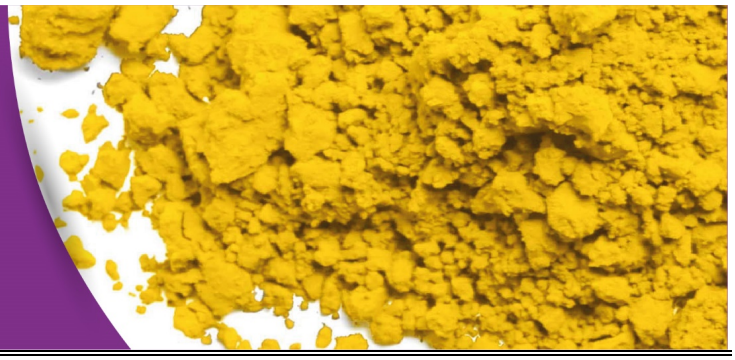


ASDC Dyeing of Synthetic Fibres
6.10 Dyes Used – Polyamide Fibres

Polyamide fibres

This discussion focusses on the dyeing of PA 6 and PA 66 fibres. As recounted above, the component macromolecular chains in both of these types of aliphatic substrate comprise amide groups (-NHCO-) separated by methylene sequences (-$(CH_2)_n$-), the polymer chains being terminated with carboxyl groups (-COOH) and amino groups (-NH_2) [or acetylamino groups (-$COCH_3$)]. Because of these structural features, PA fibres can be dyed using virtually all common application classes[1] of dye, which can be grouped according to the charge on the dye molecule within the fibre at the end of dyeing:

(i) *anionic neutral*

The terminal amino groups in PA fibres impart substantivity towards several classes of *anionic dye* namely *acid dyes* (including both *non-metallised acid dyes* and *pre-metallised acid dyes*), *direct dyes*, *mordant dyes* and *reactive dyes*. All five types of anionic dye are both *anionic* (or neutral in the case of some 1:1 metal complex dyes) and *water soluble*, the latter important characteristic being most commonly conferred by the presence of *sulfonate* (-SO_3Na)/*sulfonic acid* (SO_3H) groups in the dye molecule[2].

(ii) *basic dyes*

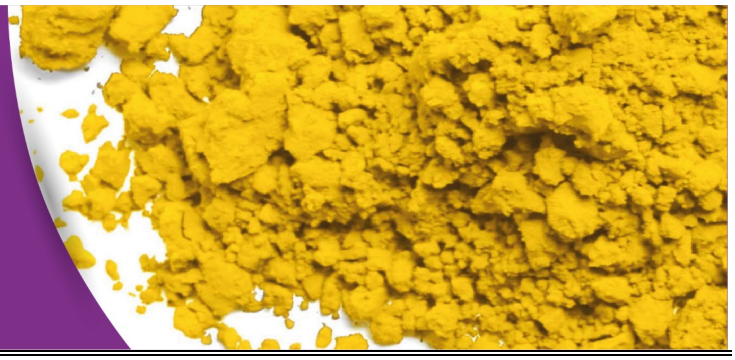
The carboxyl end groups in PA fibres impart substantivity towards basic dyes. As mentioned (section 3.2.1) the incorporation of, for example, selected sulfonic acids (eg 5-sulfoisophthalic acid) into the PA polymer enables cationic-dyeable PA fibres to be produced that display enhanced substantivity towards cationic dyes. Such fibre types enjoy mostly niche usage in the form of differential-dyeable PA fibres; as such basic dyes are little used on PA fibres.

(iii) *uncharged*

The polar and relatively hydrophobic nature of the polymer imparts substantivity towards disperse dyes, vat dyes, sulphur dyes and azoic colorants. The application conditions that are employed for these four classes of dye vary, markedly and are discussed in detail below. Of these four dye classes, disperse

[1] in this account, the classification system according to *application class* described in the *Colour Index* is employed in which individual dyes are described by C.I. Generic Name: 66. Colour Index Online; http://colour-index.com/ Bradford: Society of Dyers and Colourists; 2016 [

[2] with the exception of weakly polar 1:2 metal complex dyes



dyes enjoy greatest usage on PA fibres, with the principal use of both vat dyes and sulphur dyes being on PA/fibre blends (notably PA/cotton); azoic colorants are little used on PA fibres.

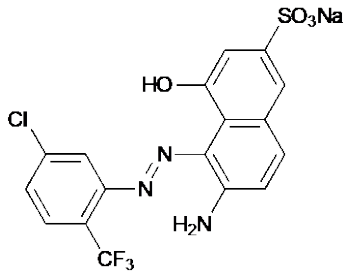
Of all of the above classes and types of dye, the most commercially important are, by some margin, acid dyes and disperse dyes, the use of other types/classes being mostly limited to niche end-uses.

Acid dyes

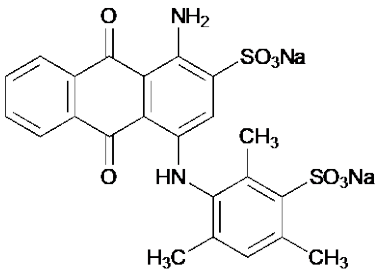
An acid dye is '*an anionic dye characterised by substantivity for protein fibres and often applied from an acid dyebath* '(35). Although the *Acid Dye* application classification in the *Colour Index* (36) contains both *non-metallised acid dyes* and *pre-metallised* acid dyes, because pre-metallised acid dyes are considered as being distinct from their non-metallised acid dye counterparts from both chemical and application viewpoints, the two types of acid dye are considered separately here.

