adopted by the Society of Dyers and Colourists [164].

- *Fibre saturation value* (A or S_f) is a fibre-specific constant, ranging in value from 1 to 3 for most commercial fibres, representing the number of accessible anionic sites per unit mass of the fibre.
- *Dye saturation factor* (f) is a dye constant, related to the purity and M_r of a dye, that represents the saturation characteristics of a given commercial basic dye.

- *Saturation concentration* (C) is the quantity of commercial dye (expressed as a percentage on mass of fibre) which saturates the given fibre; i.e. $C = A/f$.

Values of these three constants are provided by the dye manufacturer (and also the fibre maker in respect of the A or S_f value). In addition to the S_f value, the dyeing rate constant or V value of a PAN fibre can also be employed as a relative measure of the rate of dyeing of a given fibre in the initial stages of dyeing; values of this particular constant are also provided by the dye and fibre maker.

The high substantivity and low migration power of conventional cationic dyes on PAN fibres can result in problems of dye compatibility in admixture. Incompatible dyes block the uptake of each other [146] and also exhaust more rapidly than compatible dyes under the same application conditions [160, 161]. Much work has attended the characterisation of the compatibility of basic dyes in admixture [27, 35, 65, 146, 154, 160–168]. It is now widely accepted [146, 163–165] that the compatibility of a cationic dye for PAN fibre is characterised by the dye's compatibility or K value (or C or CV value) as devised by Beckmann [157]. In essence, the compatibility (K) value quantifies the adsorption of cationic dyes in admixture in terms of the diffusion coefficient and affinity of the dye. K values of cationic dyes are classified into five groups, 1 to 5 and are provided by the dye maker; in admixture, dyes of low K value exhaust before dyes of higher K value and dyes of equal K value yield virtually on-tone dyeing [146]. Commonly, cationic dyes possess K values of 3 [146] and the K values are valid under the majority of commercial dyeing conditions [146]. In addition to the K value, the standard dyeing time (e.g. T_{70} [35, 146]) provides information on the exhaustion rate of individual cationic dyes and can be used to quantify the rates of exhaustion of dyes in admixture.

The relative affinity, A_r, which is closely related to compatibility [27], is a measure of the migrating power of a cationic dye, being determined from the equilibrium uptake of the dye in the presence of a standard dye or cationic retarder for which the value of A_r is assumed to be unity [27, 146]. A high value of A_r indicates that the dye has low migrating power and its uptake is only slightly influenced by the presence of other cationic dyes, electrolytes or cationic retarders, although its uptake is markedly influenced by anionic retarders [27]. Beckmann [27] reports that the A_r values furnished by different dye makers are comparable for dyes of the same chemical constitution since A_r is unaffected by diluents in the dye. Siepmann [169] found, using several cationic dyes, that dyes of high A_r exhibited high exhaustion but low migration on PAN fibre, but also demonstrated that steric factors contributed to migration and concluded that dyes of low A_r need not necessarily possess high migration power.

3.2.10. Migrating cationic dyes

As discussed above, conventional cationic dyes characteristically exhibit rapid uptake on to PAN fibres and, with the exception of dyes of low substantivity [35, 39], possess low migration power on such substrates. This combination of properties causes problems in achieving level dyeing and recourse is made to the use of accurate pH and temperature control, compatible dyes and retarding agents. Both the high rate of exhaustion and low migration power of conventional dyes can be attributed to the dyes' high substantivity that accrues mainly from their large molecular size and highly cationic and hydrophobic nature. As their name implies, migrating cationic dyes exhibit greater migrating power on PAN fibres than their conventional counterparts; although the dyes are rapidly adsorbed by the substrate, they are able to migrate under typical dyeing conditions and thus yield level dyeings. The introduction of the first commercial migrating cationic dye range, Maxilon M in 1975 by Ciba-Geigy, was quickly followed by other ranges, as exemplified by the Basacryl MX (BASF), Remacryl E (Hoechst) and Maxilon BM (Ciba-Geigy) ranges.

Biedermann [172] reviews the work of several authors [166, 170, 171, 173–176], describing the development and physico-chemical aspects of the dyes as well as essential details of their application to PAN fibres. In essence, migrating cationic dyes are of smaller molecular size and are more hydrophilic than conventional basic dyes and therefore possess lower substantivity towards and greater diffusional power within PAN fibres; as a consequence, the dyes are rapidly adsorbed by the fibre but are able to migrate, yielding level dyeings. Despite the low molecular size and high diffusional behaviour of the dyes, their wet fastness properties on PAN fibres is excellent owing to the fact that domestic laundering is usually carried out at temperatures (commonly 60°C) below the T_g of the substrate, under which conditions the dye is unable to diffuse out of the fibre.

The dyes are applied to PAN fibres in the presence of electrolyte and a cationic retarding agent, the latter being of similar K value to that of the dyes. Conventional cationic retarders are not suitable and the admixture of migrating and conventional dyes is not usually recommended.

3.2.11. Gel dyeing

Gel- or producer-dyed PAN fibres, as exemplified by Neochrome Courtelle of Courtaulds, are available in a variety of fibre types, decitex, lustres and also shades [177]. PAN fibre is commonly wet spun from aqueous solutions of solvents such as sodium thiocyanate or DMF, residual solvent being removed from the extruded filaments by washing [178]. In gel dyeing, the washed filaments are passed, commonly in the form of tow, through an aqueous cationic (or disperse [14]) dyebath, followed by rinsing to remove surplus dye, drawing and, finally, drying [178]. The technique has also been applied to dry-spun PAN fibres [179, 180] and drawing prior to dyeing has also been described [181]. In the gel state the fibre is highly absorbent and dye diffusion within the water-filled voids of the substrate is rapid [12, 19, 182] even at the relatively low temperatures employed. Gel dyeing offers the advantages of high flexibility, small batches can be dyed economically and shade changes made easily [12, 19, 178].

3.3. Disperse dyes

The chemistry of disperse dyes is fully discussed in Chapter 1. Characteristically, disperse dyes exhibit excellent levelling but poor build-up on PAN fibres, the resultant dyeings generally possessing moderate to high fastness to light and to wet treatments but being of duller hue than those secured using cationic dyes. This dye class enjoys very limited usage on PAN fibres mainly because the build-up characteristics of the dyes are insufficient to furnish medium and heavy depths of shade and also because of the outstanding brilliance of hue, relative ease of application and excellent all-round fastness properties of basic dyes on these fibres. As a consequence of their limited usage on PAN fibres, relatively little research work has attended their application to the fibres.

3.3.1. Thermodynamics of dyeing

The uptake of disperse dyes on PAN fibres follows a Nernst (Partition) adsorption mechanism [183, 184], as observed for the uptake of the dyes on other synthetic fibres. The mechanism of the aqueous phase transfer of the dyes to PAN fibres is identical to that described in Chapter 1 for polyester fibres, namely that adsorption occurs from a dilute, aqueous solution of the dye which is replenished by dissolution of dye from the bulk dyebath dispersion; diffusion of the disperse dye within the fibre can be considered to take place by either a *solid solution* or *adsorption-at-sites* mechanism. The Nernst adsorption mechanism indicates that the nature of the interaction between disperse dyes and PAN fibres is, in contrast to that of cationic dyes and such fibres, essentially non-ionic. PAN fibres contain, typically, a high proportion of highly polar cyano groups together with a lower proportion of both weakly ($-COOH$) and strongly ($-SO_3H$, $-OSO_3H$) acidic groups. Feichtmayer and Wurz [46] suggest that dipole–dipole interaction operating between cyano groups in the substrate and polar groups in anthraquinone disperse dyes is the major contributor towards dye uptake, although dispersion and induction (dipole–

induced dipole) forces of interaction could also contribute to dye–fibre substantivity. It can be considered that in addition to such forces of interaction, others, such as hydrogen bonding, hydrophobic interaction as well as ion–dipole interaction operating between the ionic groups in the substrate and the polar disperse dyes may contribute towards dye–fibre substantivity. Hotai and Okada [185] demonstrated that both polar and non-polar forces operate between disperse dyes and PAN fibres in that both the affinity and heat of dyeing are increased by the incorporation of polar and non-polar groups into the dyes. Kaushik and Deshpande [184], in a study of the adsorption of six monoazo disperse dyes on Indacrylon (IPCL) fibre, concluded that the affinity of the dyes increased with increasing basicity of the dye, an observation that confirmed the early finding of Hadfield and Sokol [183], and also that the saturation value of the dyes increased with decreasing molecular size of the monoazo dyes. These workers [184] also demonstrated no correlation between saturation uptake and δ_t of the six dyes, although some correlation between saturation uptake and values of δ_d, δ_a and also $(\delta_d/\delta_a)^2$ for the monoazo dyes was found.

The characteristic low substantivity of disperse dyes towards PAN fibres, which is reflected in the poor build-up character [27, 73, 183, 186, 187], low exhaustion [27, 32, 34, 37, 73, 183, 184, 186, 188–190] and excellent levelling properties [37, 183, 186, 187, 190] of the dyes on the fibres, can be attributed to the hydrophilic nature of the substrate. Although PAN fibres are regarded as being hydrophobic, this hydrophobicity accrues mainly from aliphatic chain methylene (CH_2) groups which cannot be expected to provide strong hydrophobic interactions with a hydrophobic disperse dye. Furthermore, the acidic groups in the fibre can be considered to be ionised at the pH values typically encountered during dyeing with disperse dyes and will also be highly solvated by water, with the result that the hydrophobic fibre contains a reasonably high proportion of strongly hydrophilic groups. Peters [73] suggests that adsorption of a disperse dye on a fibre will be greatest when the hydrophobic/hydrophilic character of the dye matches that of the fibre. In the case of PAN fibres, it can be proffered that the fibre is substantially less hydrophobic (or more hydrophilic) than the disperse dye and thus dye–fibre substantivity is low.

The saturation value of disperse dyes on PAN fibres is considerably lower than that of the dyes on other hydrophobic fibres such as nylon and secondary cellulose acetate [183, 186, 188]. This is illustrated by the results shown in Table 3.1, wherein the greater adsorptive character of secondary cellulose acetate is apparent.

Peters [73] suggests that such differences in the affinity of a disperse dye between fibres can be attributed to differences in the amount of crystalline or other regions which are inaccessible to the dyes. This author [73] pro-

Table 3.1 Saturation values for disperse dyes [183]

	Saturation uptake (g dye 100 g^{-1} fibre)		
Dye	Acrilan	Orlon 42	Sec. cell. acet.
CI Disperse Yellow 3	2.6	1.3	7.4
CI Disperse Orange 3	6.0	2.8	10.0
CI Disperse Red 11	7.9	7.6	12.2
CI Disperse Blue 26	3.2	4.0	8.6
CI Disperse Blue 1	8.3	8.0	10.6

(Reproduced with permission from H.R. Hadfield and the Society of Dyers and Colourists)

poses that the inclusion of a volume term, *v*, which reflects the amount of water adsorbed by the fibre and is a characteristic of a given fibre, in the equation for affinity (equation (3.18)) would change the value of affinity by an amount appropriate to each fibre:

$$-\Delta\mu^0 = RT \ln \frac{[D]_f}{v\,[D]_s} \tag{3.18}$$

However, the use of this accessibilty parameter (*v*) would not fully account for the low uptake of disperse dyes on PAN fibres in view of the fact that the accessibility of the fibre to cationic dyes must be very high as these dyes exhibit high uptake on the fibres from which it can be concluded that a similar level of accessibility should operate in the case of disperse dyes.

3.3.2. Kinetics of dyeing

The diffusion of disperse dyes within PAN fibres is considered to be Fickian, as observed for other hydrophobic fibres [191], demonstrating the non-specific nature of the dye–PAN fibre interaction. Several workers [34, 188] demonstrated the temperature-dependence of dye uptake on PAN fibres, the extent of dye uptake showing a marked increase in the region of T_g (Figure 3.10). This behaviour is identical to that of basic dyes on PAN fibres and can be attributed to diffusion of the disperse dye being dependent on the T_g of the fibre, as demonstrated by McGregor *et al.* [192], who, by using a microdensitometric technique, showed that the diffusion coefficient of CI Disperse Blue 1 in Courtelle film increased with increasing temperature over the range 78.5 to 97°C and obtained a value of 293.2 kJ mol^{-1} for E^* of the dye below 90°C and 201.6 kJ mol^{-1} above 90°C.

