CHAPTER 3

Nylon dyeing

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3.1 INTRODUCTION

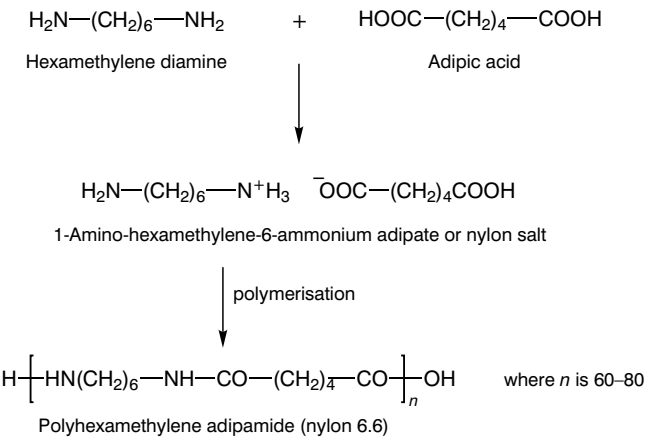
The story of William Carother's and DuPont's invention of nylon in 1938 is an example of inspirational and tenacious research leading to the first truly synthetic textile fibre [1]. Nylon has stood the test of time and, many decades later, is still highly valued in apparel and furnishing fabrics. DuPont was first into the marketplace with nylon 6.6, closely followed in 1939 by I G Farben's Perlon L (now generically known as nylon 6). Clearly, there was a race against time to establish these high-strength fibres prior to the onset of the Second World War; during the war, nylon was almost exclusively employed in parachute materials where its high strength and low density were admirably suited. At the end of the war, nylon first appeared in ladies stockings, but became rapidly established as a multi-purpose textile fibre.

The rapid solution of many coloration problems allowed the production of a wide range of shades. However, even today, there are some outstanding difficulties in terms of barré or stripiness, poor wet-fastness in full, bright shades, inadequate photostability of the base fibre and the poor light-fastness of copper phthalocyanine-based turquoise blue shades. Environmental problems, such as those related to the use of compounds of heavy metals – for example, copper – to photostabilise the fibre and to formaldehyde-containing Syntans, are becoming more important as legislation comes into force.

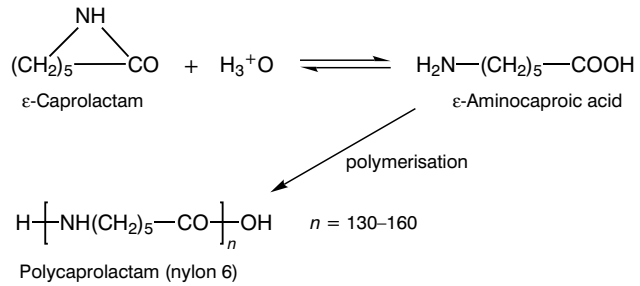
Earlier reviews of nylon dyeing processes include the excellent chapter by Ginns and Silkstone in the first Society of Dyers and Colourists textbook on blend dyeing [2] and much of the information given at that time remains equally valid today. In order to understand the various dyeing and printing processes employed for dyeing nylon, it is necessary to briefly review the chemistry and technology of nylon fibre production.

Nylon 6.6 polyamide polymer chips, the starting material for fibre production by melt spinning, are prepared by the polymerisation of hexamethylene diamine and adipic acid (Scheme 3.1). Nylon 6, or Perlon, is prepared by the condensation polymerisation of ε-caprolactam (Scheme 3.2).

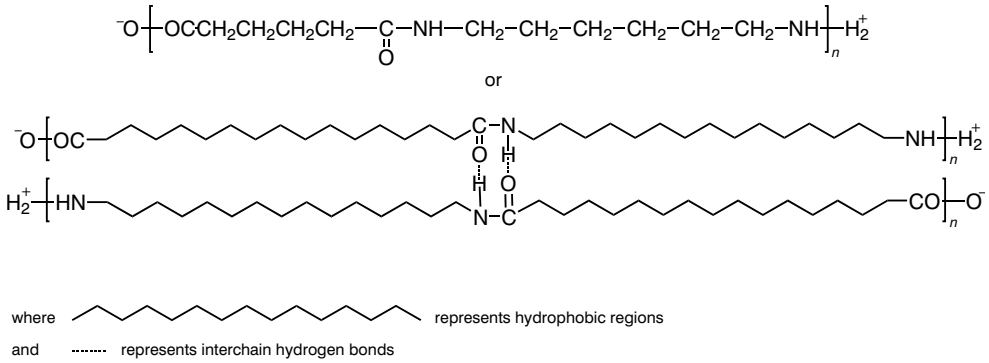
There are significant differences between these two commercially important types of nylon, some of which are manifested only on dyeing; for example, nylon 6.6 fibres show slightly higher crystallinity than nylon 6 fibres, giving rise to more rapid dyeing of the latter with anionic dyes. The two variants also have different melting points (250 °C for the former and 230 °C for the latter) and produce different amounts of oligomer during dyeing [3].



Scheme 3.1



Scheme 3.2

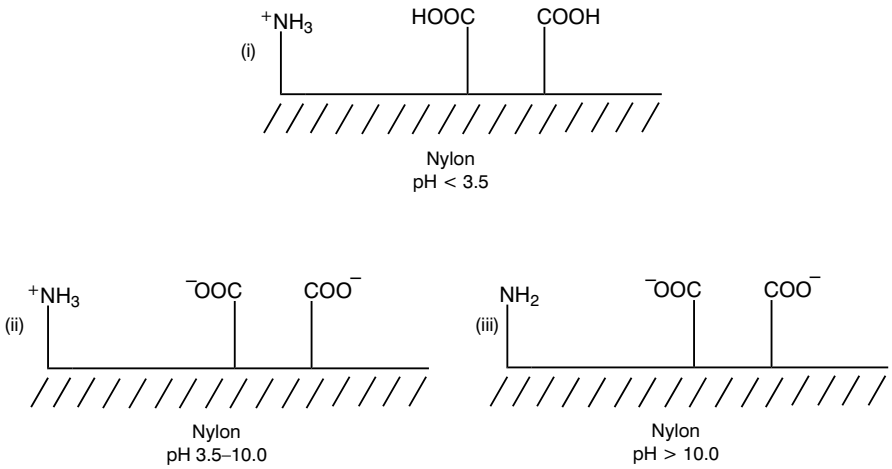


Scheme 3.3

Schemes 3.1 and 3.2 are highly simplified, especially since they give the impression that the numbers of amino and carboxyl end groups are equivalent. In practice, in order to control polymerisation and also to produce a polymer that can be consistently melt-spun, acetic acid is added to reduce the number of amino end groups. A typical nylon 6.6 fibre thus has the schematic structure shown in Scheme 3.3.

This scheme indicates that these polyamide polymers will have substantivity for hydrophobic dyes (interactions with tetramethylene and hexamethylene hydrophobic regions), anionic dyes (for example, sulphonated acid dyes interacting with protonated amino end groups) and cationic dyes (interactions with ionised carboxy end groups). In practice, nylon fibres are dyed mainly with anionic acid dyes and to a small extent with disperse dyes. The former give a wide gamut of shades with the possibility of achieving very good wet-fastness properties if high molecular weight dyes are employed, whereas disperse dyes generally suffer from poor build-up and wet-fastness properties.

Typically 1 kg of nylon 6.6 fibre contains 0.036 moles of primary amino groups and 0.090 moles of carboxylic acid groups situated at the ends of the polyamide chains. The nylon fibre thus exists in specific ionic states according to the pH of the surrounding aqueous solution (Scheme 3.4).



Scheme 3.4

These ionic states can only be, of course, an approximate picture since, in addition to the pH of the surrounding medium, the dissociation of both carboxylic acid and protonated amino groups is influenced profoundly by their environment (for example, the hydrophobic character of neighbouring groups) and by temperature. However, in spite of these reservations, states (i), (ii) and (iii) are useful models to explain the observed dyeing behaviour of nylon with ionic dyes. Thus, below pH 3.5, nylon behaves as if it possesses a net positive charge and exhibits a strong attraction for bulky anions such as simple mono-, di- and tri-sulphonated acid dyes. Above pH 3.5, nylon shows a diminishing attraction for these anions, confirming that the overall positive charge is reducing to zero. Above pH 7.0, nylon is increasingly negatively charged and has a strong attraction for cations. This ion-exchange model is clearly simplistic and the hydrophobic character of bulky ions such as water-soluble dyes can play an over-riding role due to hydrophobic interactions between, for example, the polymethylene residues in nylon 6.6 and bulky aromatic residues in dyes. Of equal importance may be the role played by interactions

between aromatic systems in the dye molecules. In this case, sorbed dye containing free aromatic rings will attract other dye molecules [4,5].

3.2 DYEING NYLON WITH ACID DYES

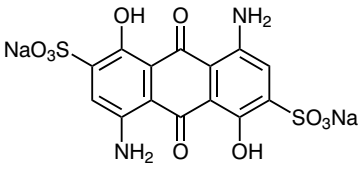
3.2.1 Dyeing theory

Acid dyes are, by definition, applicable to natural and synthetic polyamide fibres under acidic conditions, usually from boiling dyebaths. They are water-soluble, anionic dyes prepared by incorporating a number, typically 1–3, of sulphonate groups in a chromophore. In rare cases carboxylate groups are employed to achieve anionic character and water solubility. As mentioned above, the initial driving force for dyeing to occur with a simple acid dye/polyamide fibre combination is probably Coulombic, but, depending on dye structure, non-polar interactions are also capable of playing an important role. In terms of Coulombic interactions, an important factor which affects the rate of acid dye uptake, and its final saturation value on the fibre, is the total number of protonated amino sites in the fibre. In this context it is valuable to make a comparison between wool, silk and nylon (Table 3.1).

Table 3.1 Amino groups in wool, silk and nylon

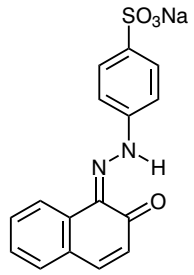
Wool	lysine primary amino histidine secondary/tertiary amino arginine guanidino α-terminal amino	0.820 mol kg^{-1}
Silk	lysine histidine α-terminal amino	0.150 mol kg^{-1}
Nylon 6.6	α-terminal amino	0.036 mol kg^{-1}

Thus one may expect the saturation values of acid dyes on these three polyamide fibres to be in the same ratio as the above basic group contents; that is, wool:silk:nylon = 23:4:1. This effect was verified experimentally by Skinner and Vickerstaff [6] who studied the equilibrium uptake of CI Acid Blue 45 (1,6-diamino-4,8-dihydroxy-3,7-disulpho-anthraquinone) (**3.1**) on the three fibres at pH 1.6 and 85 °C; the corresponding ratio obtained was 14:4:1.



