

13.9 DYEING NYLON WITH ACID DYES

13.9.1 Introduction

Nylon molecules have amino groups at the end of the polyamide chains. Nylon, like wool, can therefore be dyed with all types of acid dyes by an ion exchange process. Nylon filaments are sensitive to mechanical, thermal and chemical

stresses during filament production as well as during their assembly into fabric and its preparation for finishing. These stresses modify both the chemical and physical structure of the nylon filaments and result in changes in dyeing rate and dye uptake. If the modification of the nylon is not uniform along the length of the filament, the final colour will be uneven. Disperse dyes, which dye most synthetic fibres, migrate readily when dyeing nylon and cover such chemical and physical irregularities in the filaments (Section 15.6). Unfortunately, the washing fastness of disperse dyes on nylon is only poor to moderate, particularly in heavy shades. They are used mainly for ladies' hosiery and lingerie. The washing fastness of non-metallised acid dyes on nylon is moderate to good and the light fastness is usually good. Milling or metal-complex dyes give dyeings of superior washing fastness on nylon. Their unlevel dyeing behaviour, however, results in poor coverage of filament irregularities. The 2:1 pre-metallised dyes, in particular, give dyeings of high light fastness, as required for example for nylon automotive fabrics. Besides hosiery and apparel, carpets are a major consumer of nylon, particularly in the USA, and are usually dyed with acid dyes.

13.9.2 Preparation of nylon before dyeing

Nylon filaments are relatively free from impurities. Scouring with a detergent and soda ash (Na_2CO_3) at 70 °C usually removes spin finishes and lubricants present on the filaments and any polyvinyl alcohol or other synthetic size on woven fabric. In some instances, where white nylon fabric has yellowed from overly severe heat setting (Section 13.9.3), bleaching with peracetic acid or sodium chlorite solution is possible. Compared to fabrics from natural fibres, the preparation of those from nylon is quite simple.

13.9.3 Heat setting

Nylon is a thermoplastic polymer. When treated in hot water, the temperature is well above the glass transition temperature (T_g) of nylon. Fabrics may give considerable changes in dimensions as filament tensions introduced during manufacture relax. Heat setting avoids fabric deformation and shrinkage provided that the temperature is higher than that to which the material will be subsequently exposed.

The full width fabric is heat set using a tenter frame. The separation of the chains holding the selvages, and the speed through the oven, define the final

fabric width and length, respectively. On heating, intermolecular hydrogen bonds between amide groups break (Scheme 4.3) so that the polymer chains can move and adopt the positions required by the newly imposed dimensions without stress. At the setting temperature, new hydrogen bonds then form that stabilise the polymer structure. These new bonds are stable at temperatures up to the heat setting temperature at which they formed. They impart the required dimensional stability to the material.

Open-width fabrics are dry heat set at 190–215 °C for nylon 6.6, and 175–190 °C for nylon 6. Temperatures are lower for steam setting: 115–130 °C for nylon 6.6 and 110–120 °C for nylon 6. Since dry heat setting in hot air involves much higher temperatures than setting in steam, it involves a greater risk of polymer degradation. Dry setting sometimes results in yellowing of the material. Nylon hose are placed on shaped forms and heat set in a steam autoclave.

After dry heat setting in hot air at temperatures up to about 200 °C, the rates of dyeing of nylons 6.6 and 6 with both acid and disperse dyes decrease. This is mainly because of increased polymer orientation and crystallinity, but the number of polymer amino groups also decreases. Because of the decrease in dyeing rate and the risk of unlevel dyeing from non-uniform heat setting, it is preferable to heat set after dyeing, if this is possible. This requires a minimum level of dimensional stability at the maximum temperature of the dyeing process. Steam setting, however, increases dyeing rates with acid and disperse dyes. This latter process opens up the polymer structure making it more accessible to dyes.

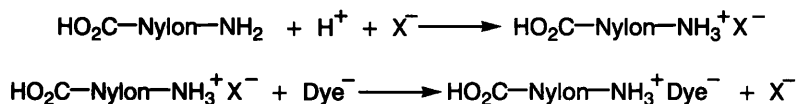
13.9.4 Adsorption of acid dyes by nylon

The dyeing of nylon with acid dyes differs in a number of respects from that of wool. A simple ion exchange process (Scheme 13.14), similar to that for dyeing wool, explains many practical dyeing observations. The limited number of amino groups in nylon and its more hydrophobic nature, however, have a profound influence on its dyeing behaviour.