The use of carriers to enhance the rate of dye diffusion was reported shortly after the commercial introduction of the fibres [34, 190]. Peters and Ingamells [119] employed several water-soluble carriers and showed that

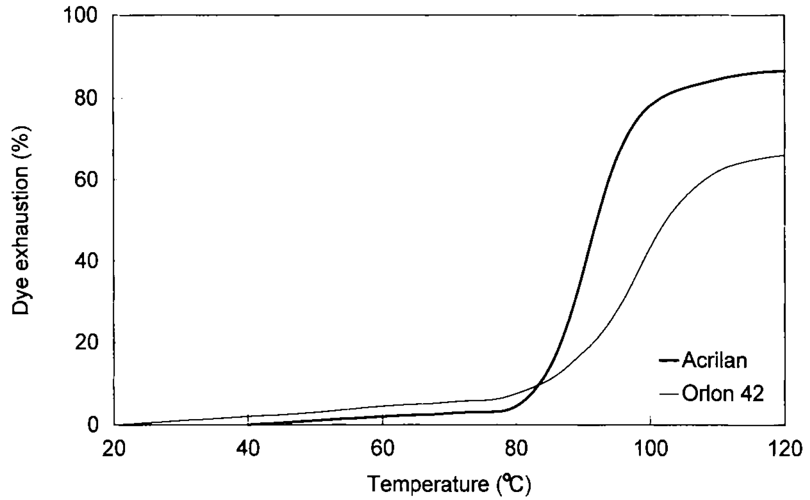


Figure 3.10 Temperature-dependence of uptake of 2% o.m.f. CI Disperse Blue 16 [188]
(Reproduced with permission of B. Kramrisch and the Society of Dyers and Colourists)

the diffusion coefficient of *p*-aminoazobenzene within Acrilan filaments increased with increase in the value of $(T \quad T_g)$ and also that the value of E^* of the dye decreased with increasing concentration of phenol in the dyebath; these workers concluded that the diffusion of disperse dyes in PAN fibres is governed by the segmental mobility of the polymer chains and that carriers increase this segmental mobility. Support for these findings was provided by the work of Gur–Arieh and Ingamells [104, 111] who demonstrated that the diffusion coefficient of CI Disperse Orange 3 in Acrilan filament increased and E^* of the dye decreased with increasing concentration of benzyl alcohol in the dyebath. Kaushik and Deshpande [193, 194] found that both the rate and extent of uptake of three monoazo dyes on Indacrylon fibre were enhanced by the addition of benzyl alcohol to the dyebath. Maximum carrier action was obtained using 0.3 mol l^{-1} benzyl alcohol which was attributed [193, 194] to the limited water-solubility of the carrier and the formation of a third (liquid) phase in the dyebath in which the dye was more soluble, as previously suggested by Balmforth *et al.* [195] to explain similar results obtained for the action of carriers on the uptake of disperse dyes on cellulose acetate fibres.

3.3.3. General considerations

Disperse dyes are applied to PAN fibres in the pH range 3.5 to 6 [27] usually in the presence of a levelling agent using recipes which are similar to those adopted for the dyeing of polyester fibres with the dyes at temperatures in the range 80 to 100°C [27]; a clearing treatment of the dyed material enables optimum fastness to be achieved [27].

References

1. J Cegarra, *JSDC*, **87** 149 (1971).
2. E Cernia, in *Man-made Fibers: Science and Technology*, Vol. 3, (eds H F Mark, S M Atlas and E Cernia), Interscience, New York, 1968.
3. F A J Ultee, *Textile Prog.*, **3** (1) 61 (1971).
4. D J Poynton, *Textile Prog.*, **8** (1) 51 (1976).
5. R G R Bacon, *Quarterly Rev. London*, **9** 289 (1955).
6. Y Tsuda, *J. Appl. Poly. Sci.*, **5** 104 (1961).
7. L H Peebles, *J. Appl. Poly. Sci.*, **17** 113 (1973).
8. I Matsubara, *Bull. Chem. Soc. Japan*, **33** 1624 (1960).
9. R Yamadera, *J. Poly. Sci.*, **50** S4 (1961).
10. O Glenz and W Beckmann, *Mell. Text.*, **38** 296, 783, 1152, (1957).
11. S Rosenbaum, *Text. Res. J.*, **34** 159 (1964).
12. S Balasubramanian, *Man-made Textiles in India*, **22** 191 (1979).
13. D Balmforth, C A Bowers and T H Guion, *JSDC*, **80** 577 (1964).
14. Courtesy of R Cox, Courtaulds Fibres Plc, Derby.
15. A R Horrocks, M Tunc and D Price, *Textile Progress*, **18** (1, 2, 3) 151 (1989).
16. K Silkstone, *Rev. Prog. Col.*, **12** 22 (1982).
17. A M Jowett, *Int. Dyer*, **154** 437 (1975).
18. I Holme, *Chimia*, **34** 110 (1980).
19. I Holme, *Rev. Prog. Col.*, **13** 10 (1983).
20. J P Craig, J P Knudsen and V F Holland, *Text. Res. J.*, **32** 465 (1962).
21. A M Jowett and M C Cobb, *Rev. Prog. Col.*, **3** 81 (1972).
22. P H Hobson and A L McPeters, in *Kirk Ohmer Encyclopeadia of Chemical Technology*, 3rd edn, Vol. 1 (ed. M Grayson), Wiley, New York, 1978.
23. J E Nettles and F Steven, *Text. Chem. Col.*, **1** 478 (1969).
24. D Heinkes, *Text. Prax. Int.*, **42** 423 (1987).
25. R Raue, *Rev. Prog. Col. Rel. Topics*, **14** 187 (1984).
26. U Mayer and E Seipmann, *Rev. Prog. Col. Rel. Topics*, **5** 65 (1974).
27. W Beckmann, in *The Dyeing of Synthetic-Polymer and Acetate Fibres* (ed. D M Nunn), Dyers Co. Pub. Trust, Bradford, 1979.
28. E N Abrahart, *Dyes and their Intermediates*, 2nd edn, Arnold, London, 1977.
29. P Gregory in *The Chemistry and Application of Dyes* (eds. D Waring and G Hallas), Plenum, New York, 1990.
30. J P Kim, PhD Thesis, Leeds University, 1990.
31. P L Meunier, *Amer. Dyest. Rep.*, **40** 51 (1951).
32. C G Lyle, J J Iannarone and R J Thomas, *Amer. Dyest. Rep.*, **40** 585 (1951).
33. R C Houtz, *Text. Res. J.*, **20** 786 (1950).
34. R I Thomas and P J Meunier, *Amer. Dyest. Rep.*, **38** 925 (1949).
35. W Beckmann, *JSDC*, **77** 616 (1961).
36. J Wegmann, *Text. Rundschau*, **9** 341 (1954).
37. J F Laucius, R A Clarke and J A Brooks, *Amer. Dyest. Rep.*, **44** 362 (1955).
38. A Wurz, *Mell. Text.*, **37** 83 (1956).
39. T Vogel, J M A DeBruyne and C L Zimmerman, *Amer. Dyest. Rep.*, **47** 581 (1958).
40. S Rosenbaum, *Text Res. J.*, **33** 899 (1963).
41. W R Remington and H E Schroeder, *Text. Res. J.*, **27** 177 (1957).
42. R J Harwood, R McGregor and R H Peters, *JSDC*, **88** 216 (1972).
43. S Rosenbaum, *J. Appl. Poly. Sci.*, **7** 1225 (1963).
44. W Biedermann and A Ischi, *JSDC*, **95** 4 (1979).
45. S Rosenbaum, *Text. Res. J.*, **34** 52, 291 (1964)

46. F Feichtmayer and A Wurz, *JSDC*, **77** 626 (1961).
47. S Cohen and A S Endler, *Amer. Dyest. Rep.*, **47** 325 (1958).
48. J Cegarra, R Puente and J Valldeperas, *Text. Chem. Col.*, **6** 170 (1974).
49. H Sand, *Kolloid. Z.*, **218** 124 (1967).
50. T H Guion and R McGregor, *Text. Res. J.*, **44** 439 (1974).
51. R McGregor and P W Harris, *J. Appl. Poly. Sci.*, **14** 513 (1970).
52. R McGregor, *Text. Res. J.*, **42** 172 (1972).
53. R McGregor, *Text. Res. J.*, **42** 536 (1972).
54. R McGregor and T H Guion, *Text. Res. J.*, **44** 433 (1974).
55. H H Sumner, *JSDC*, **102** 341 (1986).
56. H H Sumner, *JSDC*, **102** 393 (1986).
57. G Alberghina, S-L Chen, S Fischella, T Iijima, R McGregor, R M Rohner and H Zollinger, *Text. Res. J.*, **58** 345 (1988).
58. G Alberghina, M E Amato and S Fisichella, *JSDC*, **104** 279 (1988).
59. G Alberghina, M E Amato and S Fisichella, *JSDC*, **105** 163 (1989).
60. R McGregor, K Tamura and T Iijima, *J. Appl. Poly. Sci.*, **34** 2277 (1987).
61. G Alb, M E Amoto, S Fisi and H Zollinger, *Text. Res. J.*, **59** 264 (1989).
62. G Weston, unpublished results, see T Vickerstaff, *Hexagon Digest*, (19) 3 (1954).
63. W Beckmann, *3rd. Int. Conf. Surface Active Agents*, Cologne, Mainz University, 1960.
64. W Beckmann, *Bayer Farben Revue*, **9** 13 (1964).
65. U Mayer, *Mell. Text.*, **47** 653 (1966).
66. S Rosenbaum and F L Goodwin, *Text. Res. J.*, **35** 439 (1965)
67. H Sand, *Kolloid-Z, Z. Polym.*, **218** 30 (1960).
68. S L Chen, R M Rohner and H Zollinger, *Text. Res. J.*, **58** 247 (1988).
69. T M A Hossain, H Maeda, T Iijima and Z Morita, *Polym. Letters*, **5** 1069 (1967).
70. R J Harwood, R McGregor and R H Peters, *JSDC*, **88** 288 (1972).
71. F L Goodwin and S Rosenbaum, *Text. Res. J.*, **35** 333 (1965).
72. S R Sivaraja Iyer, in *The Chemistry of Synthetic Dyes*, Vol. VII (ed. K Venkataraman), Academic Press, New York, 1974.
73. R H Peters, *Textile Chemistry* Vol. 3, Elsevier, Amsterdam, 1973.
74. G Abdurakhamova, E B Lopatina, R Ya Tushkova and T Yu Tashpulatov, *Uzb. Khim. Zh.* (3) 49 (1986); *CA* **106** 34490g.
75. J P Neary and R J Thomas, *Amer. Dyest. Rep.*, **46** 625 (1957).
76. F M Carlini and C Paffoni, *Tinctoria*, **82** 102 (1985).
77. T L Dawson, *JSDC*, **97** 115 (1981).
78. H P Landerl, J J Iannarone and J J Wilson, *SVF Fachorgan*, **12** 688 (1957).
79. A Wurz, *Mell. Text.*, **38** 817 (1957).
80. W Beckmann, *Chemiesfaren*, (1960) 304.
81. C L Zimmerman and A L Cate, *Text. Chem. Col.*, **8** (11) 34/165 (1976).
82. M Bouche, *Teintex*, **33** 519,585 (1968).
83. M L Longo, D Sciotto and M Torre, *Text. Res. J.*, **52** 233 (1982).
84. G Alberti, A Cerniani and M R de Giorgi, *Ann. Chim.*, **73** 283 (1983).
85. G Alberti, A Cerniani and M R de Giorgi, *Text. Res. J.*, **56** 379 (1986).
86. M De Giorgi, A Pisano and C Ruggero, *Mell. Text.*, **70** 526 (1989).
87. V F Androsov and V L Liverant, *Tech. Text. Ind. USSR*, No. 3 98 (1966); *CA* **65** 18735d.
88. S Rosenbaum, *J. Poly. Sci., Part A*, **3** 1949 (1965).
89. R H Peters and H Wang, *JSDC*, **98** 432 (1982).
90. M L Gulrajani and R X Saxena, *JSDC*, **95** 330 (1979).
91. R Asquith, H S Blair and N Spence, *Text. Res. J.*, **47** 446 (1977).
92. R Asquith, H S Blair and N Spence, *JSDC*, **94** 49 (1978).
93. T M A Hossain, T Iijima, Z Morita and H Maeda, *J. Appl. Poly. Sci.*, **13** 541 (1969).
94. M L Williams, R F Landel and J D Ferry, *J. Amer. Chem. Soc.*, **77** 3701 (1955).
95. U Meyer, R M Rohner and H Zollinger, *Mell. Text.*, **65** 47 (1984).
96. R M Rohner and H Zollinger, *Text. Res. J.*, **56** 1 (1986).
97. T Hori, H S Zhang, T Shimuzi and H Zollinger, *Text. Res. J.*, **58** 227 (1988).
98. W R Kringbaum and N Tokita, *J. Poly. Sci.*, **43** 467 (1960).
99. R B Beevers, *J. Poly. Sci.*, **A2** (9) 5257 (1964).