3.1

Mono-sulphonated acid dyes are especially prone to the phenomenon of 'over-dyeing', in which much more dye than the predicted 0.036 mol kg^{-1} may be absorbed under prolonged 'equilibrium' dyeing conditions. Peters [7] studied the equilibrium uptake (dyeing for 3–4 days) of CI Acid Orange 7 (sulphanilic acid → β-naphthol) (**3.2**), on nylon 6.6 at 60 °C and these results are reproduced in Figure 3.1.



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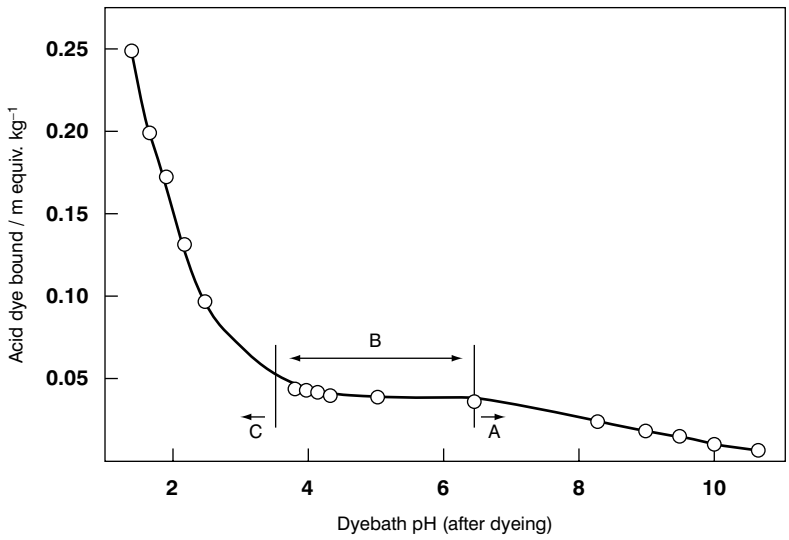


Figure 3.1 Titration curve of nylon 6.6 with CI Acid Orange 7 [7]; regions A, B and C are defined in the text

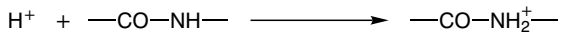
Figure 3.1 shows that this dye exhibits high neutral affinity for nylon and even under alkaline conditions significant dyeing occurs; as the pH is reduced below pH 4 the 'over-dyeing' phenomenon becomes increasingly apparent. Peters also noted that the acid dye–polyamide fibre titration curve shown in Figure 3.1 could be conveniently divided into three regions:

A a regular titration region with an anion of high affinity;

B a region of electrostatic saturation where there is a reasonable correlation between amine end group content and amount of sulphonic acid dye bound;

C a region where electrostatic saturation is exceeded and where dye uptake has no apparent maximum.

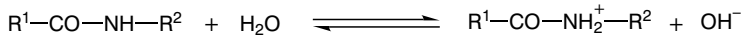
Many authors have suggested that the phenomenon of 'over-dyeing' under acid conditions is due to the protonation of amide groups in the polyamide chain, according to Scheme 3.5.



Scheme 3.5

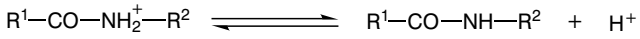
Although this is possible under strongly acidic conditions, it is most unlikely to occur in the presence of dilute acids, especially those carboxylic acids used in dyeing processes. This markedly different behaviour, compared to primary amines, is related to the fact that amides are very weak bases, with pK_b values of 15–16. The pK_b values can be calculated according to Eqn 3.1, based on the equilibrium shown in Scheme 3.6:

$$K_b = \frac{[R^1\text{–CO–}NH_2^+\text{–}R^2][OH^-]}{[R^1\text{–CO–NH–}R^2]}$$
$$pK_b = -\log K_b \qquad (3.1)$$

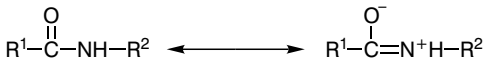


Scheme 3.6

Perhaps a simpler way of looking at these phenomena is to convert the above analysis to that of the dissociation of the theoretical conjugate acid (Scheme 3.7). The pK_a value for the above is –1 to –2, which indicates that extremely acidic conditions would be required to protonate amides. The resonance structures of the secondary amide group explain why its nitrogen atom is of very low basicity and nucleophilicity (Scheme 3.8).



Scheme 3.7



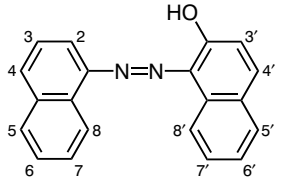
Scheme 3.8

Under prolonged exposure to even mildly acidic conditions amides will, however, hydrolyse to the corresponding protonated primary amine and carboxylic acid, which in the case of polyamides reduces the degree of polymerisation (DP). Thus the observed excessive 'over-dyeing' at low pH values (region C in Figure 3.1) may be simply due to this increasing tendency to hydrolyse. Hydrolysis will make the fibre more accessible as well as producing further

protonated amine dye sites. This explanation for 'over-dyeing' at low pH is supported by the work of Peters and O'Brian [8].

The effect on the substantivity of acid dyes for nylon, wool and human hair, of varying the number of sulphonate groups in the dye molecules, has been examined by numerous workers [9–15]. These workers quite clearly demonstrated that dye substantivity for the polyamide substrates decreases in the following order: monosulphonate > disulphonate > trisulphonate > tetrasulphonate.

White [10] prepared radio-labelled (^{35}S) derivatives of CI Acid Red 88 (**3.3**), CI Acid Red 13 (**3.4**), CI Acid Red 18 (**3.5**) and CI Acid Red 41 (**3.6**). The dyes were applied to nylon from 'infinite' dyebaths and titration curves produced. As the degree of sulphonation increased, the extent of over-dyeing decreased, the theoretical electrostatic saturation corresponding to the case of the tetrasulphonated dye.



(**3.3**; 4-monosulphonate)
(**3.4**; 4,6′-disulphonate)
(**3.5**; 4,6′,8-trisulphonate)
(**3.6**; 4,3′,6,8′-tetrasulphonate)

In the case of the mono- and disulphonates, binding forces other than Coulombic interactions predominate. However, in all cases a point of electrostatic saturation must be reached, since the negative charges on the sorbed dyes will eventually lead to a surface negative potential sufficient to repel further dye adsorption from the solution phase.

Derbyshire and Peters [16] explained these effects in terms of non-polar bonding between hydrophobic regions in the fibre and similar regions in the dye. The non-polar forces were simply defined by the above authors as Van der Waals forces.

In the light of the above observations, it is thus important to discuss the various types of molecular interactions which may occur in dye/fibre systems. In terms of non-covalent interactions, the different forces between two molecules, like or unlike, are usually divided into five categories [17]: Van der Waals forces, electrostatic interactions, induction forces, charge transfer stabilisation effects and solvophobic interactions.

The three categories large enough to be of importance in terms of dyeing processes are:

(1) **Van der Waals (VDW) interactions**, which are the sum of dispersion and repulsive energies. The thermodynamic strength of VDW interactions is less than 8 kJ mol^{-1} [4].

(2) **electrostatic interactions** between static molecular charge distributions. In dyeing processes, these include not only, for example, obvious attractions such as those between protonated amino groups in polyamide fibres and sulphonated anionic dyes, but also, according to classical definitions, hydrogen bonding [17]. A recent review points out that this may be an inadequate definition [18], but for the purposes of this analysis it is suitable.

Hydrogen bond strengths vary considerably, but for neutral molecules they lie between 10 and 65 kJ mol^{-1}, and when one of the components is ionic they rise to 40–190 kJ mol^{-1}.

(3) **solvophobic or hydrophobic interactions**. These arise from the effect of non-polar parts of water-soluble solutes on the structure of water. When such molecules are brought into aqueous solution through a relevant solubilising group (for example, sulphonate) then the water structure must change to accommodate the non-polar or hydrophobic residues. This change represents a gain in entropy for the whole system. Since most dyeing processes are restricted to aqueous systems, hydrophobic interactions are likely to play an important role in determining both dye uptake by fibres and subsequent wet-fastness. Zollinger [13], in his George Douglas lecture, highlighted hydrophobic interactions as being responsible for the above over-dyeing effects on nylon as well as the unusually high substantivity of dyes containing bulky aryl or alkyl residues for wool.

Since dyes and fibres such as wool, silk and polyester both contain aromatic residues, it is worthwhile to consider current thinking regarding π–π interactions. Hunter [4] points out that these are commonly used to explain interaction between two or more aromatic molecules, but current evidence shows that they are negligible compared to electrostatics [19].

On first sight it might be expected that, since aromatic groups are planar, maximum VDW interactions occur in a perfectly flat stacked arrangement. In water, hydrophobic interactions will also favour stacking, since the flat π-electron surfaces of the dye molecules are non-polar [20]. Thus, authors writing on dye aggregation in aqueous solution (for example, [21]) tend to draw the aggregates as perfectly stacked molecules with maximum overlap of free aromatic rings. Hunter and Sanders [22] have studied the geometry and energy contour plots of two stacked porphyrins and noted that the aromatic residues were in an offset or staggered arrangement. To explain these observations, the above authors concluded that electrostatics provide a large repulsive force which pushes the π-systems away from the usually accepted maximum overlap position; the best model involved a positively charged σ-framework sandwiched between two idealised 'π-atoms'. Continuing this analysis led Hunter [4] to the conclusion that certain face-to-face arrangements of aromatic systems lead to repulsion and other arrangements, such as face-to-edge and offset, lead to attraction. He was thus able to construct a very useful diagram, which is reproduced in Figure 3.2.

This new way of thinking about π–π interactions [4] allowed a ready explanation of the characteristic herringbone packing of aromatic hydrocarbons in the crystalline state [23] and also explained the phenylalanine–phenylalanine geometries found in X-ray crystal structure analysis results from certain proteins [24].