Non-metallised acid dyes

The dyes belong predominantly to the azo and AQ chemical classes and contain at least one or more sulfonate groups (-SO_3Na) as exemplified by C.I. Acid Red 266 and C.I. Acid Blue 129:1.



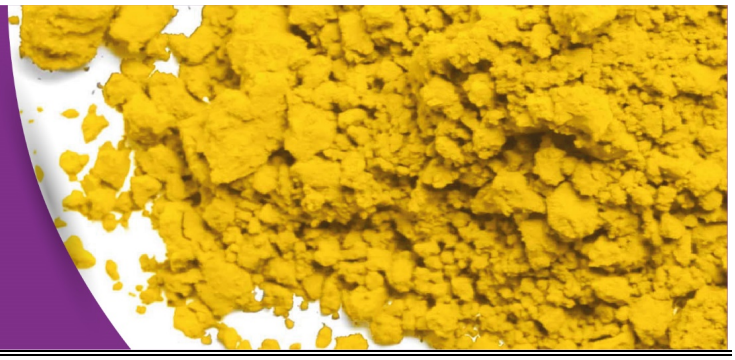
C.I. Acid Red 266



C.I. Acid Blue 129:1

The dyes vary in terms of their ability to *level* (*migrate*) during dyeing, cost, brightness, etc. and, most importantly, their fastness on PA 6 and PA 66 to different agencies (eg light, domestic laundering, perspiration, etc.). It is assumed that because the anionic dyes are applied to PA fibres under acidic/weakly alkaline conditions, the major contributor towards dye-fibre *substantivity*[3] is electrostatic forces of interaction operating between ionised anionic groups in the dye (-SO_3^-) and protonated amino groups in the fibre (-NH_3^+), although other types of intermolecular force can be expected to contribute

[3] dye-fibre substantivity is defined as *the attraction between a dye and a fibre which results in the dye being adsorbed on the fibre*: 1. Burkinshaw SM. Physico-chemical aspects of textile coloration. Chichester: Wiley; 2016.



to substantivity, including H-bonding, dipole-dipole, forces, hydrophobic interaction, etc. Of course, since dye-fibre substantivity has both mechanical and physico-chemical origins (1), it follows that various physico-mechanical aspects of dye-fibre interaction may contribute towards the substantivity of a given dye towards the substrate.

A considerable body of research has been generated regarding the mechanism by which non-metallised acid dyes are adsorbed onto PA fibres. In this context, it is generally held that the thermodynamic analysis of non-metallised acid dye adsorption is applicable to that the other four types of anionic dye used on PA fibres[4] (ie pre-metallised acid dyes, direct dyes, mordant dyes and reactive dyes), as well as that of anionic dyes in general [see (1) and the references therein].

Non-metallised dyes for PA fibres are commonly divided into three groups (67) according to their pH sensitivity[5]:

(i) Group I: dyes of low substantivity under neutral or weakly acidic conditions, that exhaust well under strong acidic conditions;

(ii) Group II: dyes that exhaust within the pH range 3.0–5.0.

(iii) Group III: dyes that display high substantivity under neutral or weakly acidic conditions (pH 5.0–7.0).

Generally, large molar mass representatives (Group III dyes) that display high substantivity under neutral pH conditions, exhibit poor coverage of barré but furnish dyeings that display good levels of wet fastness; in contrast, highly sulfonated dyes which are applied under acidic application conditions (Group I dyes), display low substantivity but high migration ability and generally provide dyeings of poor wet fastness properties on PA fibres. As the above division of the dyes implies, the application conditions employed (namely pH) depend on the particular level of substantivity displayed by the dyes. In this context, the dyes are applied at ~85-98^{o}C, between ~pH 4 to pH 8, depending on the type of dye and depth of shade applied (6); enhanced dye migration can be achieved using elevated temperatures (PA 6: 110-115^{o}C; PA 66: 110-120^{0}C) for coverage of barré (1). Dyebath pH can be controlled using acids (eg CH_3COOH), buffer systems to maintain the pH within a narrow region or by the gradual lowering of dyebath pH as dyeing proceeds; levelling agents are commonly employed to expedite level dyeing. The dyes generally exhibit lower rates of uptake on PA 66 fibres than on their PA 6 counterparts because of the greater crystallinity and more compact structure of the PA 66 variant.

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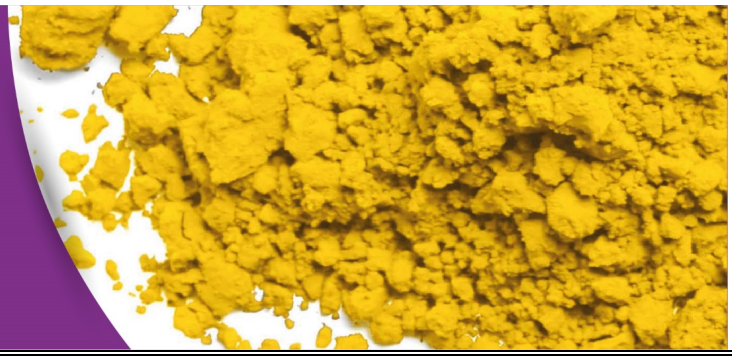
[4] this excludes the mechanisms of chroming in the case of mordant dyes and that of the covalent reaction of reactive dyes with the substrate

[5] dye makers often classify members of their dye non-metallised acid dye ranges into similar groupings



Despite the popularity of this particular dye type on PA fibres, the fastness of dyeings to wet often leaves much to be desired and, therefore, dyeings are commonly aftertreated to improve wet fastness, using either *natural tanning agents* or *synthetic tanning agents* (aka *syntans*) [section 9.2.1.3].