100. J F Fuzek, in *Waters in Polymers*, ACS Symposium Series, **127** 515 (1980).
101. G M Bryant and A T Walker, *Text. Res. J.*, **29** 211 (1959).
102. R B Beevers and S A Heap, *J. Text. Inst. Trans.*, **57** (5) T191 (1966).
103. S Rosenbaum, *J. Appl. Poly. Sci.*, **9** 2071 (1964).
104. Z Gur-Arieh and W C Ingamells, *JSDC*, **90** 8 (1974).
105. J F Bell and T Murayama, *J. Appl. Poly. Sci.*, **12** 1795 (1968).
106. D Aitken, S M Burkinshaw, J Catherall, R Cox, R E Litchfield, D M Price and N G Todd, *J. Appl. Poly. Sci., Appl. Poly. Symp.*, **47** 261 (1991).
107. J G Cook, *Handbook of Textile Fibres* Vol. 3, 4th edn, Merrow, Watford, 1968.
108. W Ingamells, in *The Theory of Coloration of Textile Fibres*, 2nd edn, Dyers Co. Pub. Trust, Bradford, 1990.
109. P A Small, *J. Appl. Chem.*, **3** 71 (1953).
110. E E Walker, *J. Appl. Chem.*, **2** 970 (1952).
111. Z Gur-Arieh and W C Ingamells, *JSDC*, **90** 12 (1974).
112. H K Reimschussel, *J. Poly. Sci., Poly. Chem. Ed.*, **16** 1229 (1978).
113. L Peters and C B Stevens, *JSDC*, **72** 100 (1956).
114. L Peters, C B Stevens, J Budding, B C Burdett and J A W Sykes, *JSDC*, **76** 543 (1960).
115. W Beal, K Dickinson and E Bellhouse, *JSDC*, **76** 333 (1960).
116. W Beal and G S A Carbishley, *JSDC*, **87** 329 (1971).
117. S Rosenbaum, *J. Appl. Poly. Sci.*, **9** 2085 (1964).
118. W Ingamells, R H Peters and S R Thornton, *J. Appl. Poly. Sci.*, **17** 3733 (1973).
119. W Ingamells and R H Peters, *JSDC*, **89** 397 (1973).
120. Z Gur-Arieh, W Ingamells and R H Peters, *J. Appl. Poly. Sci.*, **20** 41 (1976).
121. A Tokaoka and M Aki, *Sen-i Gakkaishi*, **21** 437 (1965).
122. Z Gur-Arieh, W Ingamells and R H Peters, *JSDC*, **92** 332 (1976).
123. G Alberti, A Cerniani and M R de Giorgi, *Ann. Chim.*, **74** 429 (1984).
124. T Vickerstaff, *Hexagon Digest*, **20** 7 (1954).
125. C L Zimmerman, J M Mecco and A J Carlino, *Amer. Dyest. Rep.*, **44** 296 (1956).
126. G Alberti, M R de Giorgi and G Sen, *Ann. Chim.*, **74** 421 (1984).
127. G Alberti, *Amer. Dyest. Rep.*, **71** 46 (1983).
128. G Alberti and A Loi, *Mell. Text.*, **69** 365 (1989).
129. D Aitken, S M Burkinshaw, J Catherall, R Cox and D Price, *J. Appl. Poly. Sci., Appl. Poly. Symp.*, **47** 271 (1991).
130. D Aitken, S M Burkinshaw and D Price, *Dyes and Pigments*, **18** 23 (1992).
131. G S Dodd and W Ingamells, *JSDC*, **93** 74 (1977).
132. G S Dodd and W Ingamells, *JSDC*, **93** 79 (1977).
133. T M Baldwinson, in *Colorants and Auxiliaries*, Vol. 2 (ed. J Shore), SDC, Bradford, 1990.
134. R A Clarke and L Bidgood, *Amer. Dyest. Rep.*, **44** 631 (1955).
135. S Heimann and F Feichtmayr, *Canad. Text. J.*, **83** (14) 42 (1966).
136. D Blackburn, *Int. Dyer*, **153** 418 (1975).
137. H Kellet, *JSDC*, **84** 257 (1968).
148. AATCC Metropolitan Section, *Text. Chem. Col.*, **8** (11) 34/165 (1976).
139. H P Landerl and D R Baer, *Amer. Dyest. Rep.*, **54** 222 (1965).
140. N G Morton and M E Kracht, *JSDC*, **85** 639 (1969).
141. J Park, *A Practical Introduction to Yarn Dyeing*, SDC, Bradford, 1981.
142. J Park, *Int. Dyer*, **167** 16 (1982).
143. G Alberghina, L L Longo and G Parisi, *Ann. Chim.*, **72** 399 (1982).
144. J Cegarra, P Puente and B Castro, *Tinctoria*, **85** 67 (1988).
145. J S Ward and K Meldrum, *JSDC*, **74** 140 (1969).
146. F Hoffman, *Rev. Prog. Col.*, **18** 56 (1988).
147. M E Dullaghan and A J Ultee, *Text. Res. J.*, **43** 10 (1973).
148. AATCC Midwest Section, *Text. Chem. Col.*, **8** 22/6 (1976).
149. R P Beal, M E Dullaghan, M W Goodell and A Lulay, *Text. Chem. Col.*, **6** 30/6 (1974).
150. J Cegarra and J M Fiadeiro, *Rev. Quim. Text.*, **73** 39 1984).
151. J Cegarra, P Puente and J M Fiadeiro, *JSDC*, **102** 274 (1986).

152. J Cegarra, P Puente and J M Fiadeiro, *Textilia,* **63** (1) 25 (1987).
153. J A Leddy, *Amer. Dyest. Rep.*, **49** 272 (1960).
154. W L Anderson, C J Bent and R H Ricketts, *JSDC*, **88** 250 (1972).
155. H Kellett, *Text. Manuf.*, **84** 313 (1958).
156. H Sand, *Kolloid-Z, Z. Polym.*, **218** 124 (1967).
157. W Beckmann, *11th Int. Text. Seminar, Kingston, Ontario* (1968).
158. W Beckmann and O Glenz, *Mell. Text.*, **49** 1463 (1968).
159. *JSDC*, **89** 292 (1973).
160. W Beckmann and F Hoffman, *Mell. Text.*, **64** 828 (1983); Engl edn, **12** 770 (1983).
161. W Beckmann, F Hoffman and H G Otten, *JSDC*, **88** 354 (1972).
162. U Mayer, W Ender and A Wurz, *Mell. Text.*, **47** 653 (1966).
163. D J Evans and C J Bent, *JSDC*, **87** 60 (1971).
164. Society of Dyers and Colourists, *JSDC*, **88** 220 (1972).
165. C L Zimmerman, *Text. Chem. Col.*, **7** 208 (1975).
166. W Biedermann, P Galaffasi, P Moser and H Scheidegger, *Textilveredlung*, **12** 122 (1977).
167. D P Wethermann, *JSDC*, **95** 360 (1979).
168. K V Datye and S Mishra, *JSDC*, **100** 334 (1984).
169 E J Siepmann, *Text. Chem. Col.*, **7** 46 (1975).
170. Anon, *Amer. Dyest. Rep.*, **49** 590 (1960).
171. US Patent 2,893,816 (1975).
172. W Biedermann, *Rev. Prog. Col.*, **10** 1 (1979).
173. J T Voltz, *Text. Chem. Col.*, **9** 113/22 (1977).
174. J A Koller and M Motter, *Textilveredlung*, **11** 3 (1976); *Amer. Dyest. Rep.*, **66** (3) 34 (1977).
175. W Beal, *Int. Dyer*, **157** (6) 261 (1977).
176. W Biedermann, P Galafassi, U Horn, P Moser and H Scheidegger, *Textilveredlung*, **12** 250 (1977).
177. Courtelle Technical Booklet, Courtaulds
178. P Ackroyd, *Rev. Prog. Col.*, **5** 86 (1974).
179. M Haehnke, R Mohr, K Hohmann and Hoechst A-G, EP 44062 (1982).
180. Tanaka Y, Suzuki M, Tanaka H and Toray Industries, JP 61167025 (1986).
181. F Cognini, E Sciolla and Enichem Fibre S.p.A., EP 241054 (1987).
182. I Holme, *Rev. Prog. Col.*, **7** 1 (1976).
183. H R Hadfield and W M Sokol, *JSDC*, **74** 629 (1958).
184. R C D Kaushik and S D Deshpande, *Ind. J. Text. Res.*, **14** 119 (1989)
185. M Hotai and S Okada, *Sen-i Gakkaishi*, **23** 321 (1967).
186. I M S Walls, *JSDC*, **72** 261 (1956).
187. W H Hindle, *Amer. Dyest. Rep.*, **43** 34 (1956).
188. B Kramrisch, *JSDC*, **73** 85 (1957).
189. J A Woodruff, *Amer. Dyest. Rep.*, **40** 402 (1951).
190. P L Meunier, J F Laucius, J A Brooks and R J Thomas, *Amer. Dyest. Rep.*, **42** 470 (1953).
191. R H Peters, in *Diffusion in Polymers* (ed. J Crank and G S Park), Academic Press, London, 1968.
192. R McGregor, R H Peters and C R Ramachandran, *JSDC*, **84** 9 (1968).
193. R C D Kaushik and S D Deshpande, *Ind. J. Text. Res.*, **14** 125 (1989).
194. R C D Kaushik and S D Deshpande, *Ind. J. Text. Res.*, **14** 130 (1989).
195. D Balmforth, C A Bowers, J W Bullington, T H Guion and T S Roberts, *JSDC*, **82** 405 (1966).
196. J Cegarra, P Puente and J Valldeperas, *Text. Chem. Col.*, **6** 170 (1974).
197. D Aitken, PhD Thesis, Leeds University, 1992.
198. D Aitken and S M Burkinshaw, *Dyes and Pigments*, **23** 225 (1993).

4 Microfibres

4.1. Introduction

In the previous three chapters, which discussed the basic principles underlying the dyeing of the three main types of synthetic fibre, little reference was made to the effect of fibre linear density on dyeability; this is the subject of this particular chapter in that it concerns the dyeing of microfibres. Although polyester has received by far the greatest attention in this context, polyamide and acrylic microfibres also enjoy widespread usage. However, in view of the extremely small amount of information that has been published on acrylic microfibres, this type of fibre is not discussed.

The linear density of a filament or fibre is defined as [1] *the mass per unit length of linear textile material* and is normally expressed in decitex per filament (dtexpf), where 1 dtex is *the mass in grams of 10 km of fibre* [1].

A microfibre is defined as *a fibre or filament of linear density approximately 1 dtex or less, although some commercial products may in practice be as coarse as 1.3 dtex* [1]. However, even finer fibres of <0.3 dtex are produced, these commonly being referred to as 'supermicrofibres'. Table 4.1 shows the relationship between fibre linear density and classification whilst Table 4.2 displays the fineness of fibres of various linear densities.

An appreciation of the relative fineness of polyester fibres of varying dtexpf can be gained from Figure 4.1.