The maximum electrostatic interaction for two π-electron systems was subsequently calculated as 6 kJ mol^{-1}, which is relatively weak. However, dyes are polyaromatic systems and in fibres such as wool the aromatic side-chain residues in phenylalanine, tyrosine and tryptophan often occur in the same region; thus all the small contributions, when summed, become significant.

The authors [5] contend that the previous explanations of non-polar interactions in dye/fibre

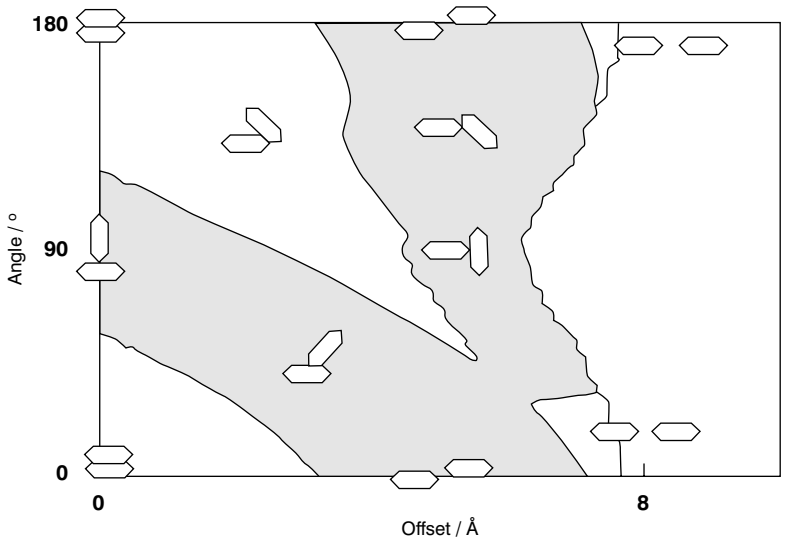


Figure 3.2 Electrostatic interaction between two benzene rings as a function of orientation. (From [4])

systems have neglected the special case of aromatic π–π interactions. Attention should be drawn to the anomaly that in aqueous systems hydrophobic interactions increasingly break down above about 60 °C and many of the above nylon over-dyeing studies were carried out in boiling aqueous solution. It is thus proposed that aromatic or π–π interactions are largely responsible for the over-dyeing effects observed and have been omitted from previous analyses. At first sight this appears to be a contentious view since undyed nylon does not contain any aromatic sites. However, as increasing amounts of dye are absorbed, initially onto protonated amino sites, those dyes containing free aromatic rings will act as new dye sites.

Holfeld and coworkers [25,26,27], in a series of papers, emphasised the influence of the nylon fibre's pre-history on its subsequent dyeing properties and related these effects to the phenomenon of barré or stripey dyeing. In this work, the existence of a surface barrier to acid dye diffusion was proposed, and subsequently proven by Coates and coworkers [28] using tracer diffusion studies with labelled chloride ion ($^{36}Cl^-$) and labelled dye anions ($D^{35}SO_3^-$). The anisotropy of the fibre varied with draw ratio; subsequently, a value for 'surface admittance' was calculated and correlated with draw ratio. At a draw ratio of 2.5 the 'surface admittance' was found to be 2.73 times that at a draw ratio of 3.5; the diffusant being $^{36}Cl^-$ labelled hydrochloric acid.

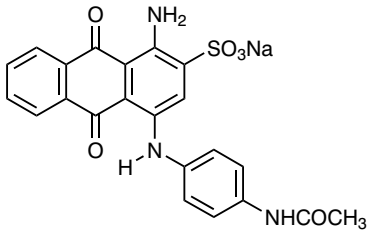
Holfeld and coworkers [25] proposed that water should be regarded as a carrier in nylon dyeing, using the analogy that carriers are compounds which provide chemical energy to supplement and replace thermal energy in dyeing and finishing. This 'carrier' effect of water in nylon dyeing causes structural changes which are reversible below 75 °C and irreversible above 95 °C. Hot steam setting up to 160 °C had a marked effect on increasing the rate of dyeing of the large molecule, CI Acid Blue 122, but no effect on that of the low molecular weight dye,

CI Acid Blue 45 (**3.1**). Steam setting usually increases the rate of dyeing and also decreases the fibre modulus despite an increase in crystallinity. Tsurata and Koshimo [29] discuss the reasons for the unexpected drop in modulus with increased crystallinity in the case of nylon 6. Peters and White [30] made a similar study on nylon 6.6 and attributed the increased dyeing rate following steam setting to changes in fibre structure, such as decreased orientation in the amorphous regions. Warwicker [31], using X-ray analysis, proposed that steam setting increased dyeing rate despite increasing fibre crystallinity, by the formation of a 'shish-kebab' type of fibre structure, which would show increased accessibility with increasing crystallinity.

In contrast to heating in the presence of moisture, dry heat always reduces subsequent dyeing rate especially with the larger dye molecules. It has been proposed [25] that dry heating produces additional interchain interactions, thus restricting subsequent dye access.

Kobsa and coworkers [32,33,34] developed a simple, rapid method of measuring the diffusion coefficients of acid dyes in nylon by adopting a semi-empirical approach. This method used a diffusion equation derived for dyeing fibres of round cross-sections from finite dyebaths, and assumed the adsorption of the acid dyes was of the Langmuir type.

Subsequently, Kobsa and coworkers [34,35] employed these diffusion coefficients to probe the structure of nylon 6.6 fibres, especially to follow changes which occurred on heat setting. In particular, Kobsa [32] studied how heat setting nylon carpet fibres at 100% RH, at temperatures ranging from 25 to 170 °C, affected the diffusion coefficients and equilibrium uptake of several common dyes during subsequent dyeing at 25 °C. He found that when the steam setting temperature exceeded 110 °C a remarkable rise in diffusion coefficient occured. At setting temperatures of 170 °C, the diffusion coefficient of CI Acid Blue 40 (**3.7**) was increased by a factor of 1000 and the equilibrium dye uptake also increased by 50% compared to an unset fibre. If the latter is an indication of dye-accessible internal volume in the fibre, Kobsa proposed that this factor must also increase by 50%, due to the steam setting procedure.



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Changes in the X-ray diffraction patterns were also studied by Kobsa [34] and revealed that the fibre possibly consists of three distinct phases:

(1) a crystalline phase melting at 182 °C at 100% RH;
(2) an amorphous phase, which exhibits a glass transition temperature (T_g) of 0 °C at 100% RH;
(3) a metastable trans-crystalline material melting between 182 and 212 °C and which produces crystalline and amorphous material on melting.

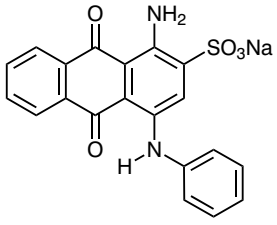
These subtle inhomogenieties in the individual nylon fibre clearly are of importance to the dyer since they give a clue as to the nature of barré when dyeing fibres of well-controlled AEG (amine end group) content.

3.2.2 Dyeing nylon with acid dyes

A characteristic feature of the acid dyeing of nylon is the phenomenon of barré dyeing – that is, the appearance of stripes in the dyed goods. Barré arises from chemical (that is, amino and carboxyl end group content) variations introduced during polymer manufacture, oxidation of amino end groups during melt spinning, and also from physical variations (in crystallinity) introduced during melt spinning, drawing and setting processes. Nowadays variations in amino and carboxylic acid end groups at the polymer manufacture stage are minimal and fuller control of physical differences is thus required. Modern fashion colours and fastness demands have recently exacerbated the barré problem since high molecular weight anionic dyes are required to meet wet-fastness requirements, and these show lower migration propensity. However, DuPont have recently introduced a new process [36] for dyeing nylon with these higher molecular weight dyes; this so-called 'Infinity' process is a patented method involving continuous addition of dye. Addition does not commence until the nylon is brought to thermal equilibrium (*c.* 70 °C) thus avoiding differential uptake of dye.

As an aid to dye selection, dye manufacturers market preferred groups of acid dyes for nylon based on their ability to cover physical and chemical differences in the fibre, their build-up properties and their compatibility in mixtures. The dyes are divided into three groups.

(1) **Group 1:** Typically these are monosulphonated dyes with little substantivity for nylon under neutral or weakly acidic conditions but which exhaust well under stronger acidic conditions (pH 3–4). The structures of dyes CI Acid Blue 25 (**3.8**) and CI Acid Blue 78 (**3.9**) are typical. These dyes, being acid levelling dyes, cover barré nylon well, but the wash-fastness of the dyeings is only poor-to-moderate.



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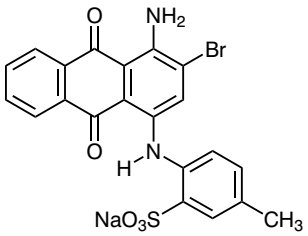

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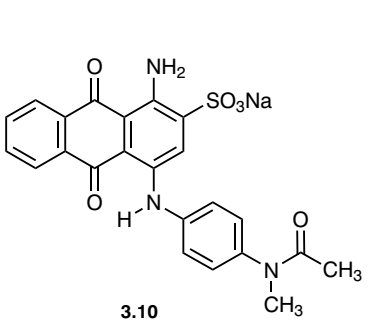
(2) **Group 2:** These dyes exhaust well at pH 3–5 and give dyeings of higher wet-fastness than Group 1 dyes. Their higher substantivity means that more care has to be taken in their application to ensure level dyeing. The structures of dyes CI Acid Blue 41 (**3.10**) and CI Acid Yellow 172 (**3.11**) are typical.



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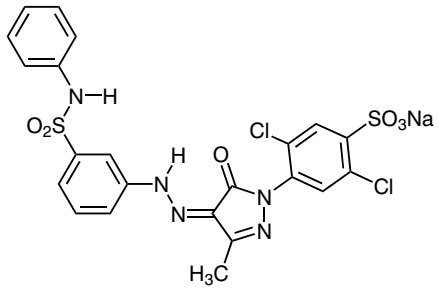

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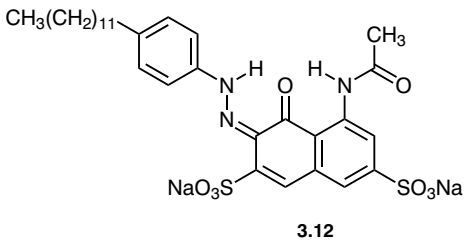
(3) **Group 3:** These dyes of greater molecular size exhibit high 'neutral' (pH 5–7) substantivity and poor levelling properties. Their coverage of barré nylon is poor, but the dyeings have good fastness to wet and washing treatments and good light-fastness. The structures of dyes CI Acid Red 138 (**3.12**) and CI Acid Blue 138 (**3.13**) are typical.