Levelling agents

Recourse is commonly made to the use of proprietary auxiliaries to ensure that level dyeing is achieved; three types of levelling agent can be used (1, 6):

(i) *anionic levelling agents*: these fibre-substantive compounds are adsorbed at the fibre surface and compete with the anionic dyes for the protonated $-^{+}NH_3$ end groups in the fibre, thereby imparting a *blocking effect* which reduces the rate of dye uptake and promotes coverage of fibre irregularities;

(ii) cationic levelling agents; these *reduce the rate of dyeing* by forming a *dye anion/cationic agent complex* in the dyebath that dissociates gradually as dyeing temperature is increased, thereby slowly releasing dye anions which are able to be adsorbed by the fibre; a non-ionic levelling agent is employed to prevent precipitation of the dye-cationic agent complex;

(iii) non-ionic levelling agents: these *retard dye uptake* by forming a complex with the anionic dye which reduces the *relative amount* of dye in the dyebath.

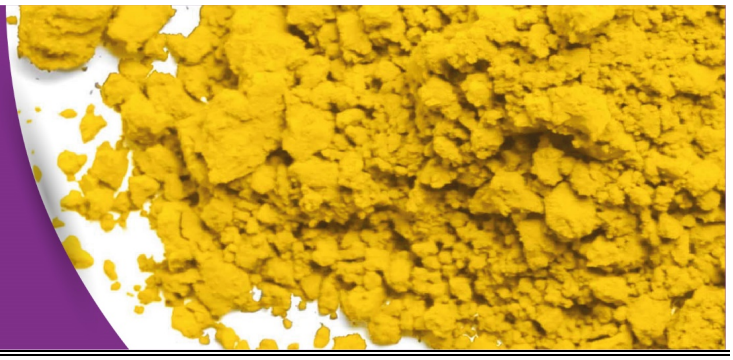
Barré effects

A problem that can occur in dyeing PA fabrics is the appearance of stripe or bars, which is commonly referred to as *barré*, that are the result of dye having been adsorbed to different levels on the different PA yarns that comprise the fabric. Such inter-yarn non-uniformity is a consequence of either *physical* or *chemical* variations in the yarn, the former being introduced during fibre processing (drawing, heat setting) or stem from crimp or linear density variations, whereas chemical irregularities are the result of fibre spinning and/or blending of yarns of different AEG (6). Generally, whilst disperse dyes typically display excellent coverage of both physical and chemical irregularities in PA fabrics, anionic dyes vary in their coverage of such irregularities.

Aftertreatment

Natural tanning agents

Natural vegetable tannin extracts are obtained from a wide range of plant sources and enjoy extensive usage in the preservation of animal skins via *tanning*. Natural tannins are water-soluble phenolic compounds that are classified as *condensed (non-hydrolysable) tannins* or *hydrolysable* (aka



pyrogallol) *tannins,* the latter class comprising two types of amorphous material, namely *gallotannins* (eg tannic acid[6]) and *ellagitannins* (eg chestnut).

In the *two-stage* full backtan process, PA fibres that have been dyed using acid dyes are subjected to consecutive aqueous treatments with tannic acid and potassium antimony tartrate. The high molar mass tannic acid is adsorbed onto protonated amino end groups in the fibre and the subsequent application of potassium antimony tartrate insolubilises the tannin by the formation of a sparingly water-soluble, *antimony tannate complex* that is located at the periphery of the dyed fibre, and which resists diffusion of the dye from the substrate during wet processing such as laundering. As the full backtan process suffers several inherent disadvantages (6), modified full backtan aftertreatments have been developed to circumvents the use of the toxic potassium antimony [see (1)].

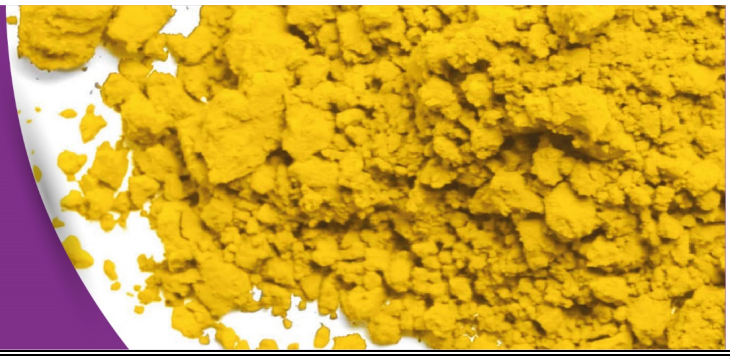
Synthetic tanning agents (*syntans*)

The inherent disadvantages associated with the use of full backtan aftertreatment (6) have resulted in its virtual replacement with synthetic tanning agents (*syntans*). Synthetic tanning agents were originally developed as alternatives for natural tannins in leather manufacture, and are of diverse composition, typically being water-soluble, formaldehyde polycondensates of sulfonated dihydroxydiphenylsulfones [see (1)]. Syntans are applied to dyed PA substrates using a *single-stage* process (eg PA 6: 70°C, 30 min; PA 66: 95°C, 30 min (6)) and do not suffer from the disadvantages displayed by their natural counterpart.