The amino group content of nylon is usually around 45 mmol kg⁻¹ but can vary from about 15–20 up to 80–90 mmol kg⁻¹ for different types. These values are much lower than the 820 mmol kg⁻¹ for wool. In dyeing nylon at moderate acidity (pH 3–4), it is therefore relatively easy to saturate all the available ammonium ion sites with acid dye anions. The equilibrium molar adsorption of polysulphonated acid dyes is particularly low because of this. A simple acid dye with three sulphonate groups per molecule will neutralise the positive charge of all

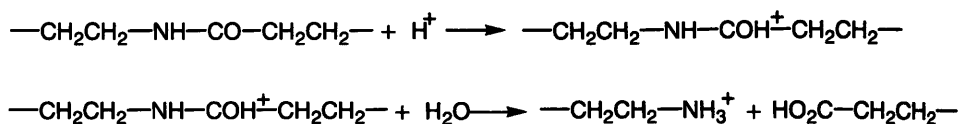
the available ammonium ion sites in the nylon at one third the molar quantity of a dye with a single sulphonate group. For a nylon with 45 mmol kg⁻¹ of amino groups, the maximum dye adsorption of a trisulphonate dye is 15 mmol kg⁻¹. This corresponds to less than a 0.9 % owf dyeing for an acid dye with a molecular weight less than 600. The equilibrium molar dye adsorption at saturation of a polysulphonated acid dye of known molecular weight and purity is, in fact, a good method of determining the amino group content of the nylon. The limited number of ammonium ion sites in nylon, when dyeing with acid dyes under weakly acidic conditions, poses problems in dyeing deep shades. In particular, the production of blacks and other deep shades is problematic, since the amount of dye that saturates all the ammonium ion sites is insufficient to give the depth of colour required.

The non-polar environment inside nylon filaments, and the large separation between the amino and carboxyl groups, may not favour a zwitterionic form in nylon, as in wool, and absorption of acid probably involves protonation of free amino groups in a non-ionic polymer (Scheme 13.14).



Scheme 13.14

Isotherms of the equilibrium adsorption as a function of pH for acid dyes of low substantivity (Figure 13.9) show that the dye initially interacts with ammonium ion groups in the nylon until these are all occupied at around pH 3. The shape of the isotherm resembles a titration curve. The amount of dye adsorbed depends on the acidity of the dyebath, which determines the number of ammonium ion sites. At low pH values, the nylon adsorbs additional dye beyond the saturation limit at pH 3. Under such acidic conditions, protonation of the carbonyl group oxygen atom of amide groups generates new cationic sites for dye adsorption. This also renders the amide group susceptible to hydrolysis at the elevated temperatures used in dyeing. Hydrolysis of an amide group forms a new amino group that, on protonation, can bind an additional dye anion (Scheme 13.15). In practice, dyeing



Scheme 13.15

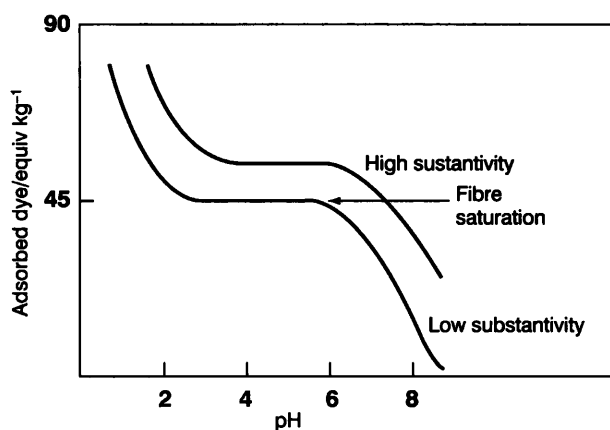


Figure 13.9 Equilibrium dye adsorption of nylon as a function of dyebath pH at constant temperature

below pH 2.5 is not possible because acid catalysed hydrolytic fibre degradation results in a loss of tensile strength.

Once a dye anion with moderate substantivity adsorbs onto an ammonium ion site in the nylon, it is quite resistant to displacement. A rapidly adsorbed dye anion can block a site and prevent adsorption of other dyes in the dyebath. The competition of acid dyes for the limited number of available dye sites can cause problems when dyeing with mixtures of incompatible dyes. Dyeing nylon with a mixture of the monosulphonated dye CI Acid Blue 47 and the disulphonated CI Acid Yellow 17 in acidic solution gives the expected green dyeing at low dye concentrations of 0.25% owf yellow and 0.17% owf blue, respectively. If dyeing is carried out using the same yellow to blue ratio but at higher dye concentrations of 1.5% owf yellow and 1.0% owf blue, however, the nylon is dyed yellow, most of the blue dye remaining in the bath. The yellow dye is more rapidly and more strongly adsorbed than the blue dye and is able to rapidly block the alkylammonium ion

sites in the nylon. It will even displace any blue dye already adsorbed by the nylon. Many pairs of dyes exhibit this type of competition behaviour.

For milling dyes, which have higher substantivity for nylon, the isotherms showing the amount of dye adsorbed at equilibrium as a function of pH are similar to those for simple acid dyes, but displaced to higher pH values and with considerable dye adsorption above pH 7. Figure 13.9 shows an example.