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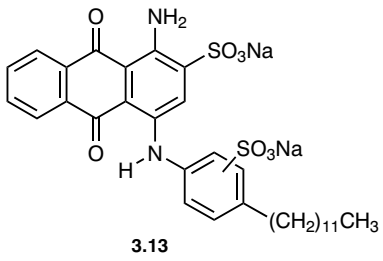


3.13

Because of the difficulty in covering the physical and chemical variations in the fibre, it is usually necessary to employ dyebath additives to control exhaustion. Anionic agents compete with the anionic dyes for available sites within the polyamide, while cationic fatty amine ethoxylated agents form complexes with the negatively charged dye, which slowly break down, releasing the dye as the temperature is raised. Recently, the use of mixtures of anionic and cationic surfactants has been advocated; the anionic 'blocking' component is designed to be rapidly adsorbed by the substrate and become concentrated on those nylon fibres which tend to be dyed most rapidly. The cationic agent aids levelness by slowing dye adsorption due to complex formation. A typical dyeing process on nylon 6.6 can therefore be presented as shown in Figures 3.3 and 3.4.

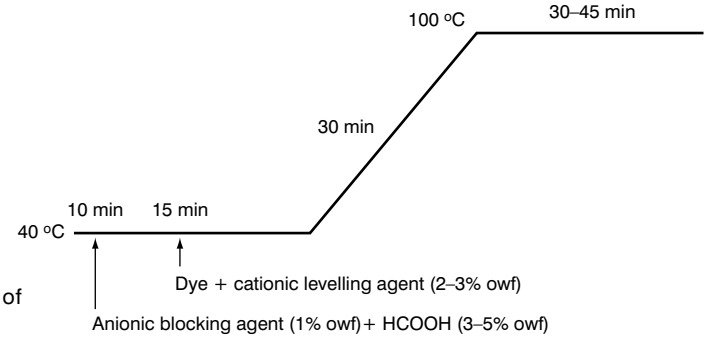


Figure 3.3 Dyeing profile of Groups 1 and 2 dyes

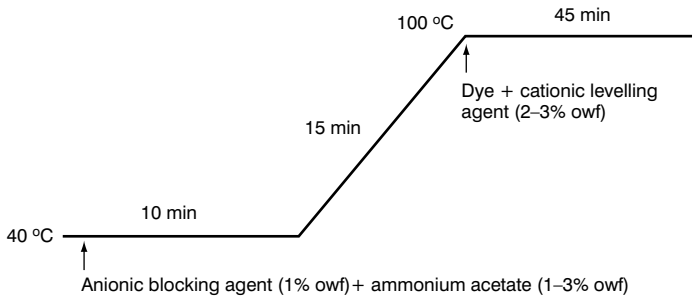


Figure 3.4 Dyeing profile of Group 3 dyes

In Figure 3.3, formic acid is used but acetic or citric acid could also be used; formic acid offers the environmental advantage of lower COD compared to the other organic acids. In Figure 3.4 the rate of rise of temperature is rapid since dyeing only occurs when the temperature is sufficiently high to break down the complex formed between anionic dye and cationic auxiliary.

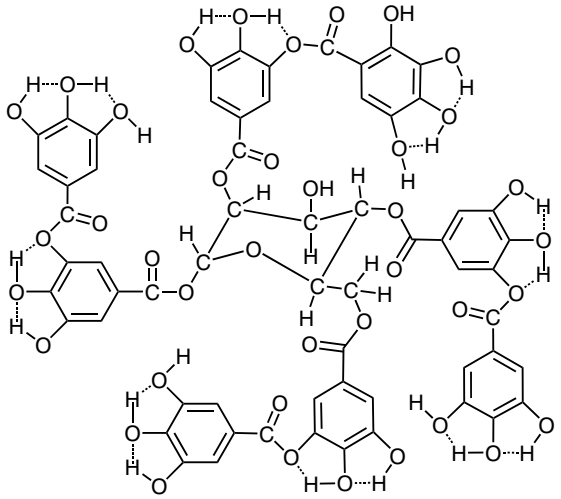
The wash-fastness properties of acid dyes (especially Groups 1 and 2) on nylon leave much to be desired and it is thus common to after-treat the dyed nylon with either natural or synthetic tanning agents (Syntans) to improve wash-fastness [37,38].

Natural tanning agents

This process is known as the 'full back-tan' and involves treating the dyed nylon with tannic acid (2% owf), at pH 4.0 (CH_3COOH) for 20 minutes at 80 °C, followed by a treatment in a separate bath containing potassium antimonyl tartrate (tartar emetic) (2% owf) at pH 4.0 for 20 minutes at 80 °C. It is considered that the full back-tan results in the formation of a large sparingly water-soluble anionic complex, located at the surface of the dyed nylon, which restricts diffusion of anionic dye molecules out of the substrate during washing. Although the full back-tan often results in quite dramatic improvement in wash-fastness of acid dyes on nylon, the process suffers from the following disadvantages:

(1) the process is in two stages, and therefore time consuming;
(2) tartar emetic is toxic;
(3) tannic acid discolours on exposure to light;
(4) back-tanning reduces the light-fastness of the dyes on nylon;
(5) the process is expensive;
(6) the effect can be partially lost on steam setting.

Major constituents of gallotannins, including tannic acid, are the polygalloylated glucoses. Shore [39] showed that the 1,2,4,6-tetragalloyl ester of D-glucose can exist as a remarkably stable structure (**3.14**).



3.14

Synthetic tanning agents

In view of the aforementioned disadvantages of natural tanning agents, a simpler after-treatment for improving the wash-fastness of acid dyes on nylon was developed employing synthetic tanning agents (Syntans). Typically, these Syntans are high molecular weight polycondensates of sulphonated phenol- or dihydroxydiphenyl sulphone-formaldehyde. It is considered that, unlike the full back-tan, Syntans do not form a 'skin' as such at the fibre surface but instead are located within the periphery [39] of the dyed substrate. Although not as effective as the full back-tan, Syntans can result in marked improvements in wash-fastness. They are generally applied at pH 3–5 (CH_3COOH or HCOOH) for 20 minutes at 80 °C. Longer treatments promote diffusion of the Syntan from the surface of the fibre towards its interior and tend to lower wet-fastness, indicating that surface deposition of the anionic polymer is important.

Syntans are still widely used despite problems of reduction in light-fastness of after-treated dyeings, slight changes in hue, firmer fabric handle and difficulties due to loss in adhesion when used in foam laminating.

The improvements in wet-fastness achieved by the use of Syntans can be partially lost due to the following factors:

(1) instability to dry heat;
(2) post-boarding sensitivity;
(3) steam-setting sensitivity.

3.2.3 Metal-complex dyes

2:1 (dye:metal) metal-complex dyes are important for nylon dyeing especially where very good light-fastness is required – for example, in automotive upholstery. Dyeings produced on nylon

using these dyes exhibit excellent build-up, good levelness in mixture shades and very good light- and wash-fastness characteristics. However, their ability to cover affinity variations in the fibre vary markedly and their application necessitates the use of weakly cationic, complexing auxiliaries to control exhaustion. It is interesting to note that some mills are refusing to use pre-metallised dyes due to ill-considered ideas regarding the safety and environmental impact of heavy metal atoms such as chromium and cobalt; responsible dye makers ensure that such heavy metals are only bound to the chromophore and are not readily available to the aqueous environment and pose no health hazards.

The dyeing of blacks on micro and fine filament yarns is currently undertaken using metal-containing dyes – for example, CI Acid Black 194. The large amounts of dye added to achieve deep blacks require Syntans, and possible after-treatment with cationics, to achieve high fastness. This after-treatment is not stable to repeated domestic washing. In the light of the above, sulphur vat dyes have been prepared for dyeing very dark blacks, thus reducing the risk of both metal and formaldehyde next to the skin. Hydron Indocarbon CLG is an example of a typical sulphur black.

3.3 DYEING NYLON WITH DISPERSE DYES

Disperse dyes cover both physical and chemical variations in the fibre very well. However, wet- and wash-fastness properties of these dyes on nylon is – with the exception of 2:1 metal-complex disperse and reactive disperse dyes – very poor, and consequently their use is restricted to applications where high wet- and wash-fastness properties are not required. The light-fastness of the dyeings is normally good.

Metal-complex disperse dyes were sold by Kuhlmann as Amichrome and BASF as Violan Fast dyes; the former are no longer available. The main advantage of this type of dye was improved level dyeing compared to more traditional 2:1 metal-complex dyes containing solubilising groups.

Reactive disperse dyes are discussed in detail in Section 3.5.2.

3.4 NYLONS WITH MODIFIED DYEING PROPERTIES

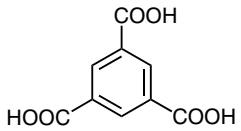
These find use predominantly in differential-dyeing yarn to produce multiple-colour or contrast effects in loop-pile tufted carpeting and in woven and knitted cloths. The fibres are made from chemically modified polyamides similar in structure to nylon 6 or 6.6 and are processed conventionally.

Since the dyeing behaviour of polyamide fibres is determined by the nature and number of end groups present ($–NH_2$ and –COOH) and by the disposition of the polymer chains, fibres with modified dyeing properties can be produced by changing either, or both, of these characteristics.

3.4.1 Deep-dyeing nylon

Modification of the polymerisation process to give a polymer with a higher amine end group (AEG) content, and consequent increased substantivity towards anionic dyes, can be achieved by:

(1) increasing the proportion of diamine in the reaction mixture (but this can lead to difficulties in controlling the polymerisation due to loss of diamine from the system at an increasing rate with increasing excess of diamine) [40];
(2) by adding *p*-toluene sulphonic acid derivatives to the system, which protects the free amino end groups during polymer and yarn manufacture, or by adding phosphinic or phosphonic acid derivatives to prevent oxidative loss of diamine [41];
(3) by producing a branched-chain polymer – for example, by copolymerisation with trimesic acid (1,3,5-benzene tricarboxylic acid) (**3.15**);
(4) by modifying the melt-spinning process such that the disposition of the polymer chains favours penetration of dye molecules – for example, by co-extruding nylon 6.6 and polycaprolactam (nylon 6).