Syntans are adsorbed at the periphery of the dyed PA fibre and form a peripheral layer of large molar mass syntan molecules which provides a physical restraint to the diffusion of acid dye molecules out of the fibre during wet treatments, such as washing. The effectiveness of syntans in improving the wet fastness of acid dyes on PA fibres can be enhanced by the subsequent application of selected compounds [eg (68-70)], which result in the formation of a low water-solubility, large molecular size complex between the cationic compound and the anionic syntan within the dyed substrate.

Although 1:2 pre-metallised acid dyes generally exhibit superior wet fastness on PA fibres to that of their non-metallised acid dye counterparts, an aftertreatment with a *synthetic tanning agent* is often employed in order to secure highest levels of wet fastness (6).

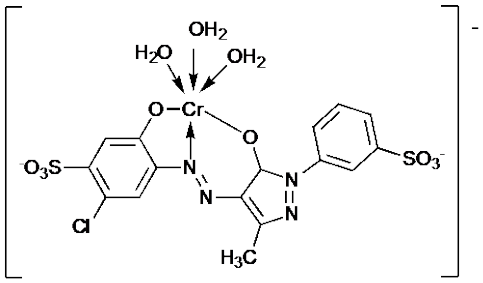
[6] tannic acid is also used as *stain resistant treatment* for PA carpet



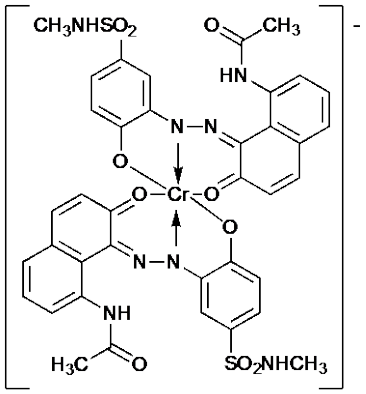
Pre-metallised acid dyes (aka **metal complex dyes**)

In the *Colour Index* (71) metal complex dyes are included in the *Acid Dye* application classification, and, therefore, the dyes are also referred to as *pre-metallised acid dyes.* The chemistry and application of this type of dye has been widely studied; see (72) for a recent account. These types of dye contain one metal atom, commonly Cr, that is complexed with either one, typically dye molecule (*1:1 metal complex dye*) such as C.I. Acid Red 183 or two, typically dye molecules (*1:2 metal complex dye*) such as C.I. Acid Black 60. The dye molecules invariably contain nucleophilic groups (–NH_2, -OH, etc.) that are able to *coordinate* with the metal atom; the dyes are commonly monoazo types as exemplified by C.I. Acid Red 183 and C.I. Acid Black 60. Both

1:1 and 1:2 pre-metallised acid dyes typically display high light fastness on PA fibres that has been attributed to shortened triplet state lifetimes and dye aggregation.



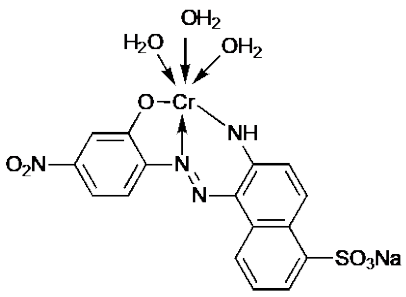
C.I. Acid Red 183



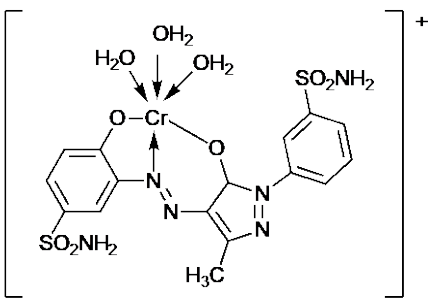
C.I. Acid Black 60

1:1 pre-metallised acid dyes

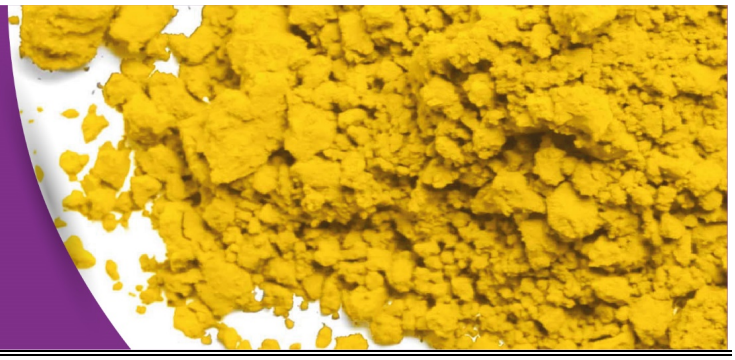
Water solubility is typically conferred by the presence of one or more sulfonic acid groups and the dyes are effectively uncharged (eg C.I. Acid Green 12) or carry an overall negative charge (eg C.I. Acid Red 183) depending on the nature of the *mondendate ligands* and both the number and nature of the solubilising groups (72); some dyes that contain no ionic solubilising group can carry an overall positive charge (eg C.I Acid Orange 76).