As in the case of wool dyeing, the ion exchange mechanism is simple and useful. It does not, however, explain the pronounced substantivity of milling and metal-complex acid dyes in neutral solution, under conditions where the nylon only has very few ammonium ion groups. In the case of these types of acid dye, the dye-fibre interaction must involve forces other than the attraction of oppositely charged ions. Obviously, dipole-dipole and hydrophobic interactions between the dye and nylon molecules play an important role in determining the high substantivity and good washing fastness of these types of dyes.

Many of the high substantivity acid dyes, particularly hydrophobic monosulphonated or non-polar pre-metallised dyes, often dye nylon in amounts well over the amino group content, even at pH values as high as 6–7. Build up of deep shades is not a problem with such dyes. This phenomenon is called over-dyeing. In some cases, it has been shown that dyeing isotherms, giving the dye on the fibre as a function of the dye remaining in solution at equilibrium, are a combination of the Langmuir and Nernst isotherms. This behaviour corresponds to ion exchange up to saturation of the available cationic sites plus over-dyeing by solution of the dye in the nylon (Figure 13.10).

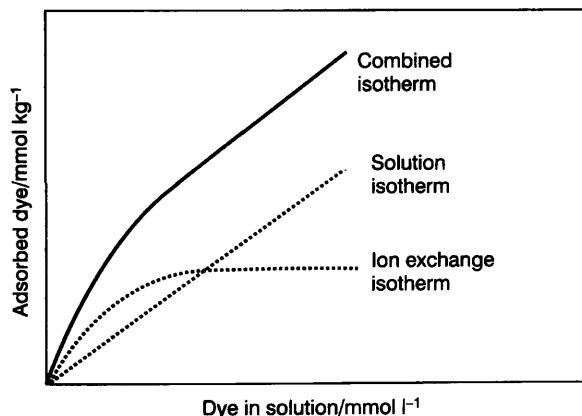


Figure 13.10 Adsorption isotherm for a metal-complex acid dye on nylon

The influence of temperature on the rate of acid dye absorption by nylon is complex. The glass transition temperature (T_g) of water-saturated nylon is probably not much greater than about 40 °C. Once the temperature exceeds T_g , the movement of polymer chain segments that is then possible should increase the rate of dye absorption as diffusion of dye molecules into the polymer matrix becomes easier. The temperature at which the initial rate of dyeing begins to significantly increase is called the dyeing transition temperature (T_D). This temperature, however, is often 20–30 °C higher than T_g under the given dyeing conditions. At temperatures somewhat higher than T_g , the voids between the chains in the amorphous polymer are too small to accommodate large dye molecules. Therefore, in spite of the increased mobility at temperatures above T_g resulting from easier polymer chain rotation, there is little dye absorption. Once the temperature exceeds the value of T_D , however, the greater ease of chain mobility creates voids whose average volume has increased to the point that allows dye molecules to enter them. The increasing size and mobility of these voids, now containing dye molecules, allows a significant increase in the rate of diffusion of dye into the polymer matrix.

13.9.5 Practical application of acid dyes to nylon

Many of the acid dyes used for dyeing nylon were first developed for dyeing wool and, like wool acid dyes, they are also classified according to their substantivity for nylon at a given dyeing pH. There are three main groups:

- (1) low molecular weight dyes of low substantivity for nylon at pH 6–7. Although these dyes have good migration during dyeing, they require an acidic dyebath containing acetic or formic acid for good exhaustion;
- (2) dyes that have moderate substantivity for nylon and good exhaustion when applied at pH 3–5 in the presence of acetic acid. These dyes have good fastness to washing on nylon;
- (3) higher molecular weight dyes of high substantivity for nylon even in neutral solution. Dyeing is usually at pH 6.5–7.0 in the presence of ammonium acetate.

The substantivity of a given acid dye for nylon is invariably higher than for wool. Even when dyeing at the boil, the extent of dye migration when dyeing nylon will be less than for wool, but the dyed nylon will have better washing fastness. Monosulphonated acid dyes are preferred for dyeing nylon since their fibre

saturation concentration is equal to the amino group content of the nylon and they build up to deeper shades better than polysulphonated dyes.

Dyeing of nylon with acid dyes starts at 40–50 °C in the presence of an appropriate acid, such as acetic acid or ammonium acetate depending on the substantivity. The temperature then gradually increases to the boil. Dyeing with weak acids is essential to avoid acid-catalysed hydrolysis and tendering of the nylon. The initial dyeing pH and the temperature gradient during the heating phase control the rate of exhaustion. The paler the shade being dyed, the higher the initial pH must be. At low concentrations of dye in the dyebath, a greater percentage of the total amount of dye present transfers to the fibre per unit time and the risk of unlevel dyeing is greater unless the bath circulation is very efficient. Many of the higher molecular weight dyes tend to exhaust very rapidly above a critical bath temperature (65–75 °C). This corresponds to the dyeing transition temperature, T_D . For this reason, the rate of heating is decreased in this temperature range. The dyebath may even be held at constant temperature for a while, around this critical value, before continued heating to the final dyeing temperature. For deep shades, addition of acetic acid, to decrease the bath pH, promotes better exhaustion as dyeing proceeds.