The origins of microfibres lay in the production of artificial suede [4–7] which first appeared in 1970 [4] and, typically, consist of a brushed, continuous ultrafine porous, non-woven fabric which has been impregnated with polyurethane [4, 8]. The supermicrofibres employed in such products

Table 4.1 Fibre count and fibre classification [2, 3]

Fibre count (dtexpf)	Fibre classification
>7.0	Coarse
7.0–2.4	Medium fine
2.4–1.0	Fine
1.0–0.3	Micro
<0.3	Supermicro

(Reprinted with permission from AATCC)

Table 4.2 Fineness of different fibres [3]

Fibre	Fineness (μm)
Polyester filament, 5.5 dtex	22.7
Wool, 90's	17
Cashmere	16
US cotton, grade 1	13.5
Silk	12
Acrylic staple, 1.3 dtex	12
Polyester staple, 1.3 dtex	11.1
Polyester filament, 0.4 dtex	6.4
Polyester filament, 0.1 dtex	3
Polyester filament, 0.05 dtex	2.1

(Reprinted with permission from AATCC)

are, typically, of 1.1×10^{-4} to <0.33 dtex [4, 5, 7, 8], being mainly polyester or polyester/polyamide mixtures although acrylic tow has also been employed [4]. Such were the excellent aesthetic properties of these artificial suede materials that fibre producers began to explore the merits of microfibres in traditional knitted and woven constructions [7].

Microfibres are now well established in many apparel markets, as well as in other outlets [3, 6, 10, 16–19, 23], being used either as single-fibre fabrics or in conjunction with coarser synthetic or natural fibres, providing fabrics of enhanced drapeability, lustre, softness and smoothness and, in many cases, novel tactile and visual aesthetics. For example, in the 1980s, very high-density woven polyester and polyester/nylon microfibre sports and outerwear fabrics were introduced that possessed a soft handle and good drapeability and which, although air-permeable, were waterproof [4, 7]. Lightly brushed fabrics were also marketed which possessed a soft touch that was likened to that of peach skin [4].

The latter types of products belong to one kind of *Shingosen*, a term, which, according to Kawasaki [9] applies to *new types of textiles made using primarily polyester filament yarn.* The shingosen, which first

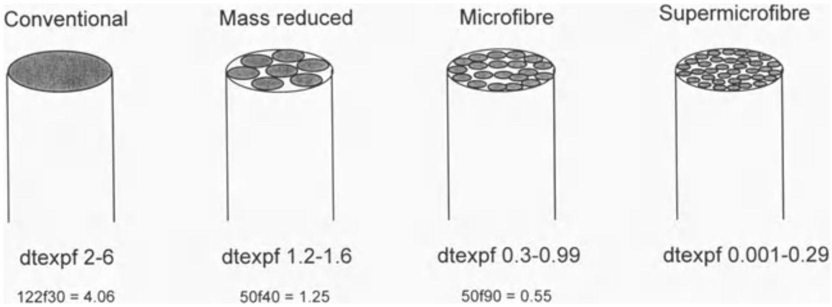


Figure 4.1 Typical dtexpf range for polyester fibres

appeared in 1988 [9], were devised in Japan as a means of increasing the apparel usage of polyester fibres and are the product of the vertical integration of various technologies involved in fibre production, such as polymer modification, yarn production, weaving and finishing [4, 9]. Although the term shingosen has been considered to mean microfibre, this is incorrect insofar as some shingosen do not contain microfibres and not all microfibre items are shingosen [4]. The earlier shingosen were lightweight woven fabrics having a silk-like handle (e.g. for shirts and blouses), these being later supplemented by middleweight yarns having a worsted-type touch (for trousers and jackets) peach skin fabrics (coats and jackets) and 'cool and dry' fabrics [9].

Whilst most microfibres are microfilaments, microstaple fibres, such as both polyester (0.44–0.55 dtex) and acrylic (0.55–0.77 dtex) [4], are also produced [24). However, although their effects, in terms of handle, drape and appearance, are similar to those achieved using microfilaments, the outlets for such fibres are determined by different criteria than those of filament yarns [10].

4.1.1. General considerations

Reducing filament linear density alters several fabric properties [10]; the effect on the flexural rigidity (R) or stiffness of a filament is given by equation (4.1) [11], in which η is the shape factor (cross-sectional shape), E the specific (tensile) modulus of the filament, T the linear density in tex and ρ the density of the filament:

$$R = \frac{1}{4\pi} \frac{\eta E T^2}{\rho} \tag{4.1}$$

From equation (4.1) it is apparent that for filaments that have been produced from the same polymer and which differ *only* in their respective filament linear density (T), the filament stiffness will decrease markedly with decreasing filament linear density, because, in this particular case, the flexural rigidity is dependent upon T^2. A reduction in filament linear density results not only in reduced stiffness of the filament but also in a reduction in the strength of the filament. However, this reduction in strength of an individual filament is offset by the corresponding increase in the number of individual filaments within a yarn to obtain the same yarn count, with the result that total yarn strength remains high [10]. Furthermore, a reduction in filament linear density is also accompanied by an increase in the surface area per unit volume of the filament, the specific surface increasing markedly with decreasing filament linear density.

In the context of dyeing, the increase in surface area that accompanies a decrease in filament linear density serves, firstly to increase the extents of both dye adsorption and desorption, these two effects resulting in, respectively, an increase in the rate of dyeing and often decreased wet and light fastness and, secondly, to reduce the visual and instrumental depth of shade obtained. In the latter context, Fothergill [12] argued that the path length of light within a textile fibre increases with increasing fibre diameter, assuming that the cross-sections are of identical shape and derived equation (4.2) to relate the concentration (*C*) of dye required to achieve the same visual depth of shade on two similar fibres (*1* and *2*) of differing dtex (*T*).

$$C_2 = C_1 \left(\frac{T_1}{T_2}\right)^{0.5} \tag{4.2}$$

Thus, according to equation (4.2), if a 1% o.m.f. dyeing was carried out on a 3.5 dtex fibre, the [redacted] same perceived depth on a 0.5 dtex fibre would be 2.65% o.m.f. Figure 4.2 shows the theoretical dye requirement, calculated using equation (4.2), for similar fibres of varying dtex, based on a 1% o.m.f. dyeing having been carried out on a 3.5 dtex fibre.

However, although exponents of 0.375 and 0.4 have been proposed for use in equation (4.2), exponents in the range 0.51–0.58 have been secured for several dye–fibre systems, the average value of 0.54 being close [13] to the theoretical 0.5 originally proposed by Fothergill. A similar treatment to that of Fothergill has been suggested by Dorsch *et al.* [14], in a study

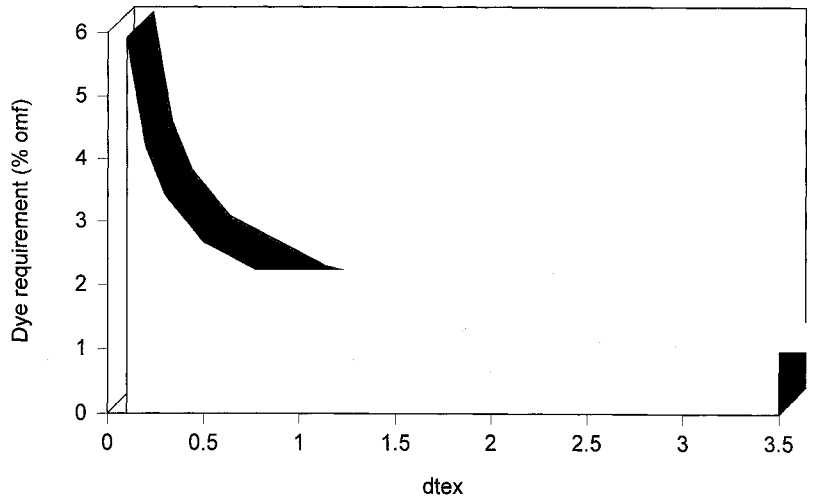


Figure 4.2 Theoretical dye requirement for similar fibres as a function of dtex (over the range 0.1–3.5 dtex) based on a 1% o.m.f. dyeing on 3.5 dtex fibre

centred on acrylic fibres. Dorsch *et al.* argued that, according to Kubelka-Munk theory (equation (4.3) in which K and S are the coefficients of the absorption and scatter of light, respectively and R the reflectance of a dyeing), as K is determined mainly by the dye and S only by the textile material, then finer fibres would appear lighter in shade than coarser fibres because of the greater amount of scattered light (S) resulting from the larger specific surface of the finer fibres. These workers [14] further proposed that as the specific surface of a filament (F) was inversely proportional to the fineness or dtex (T) of the filament, equation (4.4) was valid, from which, assuming that light scatter was proportional to specific surface, equation (4.5) depicted the variation in depth of shade (A) with fibre fineness.

$$\frac{K}{S} = f(R) \tag{4.3}$$

$$\frac{F_1}{F_2} = \frac{(T_2)^{0.5}}{(T_1)^{0.5}} \tag{4.4}$$

$$\frac{A_1}{A_2} = \left(\frac{T_1}{T_2}\right)^{0.5} \tag{4.5}$$

Using dyeings of a cationic dye on acrylic fibres of varying dtex, Dorsch *et al.* [14] showed that the theoretical depth of shade calculated using equation (4.5) coincided with instrumentally measured depths of shade for low values of dtex; however, at higher fibre linear densities the two parameters diverged markedly. As the perceived depth of shade of a dyeing on two fibres of differing fineness depends, according to Fothergill [12], on path length and, according to Dorsch *et al.* [14], on specific surface (each of which is the same phenomenon), it follows that cross-sectional shape, which involves both specific surface and path length effects, will also influence the perceived depth of shade. Indeed, it has been reported [13] that in the case of nylon carpet yarn, about 100% more dye is required to achieve the same depth of shade on trilobal cross-section yarn as is achieved on round cross-section yarn. Dorsch *et al.* [14] showed that such effects were due to differences in the amounts of light scattered by different cross-sectional shapes. In the case of acrylic fibres, these workers [14] found that S increased as the filament cross-section changed from round, through kidney-shaped to barbell-shaped and derived equation (4.6) to describe the extent of light scattering achieved for two cross-sections, namely round and barbell-shaped, wherein x was 3.54 and 5.01, respectively, for the two cross-sections.

$$S = \frac{x}{(T)^{0.5}} \tag{4.6}$$

Steilin [13] defined a *Form Index*, *FI* (equation (4.7)), derived from the circumference of the filament cross-section U and the filament cross-sectional area F (the factor 28.2 corresponding to $100/2(\pi^{0.5})$ such that the *FI* of a circle was unity), by means of which, in the cases of dyeings on polyamide and polyester, when the fibre fineness was constant, it was possible to mathematically relate changes in cross-sectional shape to changes in perceived depth of shade:

$$FI = 28.2\frac{U}{(F)^{0.5}} - 100 \tag{4.7}$$

Perceived depth of shade also decreases with increasing amount of delustrant in the substrate, this having been shown, in the case of acrylic fibres of identical dtex but differing delustrant contents, to be due to an increase in the extent of scattered light, S, that accompanied an increase in delustrant content [14]. Weigner [15] showed that in the case of 3 dtex polyester, when compared with round, bright filament, the disperse dye requirement was 20% greater in the case of round, dull, 30% greater for trilobal, bright and 40% greater in the case of trilobal, dull filaments.

4.1.2. Microfibre production

Two methods can be employed to produce microfibres, namely *conventional spinning* and *conjugate spinning*; however, there is a further method, *mass reduction* (section 4.2.1), that is used only for polyester and which produces fibres of fine rather than micro dimensions.

4.1.2.1. Conventional spinning. Although all three conventional spinning methods (melt, wet and dry) can be employed and polyester, polyamide and acrylic microfibres can be obtained [4], the direct spinning of microfibres is a complex process [21] and involves the modification of the spinning methods that are used to produce conventional dtex fibres [4, 21]. Generally, there is a limit to the fineness of fibres produced using direct spinning, as exemplified by polyester which cannot be extruded at less than approximately 0.15 g min^{-1} owing to breakage of the filament [6]. Typically, microfibres in the range 0.3–1.0 dtex are secured using conventional spinning methods [10] although filaments of 0.1 dtex have been reported [16, 20]. High-speed spinning and the drawing of fully oriented yarn (FOY) produce flat microfibre for use in woven fabrics whilst high-speed spinning of partially oriented yarn (POY) followed by drawing and texturing provides false-twist yarns suitable for knitted fabrics [21, 22].