C.I. Acid Green 12



C.I. Acid Orange 76



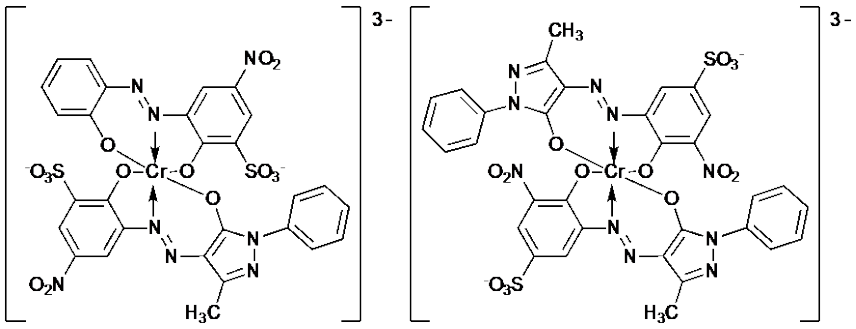
1:2 pre-metallised acid dyes

Three types of 1:2 metal complex dye have been commercially introduced, which vary in terms of the nature of the solubilising groups present in the dye ligands:

(i) *weakly polar dyes*: these typically symmetrical dye-metal complexes contain no ionic water-solubilising groups (eg C.I. Acid Black 60), water solubility being derived from the intrinsic anionicity that stems from the loss of protons from the two dye ligands and the presence of non-ionic polar substituents (eg $-SO_2CH_3$, etc.);

(ii) *monsulfonated strongly polar dyes*;

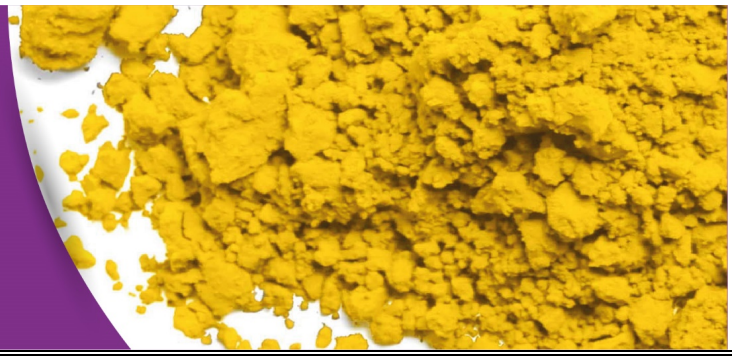
(iii) *disulfonated strongly polar dyes*: such as C.I. Acid Orange 148 and C.I. Acid Orange 142.



C.I. Acid Orange 148

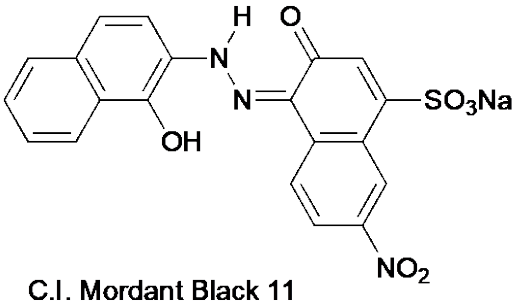
C.I. Acid Orange 142

Selected 1:1 pre-metallised acid dyes that display satisfactory saturation values and good coverage of barré are applied to PA fibres; when applied at 98°C in the pH region 4-6, in the absence of levelling agents, the ensuing reasonably bright dyeings exhibit good fastness to wet treatments and light. Selected 1:2 metal complex dyes display superior build-up owing to their lower aqueous solubility, being applied in the pH range 5-8, depending on dye type, in the presence of levelling agents at temperatures ≤110°C; the resulting dyeings display characteristically high all-round fastness.

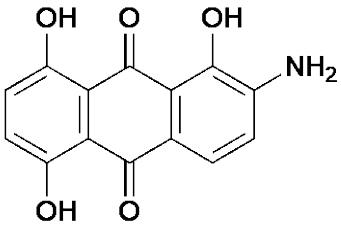


Mordant dyes

A mordant dye[7] is a dye *that is fixed by a mordant*, and a mordant is a *metallic compound, applied to a substrate to form a complex with a dye which is retained by the substrate more firmly than the dye itself* (61)[8].



C.I. Mordant Black 11



C.I. Mordant Blue 24

Mordant dyes, which are mostly azo or AQ compounds such as C.I. Mordant Black 11 and C.I. Mordant Blue 24, are anionic, water-soluble dyes that contain nucleophilic groups (-OH, -NH_2, -COOH, etc.) that are able to form a *stable co-ordination complex* with a metal ion *in situ* within the fibre. This complex formation disturbs the chromogen's π-electron density distribution which imparts a pronounced bathochromic shift to the λ_{max} of the mordant dye and, of more importance, imparts characteristically high light-fastness properties to mordants dyeings on PA fibres.

Three methods *could* be used to apply the mordant to PA fibres, as is practiced in the case of their use on wool, namely:

(i) *pre-chrome method* (aka *chrome mordant method*): the mordant is applied *before the dye*;
(ii) *metachrome method:* the mordant is applied *in conjunction with* the dye;
(iii) *afterchrome method:* the mordant is applied *after the dye.*

In the case of PA fibres, the *afterchrome* dyeing method is principally employed, utilising $K_2Cr_2O_7$ or $Na_2Cr_2O_7$ as mordant, as insufficient mordant dye-Cr complexation occurs when either the *pre-chrome* or *metachrome* application methods are used.