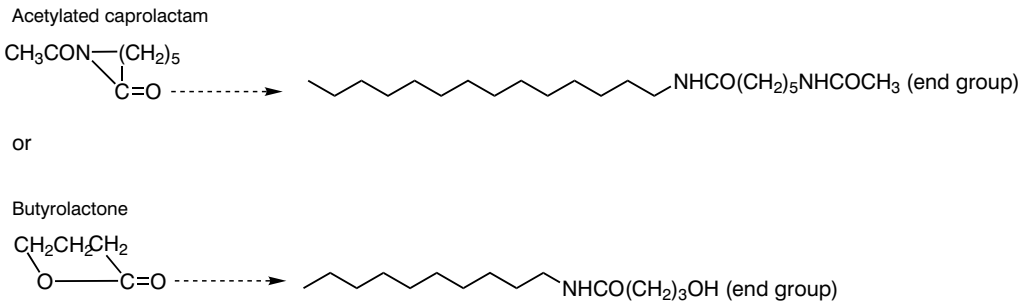


3.15

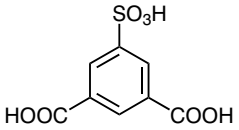
3.4.2 Basic-dyeable nylon

These fibres contain a reduced number of amino end groups and thus have reduced affinity for anionic dyes, but are readily dyed with cationic dyes. This can be achieved by:

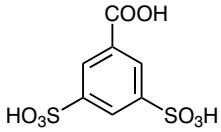
(1) addition of acetylated caprolactam or butyrolactone to the polymerisation system (Scheme 3.9);
(2) by introducing strongly acidic groups (for example, $-SO_3H$) into the fibre during the polymerisation process. Such groups can be introduced either within a chain by copolymerisation with 3,5-dicarboxybenzene-1-sulphonic acid (**3.16**) [42] or at the end of a chain by using 3,5-disulphobenzene-1-carboxylic acid (**3.17**).



Scheme 3.9



3.16



3.17

3.5 DYEING NYLON WITH REACTIVE DYES

3.5.1 Sulphonated reactive dyes

Reactive dyes contain fibre-reactive side-chains, capable of forming covalent bonds with nucleophilic sites in appropriate fibres during the dyeing process. As a class, they have been extremely successful on cotton and wool fibres, since they are capable of producing a very wide gamut of shades with excellent wet-fastness properties. However, on nylon fibres they have not been so successful, only giving sufficient covalent bonding in pale to moderate depths; in full depths the dye is present mainly as unfixed anionic dye and thus exhibits the indifferent wet-fastness properties of acid dyes. In the light of renewed current demands for bright, full shades on nylon with good wet-fastness properties, the causes of this unsatisfactory situation are worth further investigation.

Normally, 1 kg of nylon 6.6 fibre contains 0.036 moles of primary amino groups and 0.090 moles of carboxylic acid groups, both residues being situated at the ends of the polyamide polymer chains. At ambient temperatures, the nylon fibre exists in the ionic states previously described in Scheme 3.4.

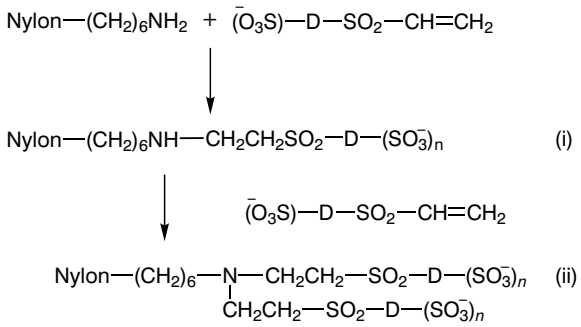
The situation shown in Scheme 3.4 is an approximation which assumes the pK_a value of the carboxylic acid residues in nylon is about 3.5 and the pK_a value of the amine conjugate acid ($–CH_2–CH_2–CH_2–CH_2–CH_2–CH_2–^+NH_3$) is about 10. Since the amino residues are the only nucleophilic sites available to covalently anchor the reactive dye, it is apparent that the maximum depth of shade, the degree of dye fixation and hence the wet-fastness of the dyeing, are very dependent on the number of such residues available in the fibre. Temperature and pH also play an important role; an increase in temperature from 25 to 100 °C lowers the pK_a values by about two units [43]. As nylon is usually dyed at or near the boil, it is often assumed that the nucleophilic primary amino sites will be available to react with the particular reactive dye only at dyebath pH values greater than neutral. However, even at pH 5 a moderate degree of reaction will be possible, since as the small amount of available unprotonated amine reacts, further nucleophilic unprotonated amine is produced to restore the dissociation equilibrium.

The reactive dyes currently available are all based on polysulphonated chromophores and sold for the dyeing of wool and cotton. To achieve adequate substantivity of such anionic chromophores for the nylon fibre it is necessary to dye under weakly acidic conditions (pH 5.0–6.0). For the reasons discussed above, such conditions are inefficient in terms of achieving a high degree of dye–fibre covalent bonding, the nucleophilic amino residues being mainly in their non-reactive protonated amine form and as such are tied up as zwitterions with anionic carboxylate groups.

Recently, DuPont and DyStar have collaborated to develop the 'Coloursafe' system, which is believed to be based on a special nylon 6.6 fibre with higher AEG than normal and selected mono- or disulphonated blocked vinylsulphone dyes (Stanalan dyes). Bright shades of good colour-fastness to washing are produced even in twice standard depth shades. Even more recently Ciba have developed the Eriofast range of reactive dyes for nylon – it is believed that these may be heterobifunctional types.

Dyes which react by a Michael addition reaction

These dyes are typified by the vinylsulphone derivatives and may conveniently be written as $D–SO_2–CH{=}CH_2$, where D represents the sulphonated chromophoric residue. The reaction of these dyes with the fibre may be written as shown in Scheme 3.10.



Scheme 3.10

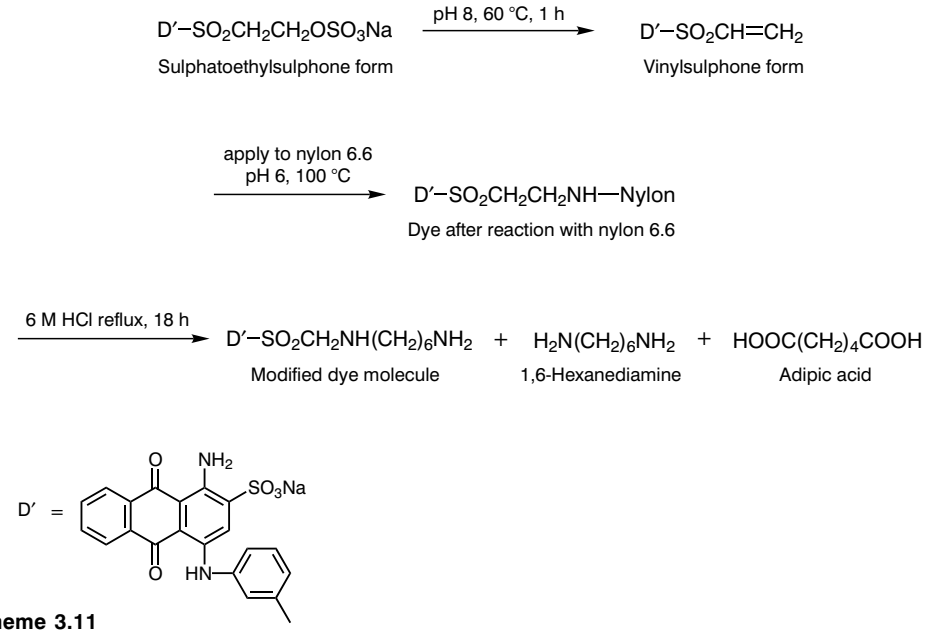
The ability of this class of reactive dyes to react firstly with the primary amino group, and then with the secondary amino group formed as a result of the first reaction, makes them potentially the most valuable type for use on currently available nylon fibres, which are intrinsically lacking in nucleophilic sites.

Assuming an average dye molecular weight of 600, then the maximum amount of vinylsulphone dye covalently bonded by 1 kg of fibre is $0.036 \times 2 \times 600$ g, which is 43.2 g, or in more usual dyers' terms 4.32% dye on mass of fibre (owf). Most commercial reactive dyes are about 50% pure; salts, buffers, antidusting agents and so on are added to give the commercially viable product. Thus, an approximate 8.6% owf fixed commercial strength dyeing should be achievable under ideal dyeing conditions. Normally, any depth greater than a 4% owf dyeing is regarded as a deep shade.

Lewis and MacDougall [44] studied the availability of the nylon amino groups for reaction with Remazol Brilliant Blue R. They based their approach on the observation of Zahn and coworkers [45] that when wool was dyed with this dye and then acid hydrolysed to its constituent amino acids, the bond between Remazol Brilliant Blue R and the nucleophilic amino acid side-chain was

resistant to the strong acidic conditions. Moreover, the blue chromophore was also unaffected. In this manner the above workers were able to isolate and quantify S-(Remazol Brilliant Blue R)-cysteine, N-ε-(Remazol Brilliant Blue R)-lysine and N-imidazole-(Remazol Brilliant Blue R)-histidine in acid hydrolysates of wool dyed in deep shades with Remazol Brilliant Blue R.

Lewis and MacDougall [44] therefore hydrolysed nylon which had been dyed to a deep shade with the activated vinylsulphone form of CI Reactive Blue 19 according to Scheme 3.11.



Scheme 3.11

The blue hydrolysate solution was filtered clear of insoluble adipic acid, neutralised and analysed using HPLC. Previously prepared model compounds were used to identify the main peak in the above HPLC analysis as the (Remazol Brilliant Blue R-1-amino)-hexane-6-amine adduct. Model studies also indicated that the di-substituted product, (bis-Remazol Brilliant Blue R-1-amino)-hexane-6-amine, was not stable to acid hydrolysis, undergoing elimination to a molecule of the vinylsulphone dye and a molecule of the mono-substituted (Remazol Brilliant Blue R-1-amino)-hexane-6-amine. The main conclusion of this study was that 0.0098 moles of $D–SO_2–CH_2CH_2–NH–(CH_2)_6–NH_2$ per kg of dyed nylon 6.6 could be recovered, indicating that only about 40% of the amine residues were available for reaction with the vinylsulphone form of this dye under the conditions employed (100 °C, 3 hours at pH 6.4).