Despite the uniform appearance of continuous nylon filaments, they are often difficult to dye level. It is common to see paler filaments on a fabric surface where they have absorbed less dye than their neighbours. This effect is called *barré*. It arises from physical and chemical differences along the polymer filament, which influence both the dyeing rate and the total amount of absorbed dye. Unfortunately, many higher molecular weight acid dyes, which do not readily migrate, emphasise these irregularities giving filaments with different depths, and even hues. Uniform coverage of *barré* in nylon is just as difficult a problem as the level dyeing of 'tippy' wool. It is discussed in more detail in Section 13.9.6.

Auxiliary chemicals in the dyebath assist level dyeing, particularly for dyes of higher substantivity and poor migration. An anionic levelling agent present in the dyebath will block a number of ammonium ion sites in the fibres. This decreases the initial rate of dye adsorption and thus promotes level dyeing. If *barré* is likely to be a problem, the goods are run for some time in a heated bath with the required acid and anionic levelling agent before dye addition. The levelling agent anions exhaust onto the nylon, the bath is cooled and the dyes are then added to start the dyeing cycle. Too much anionic levelling agent causes excessive blocking and lowers dyebath exhaustion. Some levelling agents are cationic compounds, containing a non-ionic dispersant to prevent precipitation of the dye–auxiliary

anion-cation complex. The formation of such a complex in solution retards exhaustion at low temperatures. The complex gradually dissociates as the temperature increases, liberating dye molecules that are then available for adsorption by the nylon (Scheme 13.5).

When dyeing nylon, acid dyes are often incompatible in mixtures. The dyes in a mixture must all have similar solubility and fastness properties. They will usually have the same number of sulphonate groups per dye molecule and give about the same rate of exhaustion. The dyeing will then always be on tone and there will be no hue change on repeated washing or light fading. The dyestuffs' suppliers recommend suitable trichromatic combinations.

Compatible dyes have about the same rate of exhaustion under the given conditions. Rates of exhaustion of individual dyes, however, may not always be a reliable guide to their dyeing behaviour in a mixture with other dyes. If a supplier's recommendations are not followed, selection of compatible dyes requires careful testing. The dyeing rate of a given acid dye often tends to be lower in the presence of other dyes. For example, CI Acid Violet 5 alone dyes nylon less rapidly than CI Acid Yellow 23 although both dyes are disulphonated. When dyeing with a mixture of these two dyes, under the same conditions, both dyes exhaust less rapidly, but now the violet dye adsorbs faster than the yellow. This may be related to the violet dye having a more extensive surface adsorption but a slower diffusion rate into the polymer than the yellow dye. Dyeing is never simple.

A number of direct cotton dyes are useful for dyeing nylon, particularly for deep shades. These are applied as acid dyes. They do not cover yarn irregularities well in pale shades but give reasonable fastness to light and washing.

The addition of benzyl alcohol to the dyebath (Irga-Solvent process, Ciba-Geigy) improves the coverage of barré and the washing fastness of the resulting dyeing. This process gives almost 100% exhaustion at lower temperatures (80–90 °C), in a shorter dyeing time. Re-use of the exhausted dyebath minimises the cost of the benzyl alcohol. Better levelling during nylon dyeing is also possible at temperatures above 100 °C using pressurised dyeing machines. Under these conditions, mild reducing agents such as thiourea in the dyebath scavenge oxygen that can oxidise amino groups in the nylon.

In most respects, the dyeing of nylon 6 with acid dyes resembles that of nylon 6.6. The washing out of the unreacted caprolactam monomer after filament spinning gives a more porous fibre that is easier to dye than nylon 6.6. Nylon 6 is more amorphous and has a lower melting point than nylon 6.6. It can be heat set at lower temperatures. The more open fibre structure and higher amino group

content result in greater dye exhaustion rates, better dye build-up and better migration during dyeing with acid dyes. Dyeings of nylon 6, however, have somewhat lower washing fastness than those on nylon 6.6 when compared at the same depth of shade. When dyeing nylon 6 fabric at the boil, using a winch machine, permanent stretching of the fabric can occur. It may be necessary to use a lower dyeing temperature so the goods are less plastic.

To correct unlevel dyeings on nylon, the goods are treated at pH 8.0–8.5 at the boil. At this pH, there are few ammonium ion groups and some of the dye desorbs. The bath can then be acidified and the desorbed dye re-exhausted onto the nylon. This is less successful with high substantivity acid dyes. Chemical stripping requires the use of reducing agents such as sodium sulfoxylate-formaldehyde ($\text{NaSO}_2\cdot\text{CH}_2\text{OH}$) but complete stripping may be difficult.