4.1.2.2. Conjugate spinning. Although Du Pont are credited with the first example of a potential microfilament produced using conjugate spinning technology followed by the splitting of the two components of a

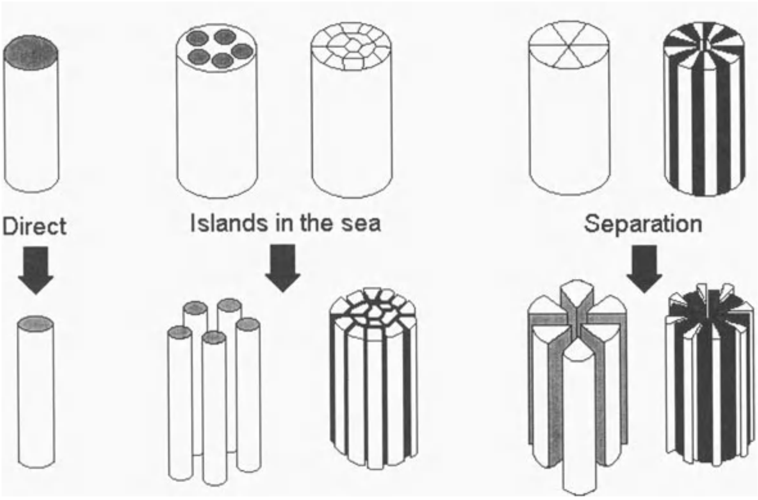


Figure 4.3 Separation and dissolution spinning methods

conjugate fibre, the production of microfibres by the combination of these two technologies was not, at the time, investigated [6] and the development of these techniques was subsequently undertaken in Japan. Two different methods, namely *separation* and *dissolution*, have been devised (Figure 4.3).

(i) Separation. This technique, which was developed by Okamoto *et al.* in the mid-1960s [6], involves the spinning of a bicomponent filament, typically one comprising nylon 6 and polyester although polyolefin/polyester and polyolefin/polyamide bicomponents have also been developed [4]. After weaving, the ensuing fabric is exposed to solvent or alkali swelling or thermal or mechanical treatment such that the two immiscible components separate resulting in individual polyamide/polyester microfilaments [4, 5, 20, 25]. The ratio of the two components as well as the shape and number of the resulting individual segments can be varied.

(ii) Dissolution. In this technique [4–6, 20], two polymers are extruded through a suitable spinneret to produce a bicomponent filament that comprises either several individual 'islands' of one component embedded within a 'sea' of the other component or a sheath of one component that surrounds the core of the other component. After weaving or knitting, one of the components is removed by dissolution in a solvent thereby producing microfilaments. Various polymers can be used for the island and sea components [6]. In the case of polyester microfilament produc-

tion, the polyester island is commonly used in conjunction with a polystyrene or alkali-soluble polyester sea component [20]. The number of islands, the ratio of islands : sea components and the cross-sectional shape of the ensuing microfilaments can be varied, the method being capable of producing supermicro polyester filaments of 1.1×10^{-4} dtex [6] as well as hollow microfibres [25]. The finest polyester supermicrofibres are produced using 'islands-in-the-sea' technology [25].

4.2. Polyester microfibres

This section concerns the dyeing of polyester microfibres with disperse dyes; the reader is directed to Chapter 1 for a general discussion of the use of this dye class on polyester fibres.

As mentioned, of all the synthetic fibres, polyester has received the greatest attention in the context of the production of microfibres; however, the trend towards finer polyester fibres dates back almost to the introduction of polyester yarn. This trend, which has been pioneered in Japan, accrued from the desire to produce a fibre that imitated silk in handle, appearance, drape and sound. Historically, the development of silk-like polyester occurred over several decades [5, 16]:

- 1960s: polyester yarns of trilobal cross-section [25] were introduced providing enhanced lustre and crispness;
- 1970s: yarns comprising filaments of differing heat shrinkages were introduced to enhance handle; mass reduction (10–15%) of the fabric further enhanced drape and moisture absorbency;
- 1980s: the use of micro- and supermicrofibres in conjunction with previous developments enabled fabrics to be produced that are remarkably silk-like in many of their characteristics.

In a comparison of various characteristics, including stiffness, scroop, smoothness and fullness/softness, of a mass-reduced polyester fabric and a natural silk fabric, Matsudaira [26] concluded that the performance of the polyester fabric approached that of its natural silk counterpart in the various parameters examined. However, as mentioned earlier, micro- and supermicrofibres are employed in a variety of outlets other than imitation silk.

Prior to dyeing, a gentle but efficient preparation stage is considered to be of vital importance in order to remove fibre processing aids (sizes, oils and waxes) and to minimise creasing and maintain the desired aesthetics [20]. Also, prior to dyeing, the fabric can be emerized to produce the popular 'peach skin' effect. This treatment, which is undertaken using specialised single- or multi-roller machines [18, 20], is usually carried out on washed goods [18, 20, 30], plain weave fabrics being emerized on both sides and gabardine and twill on one side only [3]. Prior to emerization, the fabric is prelubricated [20] with a non-permanent softener with antistatic character (to overcome the static that is built-up during emerization) [3, 20] and the emerized fabric is then heat set, the dust and lint generated during emerization being removed by washing either before [20] or after [3, 18] heat setting. Although emerizing can be carried out after dyeing [20, 27], this can result in shade change [20] and visual unevenness [27].

The increase in specific surface that accompanies a reduction in fibre linear density results in disperse dyes exhibiting a faster rate and greater extent of uptake on polyester microfibres than on 'conventional' fibres [2, 15, 20, 27–30]. It was shown [2] that when CI Disperse Blue 73 was applied at the same concentration (1.9% o.m.f.) under identical conditions to different microfabrics and to a conventional decitex fabric, the rate of dye uptake increased with increasing fibre fineness, the higher surface area of the microfibre fabrics used resulting in 10–20% more rapid dye uptake in the region 90–130°C (Figure 4.4). Furthermore, when Foron Blue RD-GLF (*Sandoz*) was applied at both 1/1 standard depth as well as 1.06% o.m.f. to different microfabrics and to a conventional decitex fabric [2], the dye displayed different rates of uptake on the different

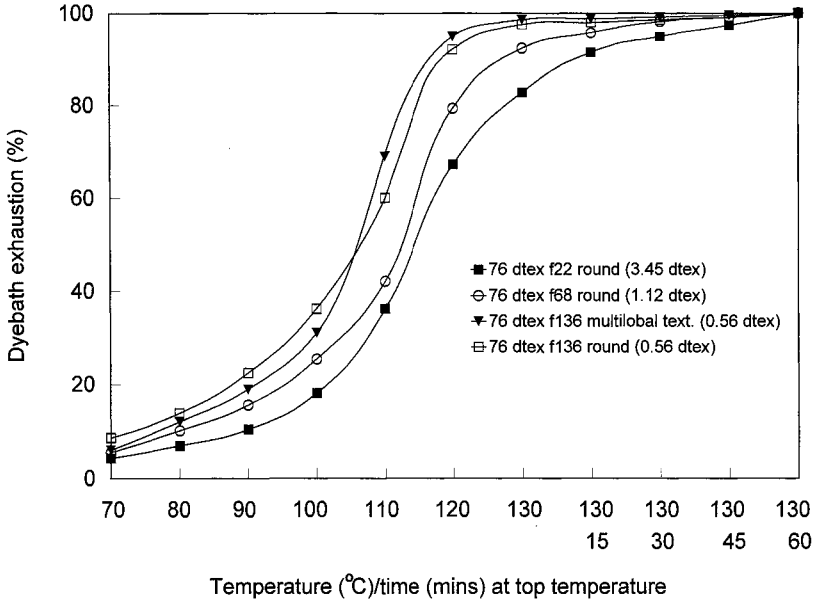


Figure 4.4 Exhaustion behaviour of 1.9% o.m.f. CI Disperse Blue 73 on conventional and micro PET fabrics [2]
(Reproduced with permission from S.Y. Kamat and Sandoz (India))

microfabrics and the rate of dye uptake on to each microfabric was greater than that on to their conventional decitex counterpart only in the lower temperature region (between 70 and 105–110°C). The greater adsorptive character of microfibres was demonstrated by the findings that when CI Disperse Blue 73 was applied in a 1/1 standard depth shade to polyester fabrics of 3.45 and 0.56 dtexpf, although virtually 100% more dye was required for the microfabric and the rate of dye uptake on to the latter fabric type was slightly greater than that on to its conventional decitex counterpart, the amounts of dye that were loosely bound to the fabrics at the end of dyeing were the same for both conventional and microfibres [2]. It has been proposed that, compared with conventional fibres, microfibres are capable of adsorbing 2 to 3 [15, 29, 30], 3 [28] or even 4 to 5 [31] times as much disperse dye, the magnitude of this differential dye uptake depending on dye structure as well as fibre fineness and cross-sectional shape, as well as fabric construction [31]. Fully penetrated dyeings are more rapidly attained on microfibres than on coarser fibres and, as a result, shorter times are required under HT dyeing conditions to achieve good dye penetration [28, 29]. The temperature range over which dye adsorption occurs as well as the time required to achieve dyebath exhaustion and fully penetrated dyeings depends on the fineness of the fibres [29]. As tightly woven microfabrics may rapidly adsorb considerable amounts of dye at low temperature, dye metering at the starting temperature of dyeing has been recommended [2].

As a consequence of disperse dyes exhibiting a faster rate and greater extent of uptake on polyester microfibres than on conventional fibres, the levelling behaviour of the dyes on microfibre is often poorer than that on conventional decitex fibres [15, 20]. This situation is exacerbated in the case of high twist yarns in high-density fabrics within which dye penetration is very poor [20]. To improve levelling, microfibre dyeing is usually commenced at a lower temperature [2, 15, 18, 20] than that employed for conventional fibres; starting temperatures of 60°C [3, 18], 70°C [15, 20, 30] as well as 30–50°C [28, 29] have been proposed depending on fibre type, fabric structure and dyeing machine [28]. Furthermore, a lower rate of rise of temperature up to the top dyeing temperature is usually employed [15, 18, 20, 28].

Additional dye coverage problems arise owing to the facts that many fabrics comprise both micro and conventional fibres [15, 20] which can result in a marked difference in dyeing rate occurring, especially at the start of the dyeing process [30]. Also, because the extent of surface reflection is greater for textured rather than flat filaments as well as for multilobal rather than round cross-sections, more dye is required to achieve the same depth of shade in the cases of textured microfilaments (Table 4.3) [3, 18] and filaments of multilobal cross-section [15]. Thus, dye coverage problems can also arise as flat filaments are often combined with tex-

Table 4.3 Relative amounts of dye required to achieve identical shade depth on 0.47 dtexpf textured and flat polyester [3]

	CI Disperse			
Polyester	Red 86	Red 302	Red 82	Blue 60
Flat	100	100	100	100
	(=2.1%)	(=2.6%)	(=1.85%)	(=2.5%)
Textured	146	120	120	124

(Reprinted with permission from AATCC)

tured yarns and filaments of varying cross-section are often combined [20]. Improvement in overall solidity of shade can be achieved by careful selection of the dyes and dyeing method as well as the use of dyebath auxiliaries [20]. It has been recommended that a holding period of 20 minutes at 96°C aids levelling because the rate of dye exhaustion increases at this temperature [18]; levelness is also promoted by the use of effective levelling and/or dispersing agent [3, 18].

To achieve the same visual (or instrumental) depth of shade on micro and conventional polyester fibres, a greater amount of disperse dye must be applied to the microfibre owing to its greater specific surface; the finer the filaments, the greater is the amount of dye required (Table 4.4). The amount of dye required to achieve a given depth of shade also increases with increasing degree of delustring [2, 15]. The build-up properties of disperse dyes on microfibre can differ from those of the same dyes on conventional fibre [20].