Lewis and MacDougall also quantified the effect of dyebath pH on the percentage exhaustion (E) and covalent fixation (F) of CI Reactive Blue 19, initially applied to nylon 6.6 in the β-sulphatoethylsulphone (SES) and vinylsulphone (VS) forms, and the results are shown in Table 3.2 (2% owf dye) and Table 3.3 (8% owf dye).

Taking exhaustion/fixation values together, it is clear that SES Dye (I) is optimally applied at

Table 3.2 Exhaustion (E)/fixation (F) of SES dye (I) and VS dye (II) *vs* pH (2% owf dyeing)

	SES Dye (I)		VS Dye (II)	
pH	E (%)	F (%)	E (%)	F (%)
2.2	94.6	3.7	99.6	20.1
3.0	89.4	5.1	99.7	29.6
4.0	87.1	7.4	99.6	55.8
5.0	85.6	30.0	99.1	85.4
6.0	96.2	85.3	97.0	88.1
7.0	95.0	97.0	93.0	86.6
8.0	88.8	93.3	85.4	92.7

Table 3.3 Exhaustion (E)/fixation (F) of SES dye (I) and VS dye (II) *vs* pH (8% owf dyeing)

	SES Dye (I)		VS Dye (II)	
pH	E (%)	F (%)	E (%)	F (%)
2.2	34.3	5.0	69.4	26.3
3.8	23.8	6.8	51.9	24.3
4.0	24.0	13.7	50.7	31.0
5.0	41.0	59.3	51.9	71.1
6.0	60.6	78.1	51.6	87.0
7.0	60.9	94.1	50.6	93.4
8.0	60.7	90.7	48.5	95.1

pH 7 whereas VS Dye (II) may be optimally applied at pH 5–6. This effect is due to the following factors:

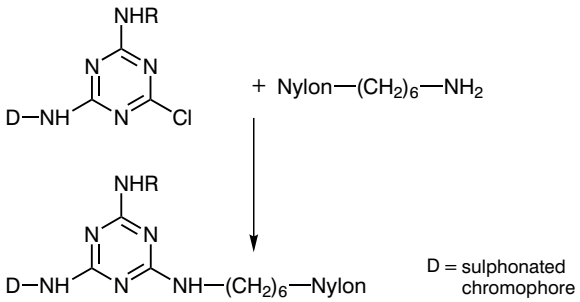
(1) SES dye is hardly converted to the reactive VS form below pH 5.0 and most optimally at pH ≥ 7.0;
(2) VS dye is still able to covalently bond with amino residues in nylon at pH 5.0; below this pH value the concentration of deprotonated, nucleophilic amino residues falls to such low levels that the covalent reaction efficiency becomes very low.

Dyeings carried out using an 8% owf depth of shade resulted in much less exhaustion of the dye compared to the 2% owf shade, because the concentration of the dye was greater than the maximum dye saturation level of the fibre. Exhaustion profiles similar to those for the 2% owf depth of shade were produced in each case when dyeings were carried out at the deeper shade. In the case of the β-sulphatoethylsulphone dye, the exhaustion was again highest at pH values greater than 6; below that the exhaustion was reduced to a minimum at pH 3–4, while increasing again below pH 3. This differs from the 2% owf depth of shade only in that the pH

value of minimum exhaustion occurs at pH 3–4 rather than pH 5. It was also shown that a maximum of 0.0305 moles (per kg nylon) of the vinylsulphone dye would covalently bond. Since only 0.0098 moles of dye-modified hexamethylene diamine could be recovered from the acid hydrolysates of dyed nylon, this indicates that two, or even three, vinylsulphone dye molecules are attached to the same amine site.

Dyes which react by a nucleophilic substitution reaction

These reactive dye systems are based on halogenated heterocyclic compounds containing nitrogen – for example, monochloro-*s*-triazines (MCT) – and are capable of only single reaction with a primary amino group. Thus a monochloro-*s*-triazine dye of molecular mass 500 will give a maximum fixation of 1.8% pure dye owf, but this limit will be difficult to attain in practice. The MCT dye will fix to nylon 6.6 according to Scheme 3.12.

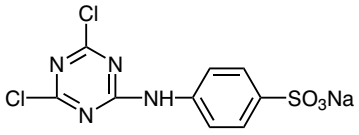


Scheme 3.12

Burkinshaw and Wills [46] also reported on the effect of pH on the exhaustion/fixation dependence of a number of reactive dyes on nylon. Surprisingly, some covalent bonding was recorded even when dyeing at pH 2–3, indicating the presence of a small number of nucleophilic amino groups.

Fixed sulphonate anion build-up and resist effects

As mentioned previously, all commercially available reactive dyes are based on polysulphonated chromophores, wool reactive dyes usually containing two sulphonate residues per chromophore and cotton reactive dyes having from two to eight sulphonate groups. When these molecules become covalently bonded to the nylon, the fibre becomes increasingly negatively charged as reaction proceeds, due to the strong ionic character of the sulphonate groups. Since these anionic dyes are initially absorbed by the fibre from the aqueous solution by electrostatic forces, the resulting negative charge build-up causes a significant reduction in substantivity. Analogous anionic dye-resist effects were achieved on nylon by Sandoz (now Clariant) using the colourless reactive resist agent Sandospace R (**3.18**) [47].



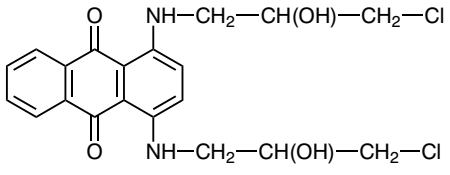
3.18

If sufficient of this reactive compound is applied to nylon – for example, by a long liquor 'dyeing' type process, or by printing procedures – and fixed, then the treated nylon cannot be subsequently dyed with acid dyes. Thus, if the treated fibre were mixed with untreated fibre and made into yarn or fabric, subsequent dyeing with acid dyes would give a melange effect. The acid dye would only dye the untreated fibre leaving the treated fibre completely white. Further styling possibilities could be achieved by over-dyeing such fibre mixtures with cationic dyes; in this case, only the pretreated fibre absorbs the cationic dye.

Sandoz (now Clariant) have further developed this idea by introducing a monochlorotriazine sulphonated reactive resist agent, Sandospace S; they also produced a cationic reactive agent, Sandospace DP, which, following application to nylon fibres, gives a substrate showing increased dye substantivity for anionic dyes. These agents, if printed, are fixed by steaming at 100 °C for 30 minutes, or if applied from a long liquor bath, by boiling for about an hour. The anionic compounds are applied at pH 4–5 and the cationic compounds at pH 7. Adequate effects are achieved at application levels of 4–5% agent (owf). It is important that, following the fixation step at the boil, the treated fibres are cleared of any unfixed or hydrolysed reactive agent, usually by an alkaline after-treatment.

3.5.2 Dyeing nylon with reactive disperse dyes

ICI developed a range of reactive disperse dyes, the Procinyls, specifically for nylon dyeing. These dyes were subsequently withdrawn from the market in the 1980s, but aspects of their chemistry and application to nylon are well worth recording. Scott and Vickerstaff [48] described the basic chemistry of this system. Five dyes were marketed: Procinyl Yellow GS, Procinyl Scarlet GS, Procinyl Red GS, Procinyl Orange GS and Procinyl Blue RS. Structures were not widely published, but the patent literature indicates that a mixture of reactive groups were used, including chlorohydrin, chlorotriazine and chloro-ethyl-aminosulphone. A Russian paper [49] on dyeing wool with Procinyl Blue RS confirmed its structure (**3.19**).

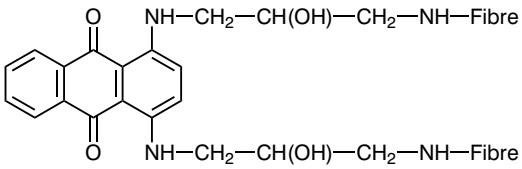


3.19

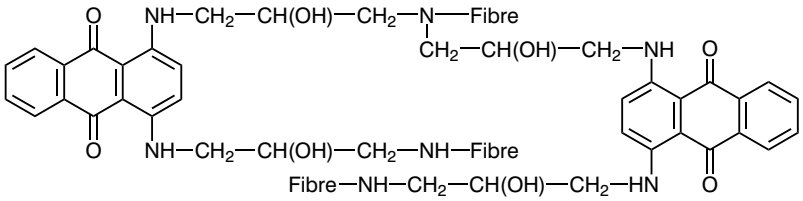
Under alkaline conditions the unreactive chlorohydrin form eliminates HCl to form the highly reactive bis-epoxide, which reacts covalently with nucleophilic sites. Using a nylon 6.6 fibre with an amino end group content of 0.042 mol kg^{-1}, Scott and Vickerstaff [48] showed that the above dye would fix to apparently higher levels than the maximum possible assuming monofunctional reaction at the primary amino residue. Dyeing was carried out initially at pH 4 at 95 °C for 60 minutes followed by alkaline fixation at pH 10.5 for a further 60 minutes at 95 °C. The results obtained are reproduced in Table 3.4. In the case of Procinyl Blue RS (**3.19**) [49], covalent bonds are possibly formed as shown (**3.20** and **3.21**).

Table 3.4 End group analysis of nylon dyed with Procinyl Blue RS [48]

Dye applied (g 100 g^{-1} fibre)	Dye fixed (g 100 g^{-1} fibre)	Dye fixed (mol kg^{-1} fibre)	Amine end groups reacted (mol kg^{-1} fibre)
0.5	0.39	0.0093	0.0056
1.0	0.78	0.0184	0.0226
1.5	1.02	0.0240	0.0256
2.0	1.23	0.0290	0.0276
2.5	1.44	0.0340	0.0386
4.0	1.84	0.0435	0.0426
6.0	2.29	0.0541	0.0426
8.0	2.37	0.0560	0.0426



3.20



3.21

The results showing over-saturation of the primary amino groups for the 6% and 8% shades in Table 3.4 indicate that products of form **3.21** are indeed present. Scott and Vickerstaff [48] argued that the excess 'fixation' was due to reaction of the reactive dye at amide bonds. Under the mild conditions of the fixation stage of the dyeing process (pH 10.5, 95 °C) this reaction is impossible as the amide nitrogen is an extremely weak nucleophile – in contrast, the secondary amine residue resulting from the first substitution (**3.20**) is a powerful nucleophile.