13.9.6 Barré

Barré is the visual difference in colour depth, and possibly of hue, along the length of dyed nylon filaments in a fabric caused by physical and chemical variations in the polymer. This gives a continuous pattern of colour stripes seen in the course direction in circular knits, as warp streaks in warp knits, or as weft or warp streaks in woven materials. Unfortunately, many acid dyes tend to accentuate barré, some dyes being more sensitive to chemical variations in the polymer filaments and others to physical variations. Filaments with chemical variations are more difficult to dye level.

Chemical irregularities in nylon filaments are mainly from a non-uniform distribution of the polymer amino groups, which causes variations in the rate of dye up-take and particularly the equilibrium dye content of the filaments. Polyamide formation is reversible and the amino group content may change as additional polycondensation or hydrolysis occur when the nylon is at high temperatures during processes such as heat setting or texturing. The number and distribution of amino groups may also vary because of their oxidation during processing.

Similar differences in dyeing rate along filaments come from variations in the degree of polymer orientation and crystallinity. These physical variations can arise from uneven treatment in processes such as filament drawing and texturing, fabric heat setting, and from uneven filament tensions during fabric construction and processing. Barré from physical variations in filaments can be minimised by using levelling acid dyes, or by promoting dye migration by dyeing above 100 °C,

using an anti-oxidant such as thiourea to protect the amino end groups. Pretreating the goods with an anionic blocking agent before the acid dyes are in the dyebath is also a common method of promoting level dyeing. Lustre variations, arising from the effects of both filament surface and internal structure on light reflection and refraction, may also give a barré effect.

There are several dyeing tests for evaluating barré on nylon. Physical variations in the filaments influence the *rate* of dyeing, and chemical variations affect the *extent* of dyeing at equilibrium. Both types of barré may even be present in the same fabric, the rate of dyeing barré being more easily detected. Because of their good migration properties on nylon, disperse dyes, such as CI Disperse Blue 3, will uniformly cover most barré except that from gross physical variations in the filaments. When using acid dyes on nylon, those capable of migration will cover barré more uniformly. Unfortunately, these are the acid dyes of lower substantivity and lower fastness to washing. When deep shades are dyed to equilibrium, the amount of this type of adsorbed dye depends upon the number of ammonium ion sites. A trisulphonated acid dye such as CI Acid Red 18, applied to nylon at the boil in weakly acidic conditions, in sufficient concentration to saturate the fibre, will readily show if any variations in amino group content are present in the filaments. CI Acid Blue 45 (disulphonated), dyed to equilibrium under similar conditions, is also widely used for this purpose. Acid dyes of higher substantivity, such as CI Acid Blue 80 (disulphonated), will dye the more accessible filaments more rapidly and are useful for detecting physical variations in the filaments because of the poor migration under the dyeing conditions.

Pressure dyeing, dyeing with added benzyl alcohol, and dyeing with additions of levelling agents, all minimise barré. Pretreatment of the nylon material in a blank dyebath at a temperature around 85–90 °C, above the prevailing dyeing transition temperature, is also beneficial. Under these conditions, the movement of polymer chain segments allows the relaxation of tensions. This gives filaments with different chemical, thermal and mechanical histories time to equilibrate before dyeing takes place. A new dyeing process for nylon, developed by Du Pont and called the 'Infinity' process, uses this principle. The process involves running the goods in a blank bath containing the appropriate weak acid, at a constant temperature above the prevailing dyeing transition temperature, usually in the range 75–90 °C. The dye solution slowly runs into the bath over about 45 min using a metering pump. The conditions are such that the dye strike is so rapid that the actual concentration of dye in the bath is essentially zero during the entire dyeing operation. The name of the process comes from the condition of infinite

exhaustion that prevails throughout dyeing. The rapid strike and poor dye migration result in yarns whose filaments are unevenly ring dyed on their exposed surfaces. This gives a higher colour yield than a well-penetrated dyeing. These ring dyeings show no decrease in washing, light and abrasion fastness when compared with well-penetrated dyeings at the same depth. By allowing the filaments to equilibrate by dyeing in a hot isothermal bath, barré is much less of a problem using this dyeing method.

13.9.7 Back-tanning

Many of the simple but brightly coloured acid dyes give dyeings on nylon of only moderate fastness to washing, particularly for deep shades. The washing fastness of such dyeings improves on aftertreatment of the dyed nylon with a solution of tannic acid containing formic acid at 90 °C (70 °C for nylon 6). This is done using a fresh bath. The anionic tannic acid is adsorbed onto the nylon surface by attraction to the cationic ammonium ion groups at the ends of the polymer chains. Subsequent treatment with a solution of tartar emetic (potassium antimonyl tartrate, $\text{KSbOC}_4\text{H}_4\text{O}_6$) produces a film of the insoluble antimony salt of tannic acid all around the filament surface. It is this film that limits desorption of the dyes during subsequent washing. When using low liquor ratio dyeing machines, a fresh bath for the tartar emetic solution avoids precipitation of the antimony salt of tannic acid in the liquor.