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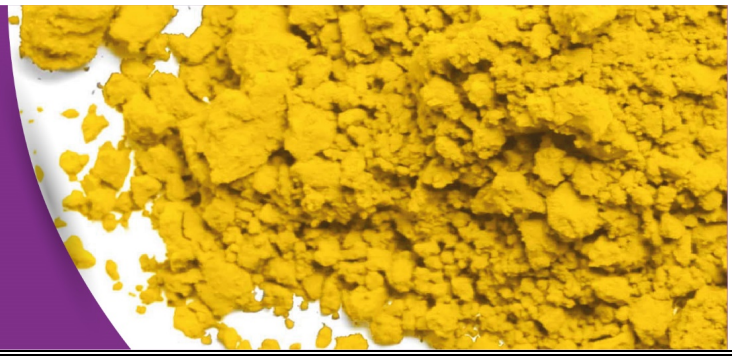
[7] the popularity of Cr compounds, commonly K or Na chromate or dichromate, in wool dyeing prompted some authors to adopt the term *chrome dye* rather than *mordant dye*; in this account, the term *mordant dye* is used, as employed in the Colour Index 71. Colour Index. Bradford: Society of Dyers and Colourists; 1971.

[8] this particular dyeing method is nowadays limited to the use of Cr salts as mordant and enjoys greatest usage in the dyeing of wool



In essence, the dye ligands coordinate with trivalent chromium, Cr(III) *in situ* in the fibre, resulting in the formation of a large molecular-size, low solubility dye-metal complex. However, as the cationic Cr(III) species display only low substantivity towards the protonated amino groups ($-NH_3^+$) in the fibre under the acidic application conditions used, the anionic, hexavalent chromium species, Cr(VI), is employed as the mordant, since this displays adequate levels of substantivity as either the chromate ($-CrO_4$) or dichromate ($-Cr_2O_7$) salt[9], which is reduced to the Cr(III) cation prior to complexation with the mordant dye ligand. As PA fibres are unable to reduce Cr (VI) to Cr(III) during the chroming stage, unlike the situation with wool which is able to itself furnish the required reduction, reducing agents (eg $Na_2S_2O_3$) must be used in the case of PA fibre dyeing, although elevated dyeing temperatures can also be employed in the absence of a reducing agent.

Typically, the mordant dye is applied to PA fibres under acidic conditions using acid-liberating salts (eg $(NH_4)_2SO_4$, NH_4COOCH_3) at ~98°C, after which, the pH is then gradually lowered to exhaust the dye and, after rinsing, the dyed material is *afterchromed*, typically using $K_2Cr_2O_7$ under acidic conditions at 95-98°C (67).

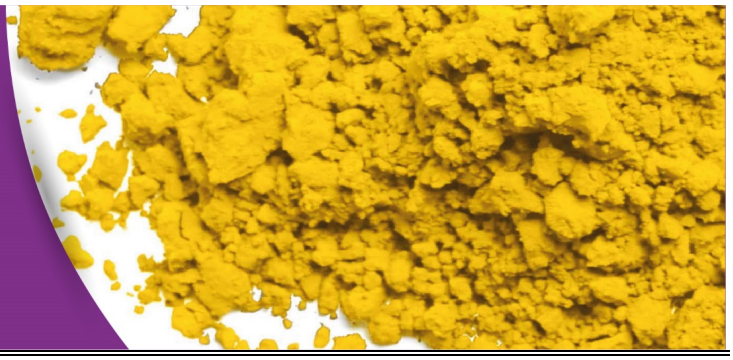
Mordant dyes are sensitive to chemical variations in PA fabrics but cover physical fibre irregularities well. Although the use of mordant dyes enables the production of economical, deep, predominantly black and navy-blue shades on PA fibres that display good all-round fastness, the use of mordant dyes is declining mostly due to environmental regulations governing the levels of hexavalent, trivalent and total chromium in wastewaters.

Direct dyes

A direct dye is *an anionic dye having substantivity for cellulosic fibres, normally applied from an aqueous dyebath containing an electrolyte* (61). The term 'direct' indicates that the dyes can be applied *directly* to cotton (and other cellulosic fibres) owing to their inherent substantivity as opposed to having to be applied *indirectly* via the use of a *mordant*[10] (metal salt or tannin), as was practiced until the commercial introduction of the first 'direct' dye C.I. Direct Red 28, under the trade name *Congo Red*, in 1885. As

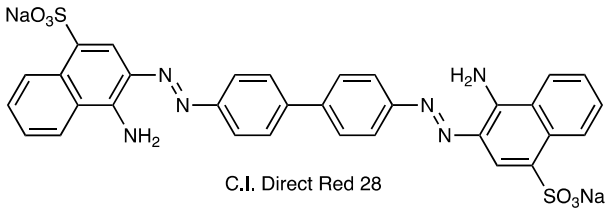
[9] one changes into the other at an appropriate pH 73. Peters RH. Textile Chemistry, Volume 3. Amsterdam: Elsevier; 1975.

[10] that was used to enhance dye-fibre substantivity, improve the fastness of a dyeing to a particular agency (eg light, water, etc.) and/or generate a different shade from a given dye

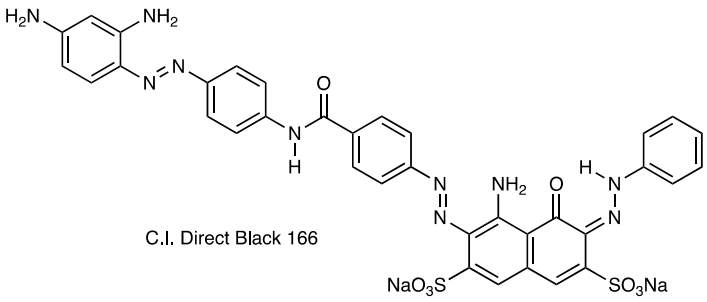


the above definition implies, the major usage of this dye class is in the dyeing of both natural cellulosic fibres (eg cotton) and man-made cellulosic fibres (eg CV, CLY,etc.).