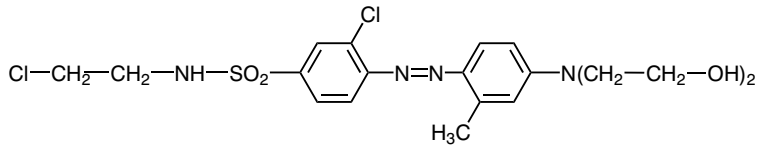
The results obtained for Procinyl Scarlet GS were even more remarkable since for full depth dyeings (10% owf), two dye molecules were able to react per primary amino group and at very heavy depths three dye molecules reacted – assuming this dye contains one reactive group per dye molecule. The results are reproduced in Table 3.5.

Table 3.5 End group analysis of nylon dyed with Procinyl Scarlet GS

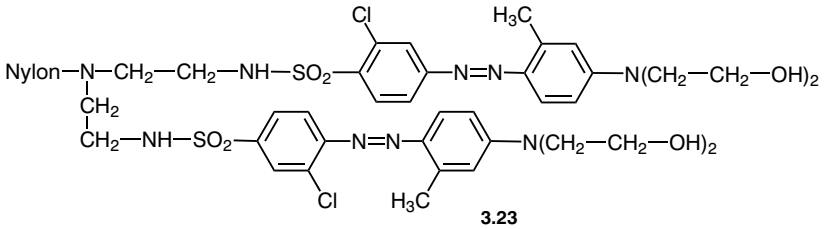
Dye applied (g 100 g^{-1} fibre)	Dye fixed (g 100 g^{-1} fibre)	Dye fixed (mol kg^{-1} fibre)	Amine end groups reacted (mol kg^{-1} fibre)
0.5	0.35	0.0074	0.0076
1.0	0.72	0.0165	0.0186
1.5	1.23	0.0258	0.0246
2.5	1.47	0.0309	0.0346
5.0	2.80	0.0590	0.0426
10.0	4.20	0.0880	0.0426
20.0	6.10	0.1280	0.0426

Again, the original explanation of reaction at amide residues contributing to excess nucleophilic sites in the fibre should be challenged; in the case of the full depth dyeings the threefold stoichiometric ratio of fixed dye to available nucleophiles can be explained by the following argument.

Assuming from the patent literature [50] that Procinyl Scarlet GS has the basic structure shown (**3.22**), under neutral to mildly alkaline conditions, two molecules of dye could be readily bonded to the fibre to give the structure below (**3.23**).



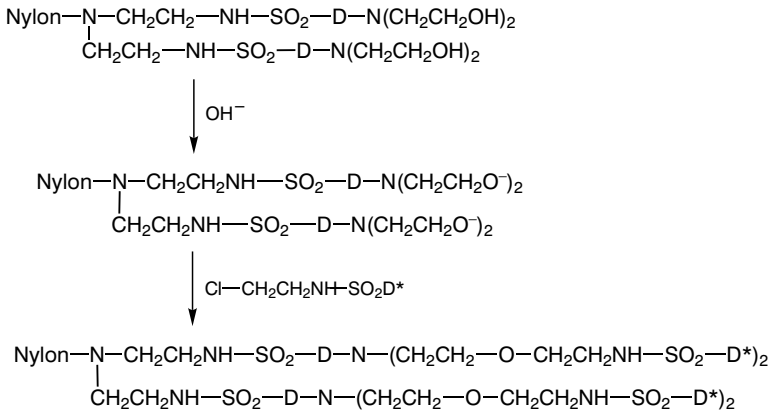
3.22



3.23

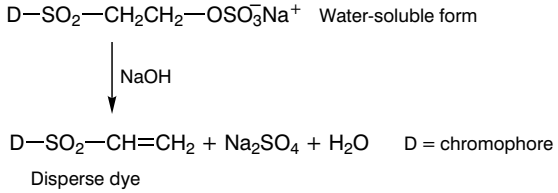
However, the recommended dyeing conditions of pH 5.5 for 30 minutes at 95 °C followed by fixation at pH 10–10.5 (1 h at 95 °C) will ensure that the side-chain hydroxyethyl groups partially ionise to give the highly nucleophilic ethanoate species; thus further reaction of non-

reacted dye can occur with this latter nucleophile, which is attached to the fibre through a previously fixed reactive dye molecule. Schematically, this reaction may be written as shown in Scheme 3.13, where D is the chromophoric residue and D* is the chromophore plus the diethanolamine side-chain.



Scheme 3.13

It may thus be seen that the fixation of this particular Procinyl dye on nylon was complicated by the presence of additional nucleophilic sites in the dye itself. In the above reactions, the actual reactive species in the dye side-chain is not the chloro-ethylsulphamoyl residue but rather the aziridinylsulphone formed by elimination of HCl under alkaline conditions. Some work [51,52] has also been reported on the dyeing of nylon with vinylsulphone disperse dyes. Good fixation was achieved without the need for an alkaline fixation stage. Lo [53] described the dyeing of nylon at pH 8 with sulphatoethylsulphone dyes in the presence of dispersing agent. As the bath temperature increased, the dye gradually changed to the active disperse vinylsulphone and thus became covalently fixed to the fibre (Scheme 3.14).

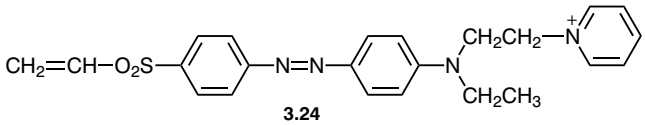


Scheme 3.14

In Japan, production has recently commenced, on a pilot scale, of reactive disperse dyes targeted at solving the important problem of producing dyed microfibre blends of polyamide and polyester with good wet-fastness properties.

3.5.3 Cationic reactive dyes

A Sandoz patent [54] has claimed vinylsulphonyl dyes containing a pendant cationic group as reactive dyes for nylon which give level dyeings of high wet-fastness. There are clearly potential advantages in using cationic reactive dyes since, under alkaline conditions, the fibre is negatively charged and the majority of the amino groups are deprotonated, thus enhancing the nucleophilic character of the fibre. High dye–fibre substantivity along with efficient dye–fibre covalent bonding should therefore be ensured under mildly alkaline conditions. A typical bright orange dye claimed in this patent had the structure shown below (**3.24**).



3.24

A recent paper by Hinks and coworkers [55] quantified the exhaustion/fixation profiles *vs* dyebath pH for the above dye applied to nylon at 0.5–4% owf. When dyed (1% owf) at pH 8, fixation values of the order of 98% were recorded and a dyebath exhaustion of 95%; this is very promising and indicates a new direction for nylon reactive dyeing products and procedures.

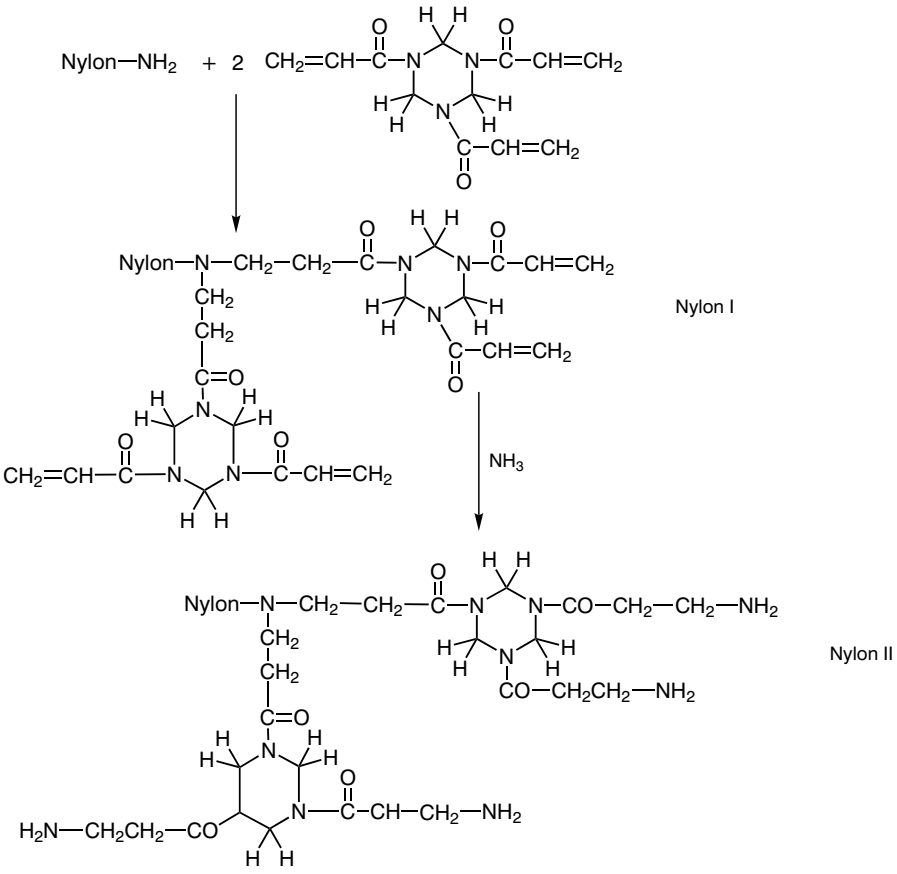
3.6 CROSSLINKING DYES ON NYLON

In a series of papers, Ho and Lewis [56,57,58,59] considered the use of crosslinking agents, either as a means to increase the number of amino functional groups in nylon, or as a means to covalently link dyes containing pendant nucleophiles to nylon. The first crosslinking agent to be studied was N,N′,N″-triacroylaminohexahydro-*s*-triazine (FAP) [56]. This compound was prepared and applied to nylon from an aqueous anionic dispersion. Subsequent reaction with ammonia produced the amine-rich substrate (nylon II) shown in Scheme 3.15.

The three substrates (untreated nylon, nylon I and nylon II) were dyed with a monochloro-*s*-triazine dye and the exhaustion/fixation curves shown in Figure 3.5 were obtained. The results were exactly as expected; dyeings on substrate nylon I indicated that the majority of the original primary amine residues were no longer available for nucleophilic substitution reactions with the MCT dye. Substrate nylon II gave the best exhaustion and covalent fixation of the MCT dye, confirming successful introduction of additional amine groups. When the substrates were dyed with aminoalkyltriazine dyes the exhaustion/fixation results shown in Figure 3.6 were obtained.