This so-called full back-tanning aftertreatment gives a somewhat stiffer, slightly yellower fabric but with improved colour fastness to washing. The process has, however, a number of disadvantages:

- (1) antimony salts are poisonous and pose an environmental threat;
- (2) the process is time-consuming, since ideally two separate baths are required after dyeing;
- (3) yellow-brown impurities in commercial grade tannic acid dull the shade;
- (4) tannic acid tends to discolour under alkaline washing conditions.

Because of the dulling and yellowing effect on the hue, back-tanning is limited to deep dyeings that tend to have poor washing fastness without this aftertreatment. The improvement in washing fastness obtained by back-tanning is lost if the fabric is heat set after dyeing, using either hot air or steam, as these processes rupture or even remove the surface film.

Because the back-tanning process is expensive and environmentally unsound,

cheaper synthetic chemicals for this purpose were developed [5]. They are called synthetic tanning agents or syntans. These are colourless, anionic, water-soluble polymers formed by condensation of formaldehyde with phenol, naphthol, or hydroxybiphenylsulphone sulphonic acids or their mixtures. Commercial syntans are complex polymeric mixtures. The average molecular weight must be as high as possible while still allowing solubility in water. Syntans are applied to dyed nylon at 80 °C at around pH 4 using acetic or formic acid in the bath. Although direct syntan aftertreatment in the exhausted dyebath is possible, a fresh bath is desirable.

The anionic syntans do not form a skin like the tannic acid/tartar emetic combination. In acidic solution, the syntan is substantive to nylon. The molecules adsorb on the filament surface by interaction with ammonium ion sites in the nylon but, because of their molecular size, they cannot penetrate far into the polymer. The layer of adsorbed syntan polymer molecules on the nylon surface presents a considerable barrier to dye transfer in either direction. They therefore improve the washing fastness of the dyeing but their presence also prevents dye penetration. Syntans are therefore useful for preventing absorption of direct dyes by nylon when dyeing cotton/nylon blends with direct cotton dyes. The improvement of the washing fastness of nylon fabrics dyed with acid dyes obtained by syntan aftertreatment is somewhat less than that of the full back-tanning process. Syntans, however, have little or no influence on the hue of the dyeing although they may slightly reduce the light fastness.

13.10 DYEING NYLON WITH METALLISED DYES

13.10.1 Mordant dyes

Nylon can be dyed with acid dyes suitable for after-chroming. Dyeing is usually at the boil using ammonium acetate or small amounts of acetic acid. After-chroming in the exhausted dyebath reduces water and steam consumption. If complexation of the dye occurs in the solution, there is a risk of deposition of the less soluble metallised dye on the nylon surface. This deposit decreases the fastness to perspiration and rubbing. To complete exhaustion, some additional acid may therefore be needed towards the end of the dyeing process. This generates more ammonium ion sites in the nylon and promotes further dye adsorption. If the extent of dyebath exhaustion is not adequate, a fresh bath is necessary for after-chroming.

Nylon, unlike wool, contains few groups capable of reducing sodium dichromate to chromic ion, the form required for complex formation with the dye. A reducing agent such as sodium thiosulphate is effective (Scheme 3.12). After-chroming is carried out at the boil using sodium dichromate and formic acid. The sodium thiosulphate is added once most of the dichromate anions have adsorbed onto the nylon. The reduction process is much slower than for wool. Efficient after-chroming of dyed nylon at 130 °C is possible without added thiosulphate. It is likely that formic acid reduces the dichromate under these conditions. Residual dichromate, left in the nylon, promotes tendering on exposure to light. Therefore, complete reduction of dichromate to chromic ion and effective complexation with the dye are essential. Despite the good fastness to washing and light of the after-chromed dyeings on nylon, this dyeing process is now restricted mainly to blacks. The after-chrome process makes shade correction and colour matching much more difficult because of the pronounced change in hue that occurs.

13.10.2 Metal-complex dyes

The dyeing characteristics of pre-metallised dyes vary widely depending on the type of metal-complex dye and on the molecular complexity and degree of sulphonation. Like all acid dyes, their application to nylon involves the usual problems:

- (1) competition for the available ammonium ion sites in the nylon and exclusion of the less substantive dyes;
- (2) difficulties in producing deep shades because of the limited number of available ammonium ion sites in nylon;
- (3) poor migration and levelling during dyeing, which accentuate barré.