Disperse dyes display lower fastness to light [2, 3, 15, 18, 20, 28–32] on microfibres than on conventional polyester fibres because of the greater fibre surface area that is exposed to light. The decreased light fastness, which can be of the order of 0.5 to 1.5 units depending on fibre fineness

Table 4.4 Relative amounts of dye required for identical shade depths on textured polyester [3]

	CI Disperse			
Count (dtexpf)	Red 86	Red 302	Red 82	Blue 60
5.6	100	100	100	100
	(=1%)	(=1.1%)	(=0.65%)	(=1.1%)
1.40	184	189	206	194
1.06	210	189	240	193
0.50	221	242	283	296
0.47	310	266	348	287

(Reprinted with permission from AATCC)

and fabric construction [2], can be partially offset by the use of proprietary UV stabilisers during dyeing [2, 20]. It has been proposed that the wet fastness of dyeings on polyester microfibre is not a major problem when suitable reduction clearing [18, 31], finishing and heat treatments [18] have been carried out. However, dyeings on microfibre do exhibit lower wet fastness than comparable dyeings on conventional fibres [29], especially in heavy depths [3, 15, 18, 20, 30], due to inadequate after-treatment [30] and when thermally treated [2, 15, 20, 30, 31]. The lower wet fastness of disperse dyes on microfibres can be attributed to the greater amount of dye present within the fibre and to the greater specific surface from which dye desorption can occur. The fastness of dyeings to sublimation on microfibre are lower than on conventional fibres [2, 28, 29, 31], this phenomenon being due to the greater amount of dye on microfibre which can result in sublimation fastness being some 1–2 points lower on microfibre than on conventional fibres [28]. In the context of the fastness properties as well as the compatibility of disperse dyes on polyester microfibres, the careful selection of dyes is highly recommended [2, 3, 15, 20, 28–32].

Consideration must also be paid to the choice of dyeing machine employed; dyeing is carried out almost exclusively on jet machines [3, 18, 20, 28, 32], employing fabric circulation rates of at least 250 m min^{-1} [32], as this machine design enables the fabrics to develop bulk [3, 18]. To minimise creasing during dyeing, the addition of a proprietary anti-crease agent is recommended [3, 20, 28, 32] and the use of deaerating agents suggested [18]. The use of effective dispersing and levelling agents is also recommended [3, 18, 20], the former agents being of importance to disperse contaminants such as oligomers, oils and waxes [20]. Dyeing is carried out, typically, in the pH range 4.4–5.0 [3, 15, 18, 20, 29, 32] using acetic acid [15, 18, 20, 29, 32] or formic acid/ammonium sulphate [3] at 130°C. For successful dyeing, the need for appropriate preparation of polyester microfabrics has been emphasised [18, 20].

At the end of dyeing, surplus dye is removed commonly by reduction clearing at 70°C [3, 18], 70–75°C [29] or 80°C [20, 32] although it has been recommended that in the case of pale and medium depth dyeings, detergent scouring at 60–70°C is sufficient [28].

4.2.1. Mass-reduced fibres

This section comprises a brief account of the principles of the mass (weight) reduction of polyester fabrics and their dyeing with disperse dyes; the reader is directed to Chapter 1 for a fuller discussion of the dyeing of polyester with this particular dye class.

Mass reduction of polyester fabrics, which has been practised for several decades and variously termed *alkalisation*, *causticisation* and *alkali* *deweighting*, relies on the fact that polyester is readily hydrolysed at high temperature by aqueous solutions of an alkali (commonly NaOH). This results in a loss in fabric mass which is accompanied by a reduction in fibre linear density and a change in several fabric properties namely, an improvement in softness, handle and wettability [33, 34], reduction of wet cling [35] and a marked reduction in the propensity to stain and to retain soil [36–38]. It has also been reported [39, 40] that by reducing the filament diameter of heat set woven fabric, alkali treatment increases the airflow through the fabric and increases yarn movement at interyarn crossover points, the latter effect improving drape and suppleness. Commonly, the typical dtexpf range for conventional polyester fibres is 2 to 6 whilst that of mass-reduced polyester is 1.2 to 1.6 [20] and thus, from Table 4.1, such fibres can be classified as 'fine'.

Although the mass-reduced polyester fibres can be considered to compete with the coarser types of microfibres, Richter [28] considers that important differences between the two fibre types are the more irregular surface of the alkali-treated fibres and the market for microfibres of weatherproof clothing with good 'breathability'. Furthermore, this author proposes that microfibres offer the advantages of lower effluent problems when compared with the high amounts of ethylene glycol and sodium terephthalate which are generated during mass reduction, together with the elimination of errors that can occur in mass-reduction treatment.

Shortly after the commercial introduction of polyester fibres, Waters [41] reported that treatment with an aqueous solution of KOH at 98°C

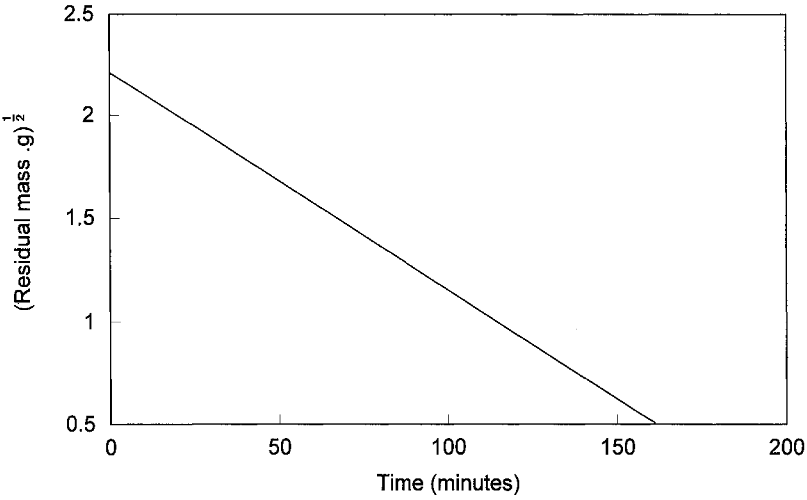
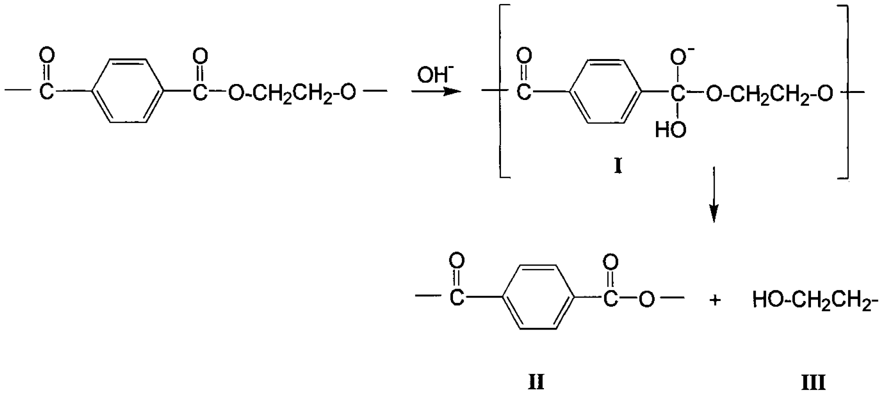


Figure 4.5 Rate of hydrolysis of PET with 200 g dm^{-3} KOH at 95°C [41]
(Reproduced with permission from the Society of Dyers and Colourists)

hydrolysed polyester fibre, as a result of which, the diameter of the filaments was reduced (Figure 4.5). The first patent concerning the use of alkaline hydrolysis to improve the tactile aesthetics of the substrate was issued in 1952 [42], this particular treatment having been applied to flat (untextured) yarn, by means of which, fabrics possessed softer tactility with a less synthetic-like handle [40]. Further developments in the 1950s led to the C–H–C process [44, 45] that involved calendering and heat setting followed by alkali treatment that enabled a fabric of enhanced lustre to be obtained without a paper-like handle [39, 43], as well as a patent specification [28] for a treatment that produced a silk-like delustering effect and softer handle. However, alkali demassing was subsequently little used [28, 39] because the enhanced fabric softness as well as the reduction in tensile strength that was also secured by alkali treatment were not at the time required [28]; during this period, the extent of mass loss involved was, typically, 2 to 5% [39]. In the 1970s, in connection with the high surplus of polyester fibres and the trend towards more comfortable fabrics of superior handle, interest in the alkali treatment of polyester was revitalised in Japan [28] and alkali-treated textured polyester fabrics with silk-like aesthetics were introduced, these having a mass loss of between 10 and 25% [44] or even up to 30% [39].

NaOH is most commonly employed, although the hydrolysing action of LiOH and KOH have been examined [46]. In the reaction with alkali depicted below, the highly nucleophilic OH^- ion attacks the electron-deficient carbonyl carbon atom in the polyester. The nucleophilic substitution reaction, which occurs via the formation of an intermediate anionic species (I), results in chain scission and the generation of terminal carboxyl (II) and hydroxy groups (III).



It is to be expected that, depending on treatment conditions, hydrolysis generates various products, from oligomers to terephthalic acid and ethylene glycol. Consequently, the loss in mass observed in practice often differs to (or is greater than) that calculated on the basis of the

Table 4.5 Hydrolysis of PET at 60°C in the absence and presence of cetrimonium bromide [48]

Treatment time (mins)	Mass loss (%)		Fibre density (g cm^{-3})	
	Absence	Presence	Absence	Presence
0	–	–	1.400	1.393
15	1.08	3.9	1.398	1.388
60	5.18	16.3	1.399	1.389
120	10.01	35.4	1.398	1.390

(Reproduced with permission from The Textile Institute)

stoichiometry of the above reaction [40, 44]. The effectiveness of the treatment, expressed in terms of mass loss, was observed to increase with increasing nucleophilicity of the attacking ion insofar as the following order was found, hydroxide < *tert*-butoxide < *sec*-propoxide < methoxide < ethoxide [47]. The rate of hydrolysis was found to be higher in the case of cationic-dyeable polyester [40, 43] possibly as a result of increased electron deficiency of the carbonyl carbons resulting from the inductive effect of the sulphonate groups within such polymers or due to differences in fine structure between the regular and anionically modified substrates [48].

Hydrolysis is topochemical, in that it is confined to the fibre surface [40–43, 49], evidence for this proposal having accrued from the findings that the density of polyester fibre, which is a measure of crystallinity, remains relatively constant with increasing mass loss [43] (Table 4.5) and also that the M_r of polyester fibre decreases only slightly as a result of hydrolysis [37, 43, 48, 49, 51]. Equation (4.8) has been devised to describe the rate of this topochemical hydrolysis, wherein R is the residual mass (%), k the rate constant for the solution and r_0 the initial radius of the fibre [48]. The use of equation (4.8) is conditional in that it applies only when the fibre radius decreases linearly with time at a given alkali concentration, no radial changes occur in the fibre structure and the fibre surface remains smooth and its cross-section remains round [48].

$$R^{0.5} = 10[1 - k/r_0)t] \tag{4.8}$$

It is considered that as chain scission proceeds, the various hydrolysis products dissolve in the alkaline solution to reveal a 'fresh' surface for further reaction, as a consequence of which, fibre diameter decreases [41, 48]. However, surface pitting also occurs [28, 33, 34, 39, 44, 51], this being especially pronounced in the case of delustred fibre [39, 48], the latter observation having been attributed [39, 44] to removal of TiO_2 particles from the substrate. It has been suggested [40] that at up to 10% mass loss, alkali treatment primarily consists of progressive surface erosion whereas in the case of mass loss above 10%, mass reduction pro-

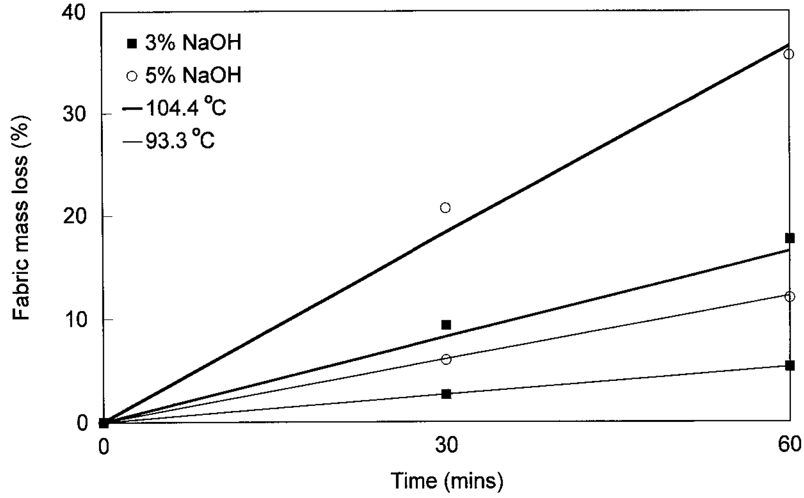


Figure 4.6 Mass loss of untextured PET fabric as a function of temperature, [NaOH] and time of treatment using a high liquor ratio [40]
(Reproduced with permission from AATCC)

ceeds through enlarged surface cavitation. Alkali treatment reduces the strength of the substrate although the loss in strength is not directly proportional to mass loss, in that loss in strength is often greater [28, 39, 40].