The results clearly show that the nucleophilic dye reacts efficiently with substrate I, which contains activated double bonds; the other substrates do not form covalent bonds with this type of dye.

The crosslinking agents, 2-chloro-4,6-di(4″-sulphatoethylsulphonyl-anilino)-*s*-triazine (XLC) and 2-chloro-4,6-di(4″-vinylsulphonyl-anilino)-*s*-triazine, (XLC-VS) were also found to be very valuable [57,58]. Water-soluble XLC and XLC-VS dispersions showed much higher



Scheme 3.15

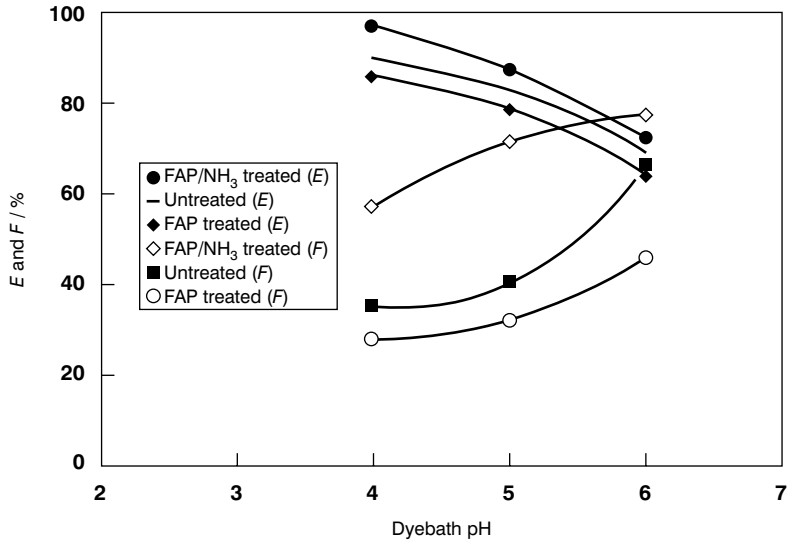


Figure 3.5 Exhaustion and fixation of monochlorotriazine reactive dye on nylon and modified nylons, *vs* bath pH

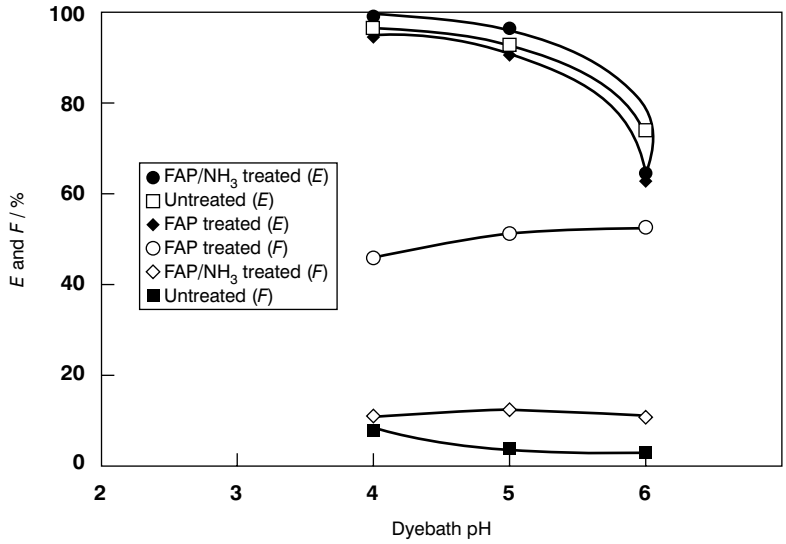


Figure 3.6 Exhaustion and fixation of aminoalkyl dye on nylon and modified nylons, *vs* bath pH

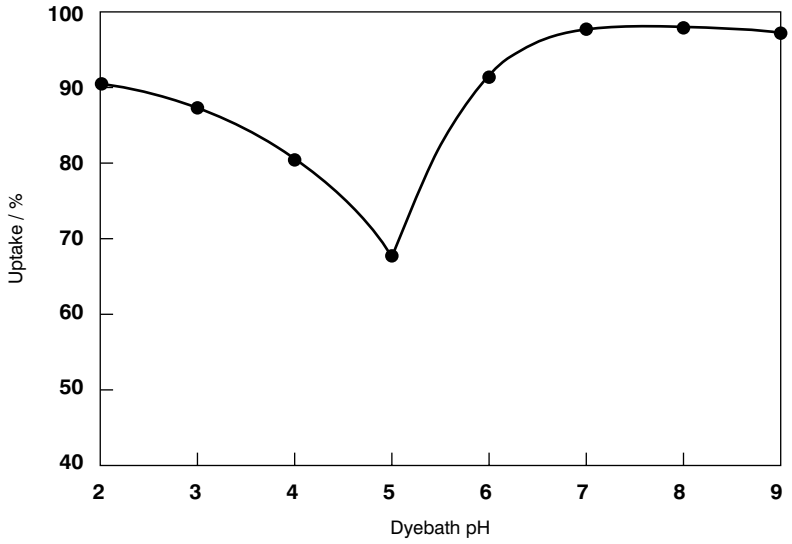
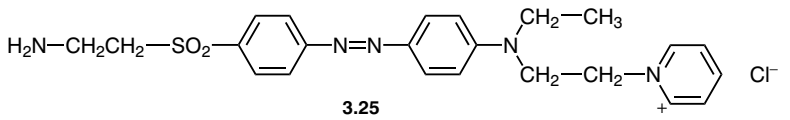


Figure 3.7 Uptake of XLC by nylon *vs* bath pH

substantivity for nylon 6.6 than did FAP. The effect of pH on the uptake of XLC by nylon 6.6 is shown in Figure 3.7.

Figure 3.7 confirms that below pH 5 XLC behaves like a colourless acid dye, but above pH 5 it increasingly behaves like a reactive disperse dye; it is well known that the β-sulphatoethylsulphone residues convert to vinylsulphone at pH values greater than 5 and it is this form which behaves as a colourless reactive disperse dye.

It was expected that the most promising application of such crosslinking systems would be to dye with a nucleophilic aminoalkyl dye first and then to add the fibre substantive crosslinker to bring about covalent bonding by reaction with amino groups in the dye and the fibre. The nucleophilicity of both the fibre and the aminoalkyl dyes is enhanced as the dyebath pH increases and is at a maximum > pH 8; sulphonated aminoalkyl dyes do not show sufficient substantivity under these weakly alkaline conditions, and cationic aminoalkyl dyes were therefore studied; a particular cationic dye (**3.25**) was synthesised and its uptake by dyed nylon 6.6 at various dyebath pH values was observed [59].



3.25

Figure 3.8 shows the results obtained. As expected, the dye showed maximum uptake above pH 8 due to the decreasing quantity of protonated amino groups present in the nylon substrate as the dyebath pH increases.

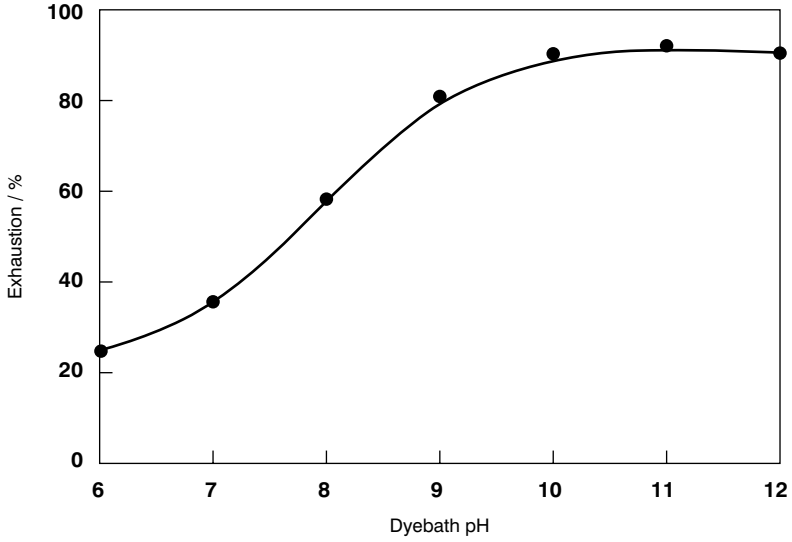


Figure 3.8 Uptake of aminoalkyl cationic dye by nylon *vs* bath pH

The optimum conditions to apply the aminoalkyl cationic dye and XLC crosslinking agent involved dyeing at pH 10 at the boil for 1 hour and then reducing the pH to 8, adding XLC and running for a further 60 minutes to achieve fixation. Figures 3.9 and 3.10 show typical exhaustion/fixation results achieved without and with this crosslinker, respectively. Clearly covalent bonding of dye to fibre only occurs in those samples after-treated with the crosslinker.

Thus, the development of cationic aminoalkyl dyes and crosslinking systems offers scope to obtain level dyeings of high wet-fastness properties on nylon fibres.

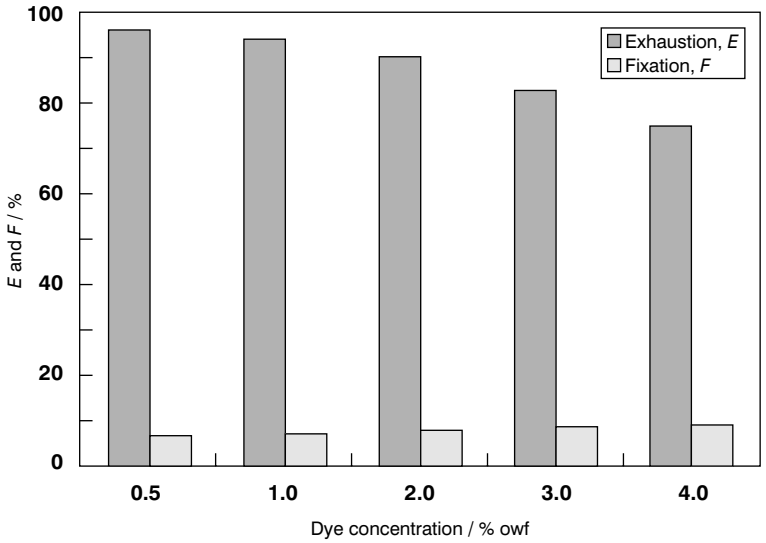


Figure 3.9 Effect of aminoalkyl cationic dye concentration on dye exhaustion and fixation