The 2:1 metal-complex dyes have very good light fastness in pale shades and good washing fastness, even in deep shades. Many weakly polar 2:1 dye-metal complex dyes, particularly those without sulphonate groups in the dye ligands, have good build-up properties on nylon, because of over-dyeing (Section 13.9.4). In deep shades, they absorb in amounts exceeding the amino group content of the nylon and therefore must interact with the fibre by forces other than ionic forces. They do not therefore give blocking effects. Most 2:1 dye-metal complexes, however, accentuate physical irregularities in the nylon filaments and cause barré. Dyeing with either a weakly dye-complexing (cationic) or site-blocking (anionic) auxiliary levelling agent in the dyebath overcomes this problem. Alternatively, dyeing at

120 °C (110 °C for nylon 6), in the presence of an anti-oxidant to avoid amino group oxidation, promotes better levelling.

The 2:1 pre-metallised dyes have poor migration during dyeing of nylon, and level dyeing requires good control of the dyeing process. Dyeing is usually started at pH 7. The goods are pretreated with a suitable levelling agent and ammonium sulphate. The dyes are added and the temperature raised to the boil. Some dyes may have very rapid strike at 60–70 °C. A decreased rate of heating in this temperature range lowers the risk of unlevel dyeing.

The very acidic dyebaths used in wool dyeing with 1:1 dye–metal complex dyes will cause hydrolysis of the nylon. Some dyes of this type will dye nylon using acetic acid at pH 4–6 with a weakly cationic levelling agent. They give dyeings of good washing and light fastness.

13.11 LIGHT AND OZONE FADING OF ACID DYED NYLON

Nylon fabrics dyed with acid dyes generally have moderate to good light fastness. All auxiliary chemicals used in dyeing or for aftertreatments should be tested to ensure that any residue left in the fabric does not decrease the fastness to light. This also applies to ozone fastness. Ozone is a major constituent of polluted urban air and is a powerful oxidising agent capable of rapidly destroying the colour of many types of dyes.

Nylon is a major fibre for production of automotive fabrics and carpets because of its superior properties. It is, however, becoming increasingly difficult to meet the car manufacturers' demands for light fastness ratings of 6 (Section 24.3.4) or even higher. Some nylon fabrics are aftertreated with copper derivatives (1–2% owf) to improve their fading resistance but with the increased risk of environmental contamination by copper. Automotive carpets and fabrics are often aftertreated with colourless ultraviolet photostabilisers. These strongly absorb ultraviolet light on the nylon surface and protect both the fibre and the dyes in it from photodegradation. The light fastness is therefore better. These chemicals function like sun screen products, the absorbed ultraviolet light being converted into heat. For automotive interior fabrics and carpets, the UV stabilisers do not need to have any significant degree of washing fastness but they must be colourless, odourless and non allergenic.

The fading of the colour of dyed nylon by ozone in industrial environments is a surface phenomenon. The fastness to ozone is therefore lower for dyeings that have poor dye penetration into the filaments. The ozone fastness, however,

increases with increase in the extent of dye–fibre interaction. For dyes with the same chromophore, the ozone fastness on nylon increases in the following order: disperse dye, disulphonated acid dye, monosulphonated acid dye, and reactive dye. Unfortunately, even reactive dyes (Chapter 16) cannot meet the ozone fastness demanded for automotive carpeting. Testing of ozone fading is not easy but is necessary because there is no relation between colour fading by ozone and by light.

13.12 NYLON CARPET DYEING

Manufacture of tufted carpets consumes large quantities of nylon multi-filament yarn. Modern filaments often have unusual properties compared to the original cylindrical nylon filaments. They may have trilobal cross-sections that hide dirt more effectively, and even conductive surfaces or cores that effectively dissipate static electricity. In addition, fluorocarbon finishes reduce soiling, stain blockers hinder penetration of anionic colorants in spilled food and drink, while ultraviolet photostabilisers improve the stability of the both the nylon and the dyes present towards light.

Considerable quantities of wide, tufted nylon carpeting are dyed continuously, particularly in the USA. The nylon filament yarn is textured to give it bulk, and heat set before tufting using dry heat or steam. Tufting involves punching of the multi-filament yarn through the primary backing and forming and tying of the filament loops. These may or may not be cut to form the pile.

13.12.1 Continuous dyeing of nylon carpets with acid dyes

For large quantities of carpet in a single colour, continuous dyeing is by far the most economic method of coloration. Great lengths of evenly dyed carpet, up to 12 m wide, require even dye application and fixation. Before application of the dye solution, the carpet is often well wetted with a solution of a wetting agent such as disodium di-octylsulphosuccinate. Steam set yarns are much easier to dye than dry set yarns. Addition of gum to the wetting agent solution promotes uniform wetting and helps to eliminate ‘frostiness’ at the pile surface caused by the migration of the dye away from the fibre tips during steaming. The pre-wetted carpet may be vacuum extracted before dye application. A high pick-up (300–400%) of thickened dye solution is run onto the pile surface across the full carpet width. A variety of systems are available for this step. Pre-wetting avoids pools of dye solution on the pile surface that run into pools on the carpet backing. A carpet of

weight 1.0 kg m^{-2} , 12 m wide, moving at 20 m min^{-1} with a 300% pick-up of dye solution, requires 720 kg min^{-1} of dye solution. Liquid acid dyes are necessary for rapid preparation of solutions by simple dilution. Dye solution may also be applied continuously to dry carpet, in which case wetting agents are in the dye solution. By using separated streams of different dye solutions, various multi-colour effects are possible (Section 23.9).