The extent of fibre degradation imparted by alkali treatment depends on the concentration of alkali, temperature, duration and liquor ratio of treatment, type of cationic surfactant employed and fabric construction. In the context of the first three of these variables, it is considered [39, 40] that their influence decreases in the order temperature > alkali concentration > time of treatment (Figure 4.6).

The rate of demassing can be controlled by temperature [28]; whilst the hydrolysis of PET begins only at temperatures above its T_g (80 to 90°C) [28], under batchwise conditions, the rate of loss in mass imparted by alkali treatment increases almost exponentionally with increasing temperature above about 80–90°C [28, 39, 40, 52]. The extent of mass loss increases with increasing concentration of NaOH during batchwise treatment [39, 40, 52]. However, owing to consumption of NaOH during the process [40, 43, 44], the rate of mass loss that occurs at a given concentration of alkali decreases with increasing time [39, 40] and, consequently, an excess of alkali must be employed [43].

At constant treatment time, a curvilinear relationship between mass loss and alkali concentration was observed [37] and the variation of (mass loss)$^{1/2}$ with time was shown to be rectilinear [48]. Latta [44] derived a rate expression for the hydrolysis of polyester with NaOH from the findings that the second-order (with respect to [OH^-]) cleavage of the polymer chain was the rate-determining step and that subsequent terminal group generation was a first-order reaction. A linear relationship has been secured for the extent of hydrolysis as a function of time of treatment [37, 40–43, 50, 52] although if an excess [OH^-] is not used, a curvilinear relationship is obtained [53].

Several workers have demonstrated that the rate of mass loss, at a given temperature and given [OH^-], increases markedly in the presence of a quaternary ammonium surfactant [39, 40, 43, 54] (Table 4.5). It has been shown [46, 54] that the efficiency of such accelerated hydrolysis depends on the constitution of the cationic surfactant. The acceleration effect imparted by cationic surfactants has been attributed [55–57] to the agents suppressing the negative charge on the intermediate anionic species (I) which thus decreases ion–ion repulsive effects operating between (I) and the hydroxide ion and thereby facilitates transfer of the OH^- ions into the polymer. Zeronian and Collins [48] suggest that such interaction between the cationic surfactant and the intermediate anion (I) would, by means of an inductive effect, increase the electron deficiency of the carbonyl carbon atoms, resulting in an increase in susceptibility of the polymer to hydrolysis. It has been reported that cationic surfactants can have a detrimental effect on the strength of the substrate [39, 40]. The extent of hydrolysis of polyester can be assessed, with the aid of a calibration series, by means of the staining of the fabric with cationic dyes [28, 44].

Commonly, prior to alkali demassing, the fabric must be carefully desized [28], scoured and bulked [44] and usually heat set [28, 40, 44]. Alkali treatment can be carried out either batchwise or continuously [28, 39, 57]; Shet *et al.* [56] considered that a pad-dry heat (60°C) technique was more effective, in that greater mass loss was achieved, than in a batchwise process that employs a large liquor:solids ratio. Richter [28] recommends both a batchwise procedure involving treatment at 110°C for 60 minutes using 10 to 20 g l^{-1} NaOH (100%) and a continuous process comprising padding with 100 to 200 g l^{-1} NaOH (100%) followed by steaming for 2 to 6 minutes at 110–115°C, both treatments being carried out in the presence of a cationic surfactant.

In the context of dyeing with disperse dyes, uniform alkaline treatment is essential for levelness of dyeing, relatively small variations in treatment resulting in uneven delustring which, in turn, gives rise to the ensuing dyeings having a 'cloudy' appearance; although mass-reduction can be carried out after dyeing, cloudy dyeings can still result [28]. The effects of the increase in fibre-specific surface that accompanies a reduction in fibre linear density are very similar to those previously discussed in the preceding section that concerned the dyeing of microfibre polyester, namely that the dyes exhibit a faster rate and greater extent of uptake and, also, that more dye must be applied in order to achieve a given

Table 4.6 Effect of treatment with 200 g dm^{-3} KOH at 100°C on mass loss and disperse dye uptake [41]

Time (min)	Mass loss (%)	Dye uptake (%)
0	–	10
30	42	12
45	85	18

(Reprinted with permission from the Society of Dyers and Colourists)

depth of shade on mass-reduced fibre [28]. Waters [41] first observed the increase in dye uptake that accompanied the mass reduction of PET (Table 4.6).

It has been proposed that, in the case of deep shades, mass-reduced polyester fabrics require some 1.5 to 2.5 times more dye than is required for non mass-reduced fabrics [28]. Consequently, as in the case of the dyeing of microfibres, the starting temperature of dyeing is reduced, typically to between 40 and 50°C [28]. Furthermore, dyeings on mass-reduced fabrics generally display lower light- and wet-fastness properties than dyeings on non-mass-reduced fabrics. The light fastness can be further impaired if the dyeings are subjected to thermal treatment that gives rise to dye migration [28].

4.3. Polyamide microfibres

Polyamide microfibres have been available for several years [2, 17, 58–61] and enjoy usage in outlets such as sports/leisure wear, underwear and as 'cotton-look' outerwear [17, 59]. This section concerns the dyeing of such microfibres with acid dyes. The reader is directed to Chapter 2 for a general discussion of the use of this dye class on nylon fibres.

As with polyester microfibres, the greater extent of surface reflection that ensues from the greater surface area of polyamide microfibres results in dyeings on microfibre appearing visually lighter in shade than identical depth dyeings on conventional decitex fibre; this has been demonstrated by several workers [2, 15, 61–64]. Weigner [15] considers that, depending on fibre titre and lustre, polyamide microfibre may require up to 100% more dye than conventional fibre. In a study [65], using reactive disperse dyes and a conventional disperse dye, of conventional (78f46; 1.7 dtexpf) and microfibre (85f92; 0.9 dtexpf) knitted nylon 6.6 fabrics, each of AEG content 66.4 g-eqv. 10^{-6} g [66], it was found that in order to achieve a 1/1 standard depth of shade on both types of fibre, between 25 and 33% more reactive disperse dye had to be applied to the microfibre than conventional fibre and considerably more disperse dye was required on

Table 4.7 Dye concentration (% o.m.f.) required to give standard depth dyeings on conventional and microfibre nylon 6.6 fabric [65]

Dye	Standard depth	Conventional	Microfibre
A	1/1	0.3	0.4
B	1/1	0.2	0.25
C	1/1	0.25	0.3
D	1/3	0.33	2.0

(Reprinted from *Dyes and Pigments*, **25**, S.M. Burkinshaw and G. Collins, The dyeing of conventional and microfibre nylon 6.6 with reactive disperse dyes, pp. 32–48. Copyright 1994, with kind permission from Elsevier Science Ltd., The Boulevard, Lanford Lane, Kidlington, OX5 1GB, UK)

microfibre to achieve a 1/3 standard depth shade (Table 4.7). Further, in a study of the dyeing of the same microfibre and conventional decitex nylon 6.6 knitted fabrics using six non-metallised acid dyes and three monosulphonated 1 : 2 metal-complex dyes [64], it was observed that the colour strength (*K*/*S* value) of dyed microfabric was consistently lower than that of its dyed conventional counterpart for each of the five depths of shade (0.5, 1, 2, 3 and 4% o.m.f.) and each of the three temperatures

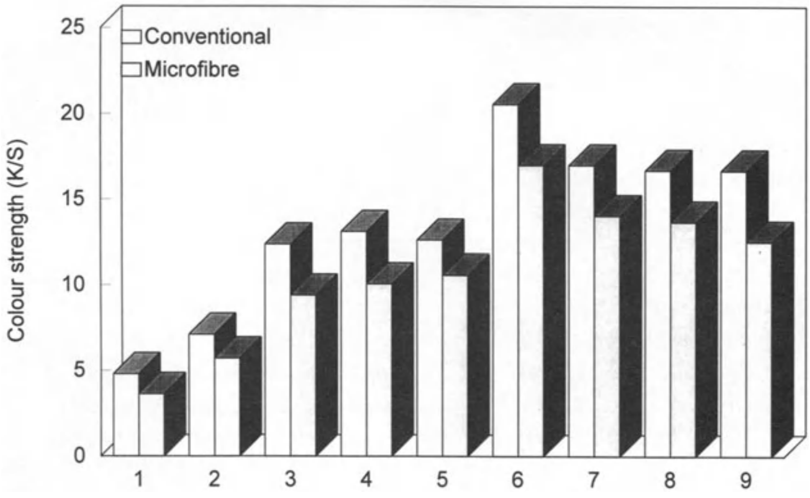


Figure 4.7 Colour strength achieved for 2% o.m.f. dyeings on conventional and microfibre nylon 6.6 fabrics at 98°C (1: CI Acid Blue 41; 2: CI Acid Yellow 42; 3: CI Acid Red 337; 4: CI Acid Blue 129; 5: CI Acid Yellow 159; 6: CI Acid Red 229; 7: CI Acid Blue 348; 8: Neutrilan Yellow S-2G; 9: CI Acid Red 359) [64]

(98, 115 and 120°C) employed. Furthermore, the difference in colour strength of identical depth dyeings on micro and conventional fibres varied markedly for each of the nine dyes used (Figure 4.7). The visual depth of shade obtained on polyamide microfibre also decreases with increasing degree of delustring and is influenced by the cross-section of the fibre [2, 15].

As the polymer used in polyamide microfibre is often the same as that employed in conventional fibres [66], microfibre can be dyed in a manner similar to its conventional counterpart [15]. It has been shown [64] that when nine acid dyes were applied, under identical conditions, to micro and conventional decitex nylon 6.6 fabrics, although the colour strength of identical depth dyeings on microfabric was lower than that on its conventional decitex counterpart, there was very little difference in the hue (*H*°) and chroma (*a**, *b**, *c**) of the same dyeings on each type of fibre. However, differences do exist between the dyeabilities of micro and conventional polyamide fibres. Although it has been proposed [2, 15] that both the rate and extent of dye uptake of non-metallised acid and also metal-complex dyes on microfibre differ only slightly from those achieved on conventional fibres, it was shown [2] that the rate of uptake of the non-metallised acid dye, CI Acid Red 261, on to nylon 6.6 microfibre (1

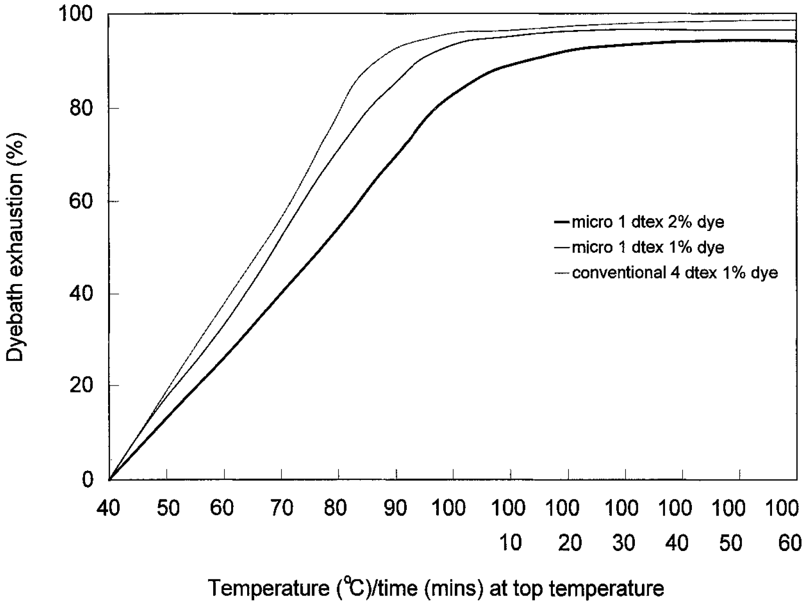


Figure 4.8 Rate of uptake of CI Acid Red 261 on conventional and micro nylon 6.6 at pH 5 (2)

(Reproduced with permission from S.Y. Kamat and Sandoz (India)) dtex) was lower than that achieved on to conventional (4 dtex) nylon 6.6 fibre when the dye had been applied under identical conditions, at 1% o.m.f., to each fibre type (Figure 4.8).