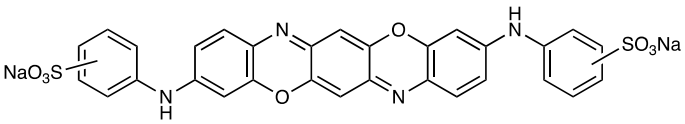
Although direct dyes are predominantly azo structures, such as C.I. Direct Black 166, some non-azo classes feature, as represented by C.I. Direct Blue 106. Selected direct dyes provide economically attractive dyeings on PA fibres; an aftertreatment with a syntan improves the wet fastness of the dyeings (6, 74).



C.I. Direct Red 28

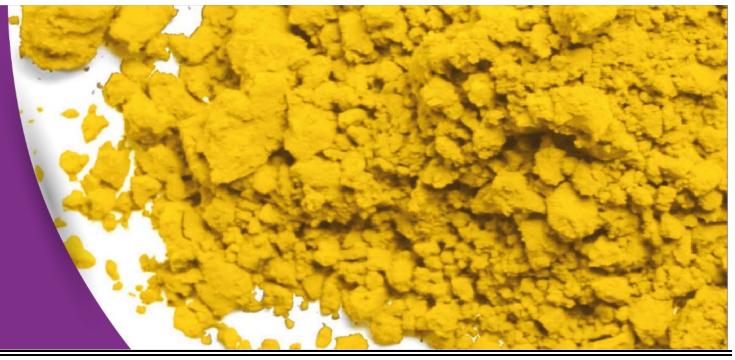


C.I. Direct Black 166



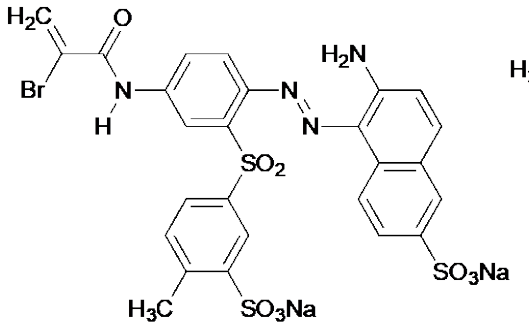
C.I. Direct Blue 106

Direct dyes structurally resemble non-metallised acid dyes insofar as the typically large molar mass, planar, azo dyes contain sulfonate groups. In essence, selected direct dyes are applied to PA fibres using conditions employed for Group III non-metallised acid dyes, as they are large molar dyes that display high substantivity under neutral pH conditions, but emphasise physical fibre irregularities, are sensitive to chemical variations and display low migration. For example, direct dyes can be applied fibres under acidic conditions using acid-liberating salts to reduce the final dyebath pH to 5.0, at ~80-98°C; further pH reduction may be necessary to achieve complete dye exhaustion (67).

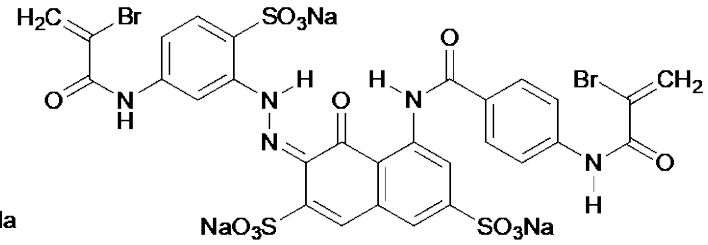


Reactive dyes

See (1) and the references therein for a detailed account of this topic. A reactive dye '*under suitable conditions, is capable of reacting chemically with a substrate to form a covalent dye-substrate linkage'* (61). In essence, reactive dyes possess one defining structural characteristic that distinguishes them from their acid dye, direct dye and mordant dye counterparts, and, indeed, from all other classes of dye, namely the presence of one or more *reactive systems* (eg *α-bromoacrylamido*) that is attached to the *chromogen*[11] and which imparts to the dye molecule the ability to form a covalent bond with nucleophilic groups in the substrate; indeed, structurally, reactive dyes for PA fibres are, in essence, acid dyes that carry one or more reactive system (eg C.I. Reactive Red 84 and C.I Reactive Red 84).



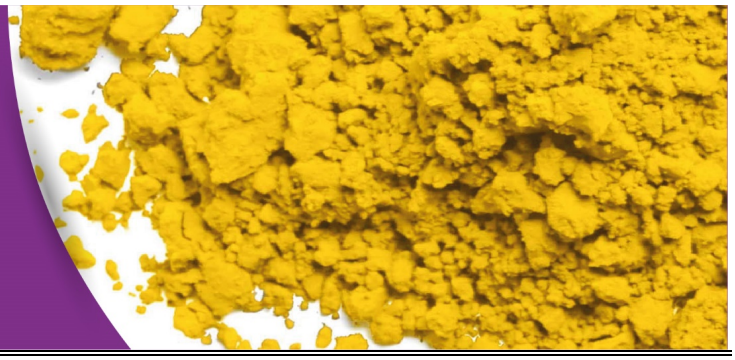
C.I. Reactive Red 84



C.I. Reactive Red 83

As a consequence of the covalent reaction that occurs between the chromogen and the fibre, at the end of dyeing, the chromogen is covalently attached (ie *fixed*) to the fibre and, therefore the ensuing dyeing displays characteristically excellent fastness to wet treatments. Because of the ability of reactive dyes to become covalently linked to the substrate, reactive dyes differ profoundly to all of the other types of dye that can be used on PA which rely upon *mechanical retention* (eg vat dyes, sulphur dyes, azoic colorants) and *physical adsorption* (acid dyes, direct dyes and mordant dyes) for dyeing to be achieved. The nucleophilic sites in the PA fibre with which reactive dyes form a covalent bond are the terminal amino groups, $-NH_2$.