The wet carpet is then steamed for 3–5 min, preferably in dry saturated steam at 100°C . If dye penetration into the fibres during steaming is not adequate, the colour fastness properties may be inferior, particularly the ozone fastness. The latter can increase from 2–3 up to 4–5 as the steaming time increases and the dyes penetrate deeper into the filament interior. Finally, washing the carpet removes unfixed dyes, residual gum and auxiliary chemicals. When only small lots of carpet are involved, dyeing is carried out using winch machines.

13.12.2 Stain blockers [6]

Stain blockers improve the stain resistance of nylon carpets towards anionic dyes in spilled food and drink. The original stain blockers were of low substantivity and the appreciable amounts remaining in the bath increased the BOD problems of the effluent (Section 8.5.1). They also turned yellowish on light exposure. A pale blue carpet would therefore become greener in the exposed areas. Current formulations include the stain blocker and fluorocarbon polymers, and are more stable. The fluorocarbon polymer forms a film on the nylon surface that resists the spreading of both oil and water and to which particles of dirt do not adhere readily. The build-up of static electricity is also reduced. Stain blockers are anionic polymers similar to the syntans used for the aftertreatment of nylon dyed with acid dyes (Figure 13.11). Because of their anionic nature, they repel the anionic colorants in spilled foods and the polymer film on the surface of the nylon fibres provides a physical barrier to the penetration of non-ionic materials.

The fluorocarbon polymer and stain blocker are usually applied after dyeing since they interfere with dye fixation. Application procedures and conditions depend upon the particular products selected. Continuous application of the stain blocker, by spray, foam, or liquid jet, to the wet carpet after continuous dyeing is common. The lack of colour of these products requires extra care to ensure their uniform application for the best performance in use. The dispersion contains stain blocker, magnesium sulphate and fluorocarbon polymer. Acids such as acetic, formic, citric, or sulphamic acid will give a pH of 2.0–4.5, depending upon the

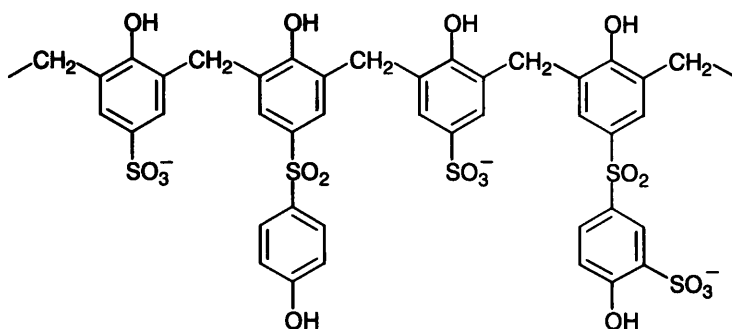


Figure 13.11 Partial chemical structure of a stain blocker

product selected, the nylon type and heat setting method used. The carpet is then steamed. The magnesium ions lower the aqueous solubility of the anionic stain blocker thus favouring transfer to the filament and the formation of an insoluble polymer film on the surface. Hydrogen bonds between the hydroxyl groups of the stain blocker molecules and amide groups in the nylon hold it onto the fibre surface. This is augmented by coulombic attraction between the blocker's sulphonate groups and ammonium ion groups in the nylon surface. This promotes substantivity of the stain blocker for the nylon but its molecular size prevents penetration into the polymer.

Treated carpets have good water resistance, in the absence of surfactants. If water penetrates into the nylon fibres, coloured anions will not. The anionic layer of polymer blocker on and just inside the nylon surface repels them. Excessive steaming may cause a loss of the stain blocking effect if the polymer diffuses too far into the nylon. The degree of penetration is clearly less, the higher the molecular weight of the polymer. Stain blockers offer no resistance to non-ionic stains such as those from coffee and mustard. They also interact strongly with cationic chemicals found in some cleaners and creams. The use of anionic stain blockers on nylon carpets has increased dramatically despite their far from ideal performance. Some would claim that their market success involves more consumer persuasion than consumer demand.

13.13 DYEING MODIFIED NYLONS

There are a number of modified nylon polymers available having different substantivities for both acid and basic dyes (Section 4.2.4). Light dyeing, normal dyeing, deep dyeing and ultra deep dyeing types are available for dyeing with acid

dyes. These have increasing amino group contents, respectively, but all dye to the same depth with disperse dyes. In addition, there are also basic dyeing varieties of nylon, containing anionic groups capable of binding cationic dyes (Section 4.2.4). Mixtures of different nylon types in a carpet give attractive tone-in-tone and multi-colour effects because of their differential dyeing behaviour.