Other workers [63] have observed that in the case of the dyeing of micro (0.9 dtexpf) and conventional (1.7 dtexpf) nylon 6.6 knitted fabrics with 1% o.m.f. CI Acid Blue 25, in the initial stages of dyeing (after 15 minutes at 40°C), dye uptake was greater on microfibre. As dyeing proceeded and dyeing temperature was increased, the rate of dye uptake on to microfibre decreased and, at the end of dyeing at 98°C, complete (i.e. 100%) dyebath exhaustion was secured for both types of fibre. The more rapid rate of dyeing observed for microfibre fabric in the early stages of dyeing was attributed [63] to the substrate's greater surface area.

Examination of the dye distribution across dyed filaments during the course of dyeing revealed [63] that in the early stages of dyeing (at low temperature), most of the adsorbed dye was, for both fibre types, situated at the fibre periphery, but the extent of this 'ring dyeing' was greater for microfibre, this latter finding, again being attributed to the greater surface area of the micro yarn. Furthermore, it was found that the extent of this 'ring dyeing' decreased to a greater degree in the case of conventional fibre with increasing time and temperature of dyeing and, at the end of dyeing, whilst 'ring dyeing' was absent in the case of conventional fibre, this was not the case with the microfibre [63]. The greater propensity of the microfibre to ring dye was considered [63] to be due to the rate and extent of dye diffusion within the microfibre being lower than that within its conventional counterpart owing to the lower internal volume of the former type of fibre.

It was demonstrated that the extent of dyebath exhaustion achieved for 1% o.m.f. CI Acid Red 261 [2] was slightly lower on nylon 6.6 microfibre (1 dtex) than on conventional (4 dtex) nylon 6.6 fibre when the dye had been applied under identical conditions to each fibre type. This was confirmed in a subsequent study of the dyeing of both micro and conventional nylon 6.6 fabrics with four non-metallised acid dyes [63], in which it was found that the difference in final dyebath exhaustion obtained on micro and conventional fabrics increased with increasing concentration of dye applied over the range 0.5 to 4% o.m.f. The following argument was proposed to explain the observed lower extent of dyebath exhaustion in the case of microfibre fabric [63]. During the dyeing of both micro and conventional substrates, the dye molecules will be adsorbed on to the fibre surface and thence diffuse within the interior of the fibre. The rate of dye diffusion within the fibre can be considered to be governed by the concentration of dye at the fibre surface and the available volume within the interior of the substrate in which the dye molecules diffuse. Thus, when both the surface dye concentration and the internal volume are high, the rate of dye diffusion within the fibre (and thus the rate of dyeing) will also be high. However, if the surface dye concentration and the internal volume are low, the diffusion rate will be low. In the case of microfibres, dye adsorption at the fibre surface was found to be high owing to the fibre's large surface area, whilst, in comparison, the available internal volume will be low. Hence, it was envisaged that as dyeing proceeds, there was a limit to the amount of dye that could be accommodated within the comparatively low internal volume of the substrate which, in turn, limited the rate of dye uptake and, therefore, the extent of dyebath exhaustion. Support for this argument was considered [63] to arise from the observation that the difference in dyebath exhaustion secured for dyeings of micro and conventional fibres increased with increasing concentration of dye applied. This was taken to indicate, in the case of microfibre, that even though at higher concentrations of applied dye more dye might be present at the fibre surface, this dye cannot diffuse into the small available internal volume of the substrate.

Owing to its smaller decitex and greater surface area, because more dye has to be applied to polyamide microfibre to obtain the same visual depth of shade as its dyed conventional decitex counterpart, then for dyeings of the same visual depth, the wet fastness of a given dye on polyamide microfibre is lower than that on a conventional decitex fibre [2, 15, 62, 64]. Also, it was shown [63] that when the same concentration of dye was present within micro and conventional nylon 6.6 fabrics, the dyed microfabric exhibited lower wash fastness, this being due to the larger surface area of the microfibre from which dye desorption occurred. Although the aftertreatment of dyeings with either syntans [2, 61, 67] or the full backtan [67] can improve the wash fastness of acid dyes on microfibre polyamide, it has been demonstrated [67] that, when the same amount of several non-metallised acid dyes was applied to 0.9 and 1.7 dtexpf nylon 6.6 knitted fabrics, a commercial syntan was less effective in improving the wash fastness of the dyed microfibre, even though, owing to the greater surface area of microfibre, more syntan had been adsorbed on to this particular type of substrate. The mechanism of adsorption of syntans on both conventional and microfibre polyamide fibres is discussed in Chapter 2.

Non-metallised acid and, to a lesser extent, metal-complex dyes, exhibit lower light fastness on microfibre, especially on strongly delustred fibres [2, 15]; reductions of between 1 and 3 points can be encountered [2]. It is considered [15] that manganese, which is incorporated in dulled fibres to enhance the light resistance of the substrate, is removed from microfibres during dyeing under acidic conditions because of the large surface area of the fibre, with the result that not only is the light resistance of the fibres impaired but also the light fastness of dyeings is decreased. It has been found that the manganese content falls by up to 70% following treatment under acidic conditions [15]. Thus, in order to achieve maximum light fastness, dyeing with acid dyes should be carried out under weakly acidic/

neutral conditions; for example, non-metallised acid dyes can be applied at pH 6 to 7 [2, 15] and 10:2 pre-metallised acid dyes at pH 6 to 9 [15]. Generally, the light fastness of pre-metallised acid dyes is higher than their non-metallised counterparts on polyamide microfibre [2, 15, 64].

References

1. *Textile Terms and Definitions*, 9th edn (ed. M C Tubbs and P N Daniels), Textile Institute, Manchester, 1991.
2. Anon., *Colour Chronicle*, Sandoz, Oct./Dec. (1992) 1.
3. J Baumann and G Jerg, *Text. Chem. Col.*, **22** (12) (1990) 12.
4. Anon., *Jap. Text. News*, (5) (1992) 83.
5. T Hongu and G O Phillips, New Fibres, Ellis Horwood, New York, 1990.
6. M Okamoto, in *Tomorrow's Ideas and Profits: Polyester 50 Years of Achievement* (ed. D Brunnschweiler and J W S Hearle), Textile Institute, Manchester, 1993, p. 108.
7. J E Berkowitch, in *Tomorrow's Ideas and Profits: Polyester 50 Years of Achievement*, (ed. D Brunnschweiler and J W S Hearle), Textile Institute, Manchester, 1993, p. 112.
8. T Yasui and T Matsura, in *Tomorrow's Ideas and Profits: Polyester 50 Years of Achievement*, (ed. D Brunnschweiler and J W S Hearle), Textile Institute, Manchester, 1993, p. 210.
9. K Kawasaki, in *Tomorrow's Ideas and Profits: Polyester 50 Years of Achievement* (ed. D Brunnschweiler and J W S Hearle), Textile Institute, Manchester, 1993, p. 326.
10. I Heidenreich and H Ninow, *Economist Intelligence Unit, Text. Int. Outlook*, (40) (March) (1992) 37.
11. W E Morton and J W S Hearle, *Physical Properties of Textile Fibres*, 2nd edn, Textile Institute and Heinemann, London, 1975.
12. F Fothergill, *JSDC*, **60** (1944) 93.
13. F Steilin, *Mell. Text.*, **64** (1983) 212.
14. P Dorsch, H Wilsing and K-H Peters, *Mell. Text.*, **62** (1981) 188.
15. D Weigner, *Int. Text. Bull.*, (3) (1992) 23.
16. D Brierley, *Review of the Development of Polyester Microfibre*, Zeneca Internal Report, 1992.
17. Anon., *Textile Month*, (1) (1992) 23.
18. A Partin, *Amer. Dyest. Rep.*, (11) (1991) 45.
19. G Honorati, in *Tomorrow's Ideas and Profits: Polyester 50 Years of Achievement* (ed. D Brunnschweiler and J W S Hearle), Textile Institute, Manchester, 1993, p. 220.
20. *Polyester Microfibre Handbook*, ICI Specialties, April 1991.
21. R Bianchi and R Maglione in *Tomorrow's Ideas and Profits: Polyester 50 Years of Achievement*, (ed. D Brunnschweiler and J W S Hearle), Textile Institute, Manchester, 1993, p. 196.
22. M L Jacques, *Textile Asia*, (11) (1992) 50.
23. P Leadbetter and S Dervan, *JSDC*, **108** (1992) 369.
24. S Davies, *Text. Horizons*, **8** (1989) 49.
25. O Wada, *J. Text. Inst.*, **83** (1992) 322.
26. M Matsdaira, *J. Text. Inst.*, **83** (1992) 24.
27. J Hilden, *Int. Text. Bull. Dyeing, Printing, Finishing*, (3) (1991) 34.
28. G Richter, *Colourage Annual*, (1991) 55.
29. *BASF Technical Information Bulletin 232/3e*, Jan. (1993).
30. D Weigner, *Mell. Text.*, **73** (1992) 743.
31. S M Burkinshaw, unpublished results.
32. K H Rostermundt, *Text. Prax. Int.*, **56** (1991) 56.
33. L M Olson and M Wentz, *Text. Chem. Col.*, **16** (1984) 48.
34. E M Sanders and S H Zeronian, *J Appl. Poly. Sci.*, **27** (1982) 4477.
35. G Elefante and F Giammanco, *Chemiefasern/Textilindustrie*, **36** (1986) 892.
36. N T Liljemark and H Asner, *Text. Res. J.*, **41** (1971) 732.

37. J Dave, R Kumar and H C Srivastave, *J. Appl. Poly Sci.*, **33** (1987) 455.
38. H Hendrix, *Z Ges. Textilindustrie*, **63** (1961) 962.
39. A A-M Gorrafa, *Text. Chem. Col.*, **12** (1980) 83.
40. K D Houser, *Text. Chem. Col.*, **15** (1983) 70.
41. E Waters, *JSDC*, **66** (1950) 609.
42. J D H Hall and J R Whinfield and ICI, USP 2,590,402 (1952).
43. S H Zeronian and M J Collins, *Text. Chem. Col.*, **20** (4) (1988) 25.
44. B M Latta, *Text. Res. J.*, **54** (1984) 766.
45. N J Gajjar and Du Pont, USP 20,828,528 (1958).
46. N K Nayak and V A Shenai, *Text. Asia*, **13** (8) (1982) 59.
47. C G G Namboori and M S Haith, *J Appl. Poly. Sci.*, **12** (1968) 1999.
48. S H Zeronian and M J Collins, *Text. Prog.*, **20** (2) (1990) 1.
49. H Ludewig, *Polyester Fibres*, Wiley, New York, 1971.
50. S H Zeronian, M J Collins, L D Fisher and S L Hawk, *J Ind. Fabr.*, **3** (2) (1984).
51. M S Ellison, L D Fisher, K W Alger and S H Zeronian, *J. Appl. Poly. Sci.*, **27** (1982) 247.
52. C G G Nabboori, *Text. Chem. Col.*, **1** (1969) 50.
53. S M Gawish and G Ambriose, *Amer. Dyest. Rep.*, **75** (1986) 30.
54. S M Gawish, M Bourgeois and G Ambriose, *Amer. Dyest. Rep.*, **73** (12) (1984) 37.
55. E McIntyre, in *Handbook of Fibre Science and Technology*, Vol. IV. (ed. M Lewin and E M Pearce), Marcel Dekker, New York, 1985.
56. R T Shet, S H Zeronian, H L Needles and S A Siddiqui, *Text. Chem. Col.*, **14** (1982) 233.
57. D Balmforth, *Text. Chem. Col.*, **14** (1982) 118.
58. M L Jacques, *Textile Asia*, (11) 50 (1992).
59. Anon., *Textile Month*, (1) (1992) 29.
60. Anon., *Textile Month*, (1) (1992) 32.
61. Anon., *Int. Text. Bull.*, (2) (1994) 10.
62. K D Maseka, PhD Thesis, Leeds University, 1994.
63. S M Burkinshaw and K D Maseka, *Dyes and Pigments* (in press).
64. S M Burkinshaw and S D Cox, Unpublished results.
65. S M Burkinshaw and G W Collins, *Dyes and Pigments*, **25** (1994) 31.
66. D J Marfell, Du Pont Fibres (UK), *Personal communication.*
67. S M Burkinshaw, R Gordon, D J Marfell and K D Maseka, *Proc. of the 1994 AATCC Int. Conf. and Exhibition*, Charlotte, 1994.

Dye index

The dyes below are those for which the structure has been given

Subject index