[11] a chromogen is *a chemical compound that is either coloured or can be made coloured by the attachment of suitable substituents - the chromophore and the auxochrome(s) are part of the chromogen where* a chromophore is a *chemical group which, when present in a compound (the chromogen), is responsible for the appearance of colour - colorants are sometimes classified on the basis of their chief chromophore (eg azo dyes contain the chromophore –N=N-)* and an auxochrome is *a substituent group in a chromogen that influences its colour*: 61. SDC. Colour terms and definitions, 2nd edition. Bradford: Society of Dyers and Colourists; 1988.



Prior to covalent bond formation with the substrate, the mechanism of adsorption of reactive dyes on PA fibres accords with that of non-metallised acid dyes (1).

Although the commercial introduction of reactive dyes for cotton and other cellulosic fibres (eg CUP, CV, etc.) some 60 or so years ago promptly resulted in this particular class of dye becoming the most popular of the five classes of dye that can be used on these substrates[12], this did not happen in the case of reactive dyes specifically intended for use on wool fibres and, especially, reactive dyes aimed at PA fibres. Indeed, very few commercial reactive dye ranges have been marketed for use on PA fibres, with the result that this class of dye nowadays occupy only a small market share compared to that of their non-metallised acid and pre-metallised acid dye counterparts.

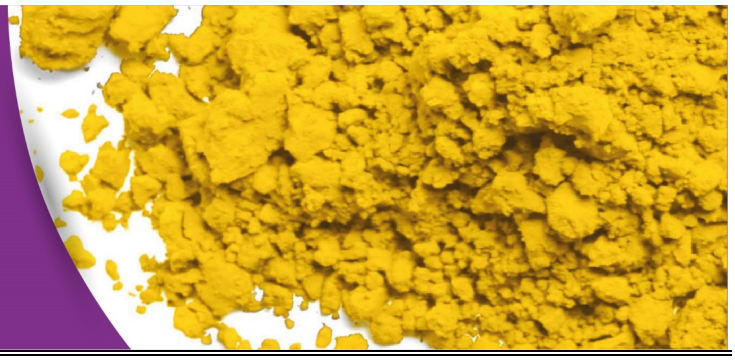
Selected examples of reactive dyes marketed for use on both cellulosic fibres and wool can be applied to PA fibres from weakly acidic dyebaths (pH 4-6) in the presence of a levelling agent. However, such dyes tend to be very sensitive to fibre irregularities and the extent of dye fixation achieved is typically low, so that only pale/moderate depths of shade are secured for regular AEG fibres. The low depths of shade achieved on PA fibres using anionic reactive dyes arise from the relative paucity of nucleophilic sites (-NH_2 groups) in the substrate (1), a situation that contrasts to that in the two natural polyamide fibres, wool and silk (Table 4), on which deep shades can be obtained using anionic reactive dyes.

Table 4 Amino end group content of different fibres (75)

fibre	AEG/ m eq kg^{-1}
wool	800-900
silk	120-200
PA	30-50

By way of brief explanation, reactive dyes are able to exploit the ability of the terminal -NH_2 groups in PA fibres to act as *nucleophiles* with which the reactive system within the dye molecules can *react* to form a covalent linkage. Covalent dye fixation (ie the formation of a covalent dye-fibre bond) can *only occur* when the amino end groups are *unprotonated* under neutral conditions (ie ≥ pH ~8); thus, anionic reactive dyes *do not* covalently bond with protonated terminal amino groups (-$^{+}NH_3$) in the fibre. In this context, it is unfortunate that whilst weakly acidic conditions *maximise dye-fibre substantivity* (ie anionic reactive dye uptake), because of the pK_a of the amine conjugate acid in PA fibres (eg PA 6: –$(CH_2)_6$-

[12] direct dyes, vat dyes, sulphur dyes, azoic colorants and reactive dyes



NH_3^+ = ~10 (76)), then such weakly acidic dyeing conditions favour the formation of non-nucleophilic, protonated amino groups, $-^+NH_3$, with the result that very few nucleophilic, unprotonated amino end groups, $–NH_2$, are available for reaction with the dye. The conflicting requirements of dye exhaustion requiring acidic conditions and dye-fibre reaction requiring higher pH values was clearly demonstrated in a study (77) of the effects of pH on the exhaustion and fixation of modified vinyl sulphone reactive dyes on microfibre PA 66. Whilst the extent of *covalent dye fixation, %F*, of the dyes increased as dyebath pH increased over the range pH 3-8, because of the consequent increase in the number of unprotonated, nucleophilic $–NH_2$ groups in the fibre, the *total reactive dye fixation, %T*, which is a measure of the proportion of the dye originally applied to the substrate that is covalently bound (1), decreased in the pH region 7-8 owing to reduced dye exhaustion within this particular pH range (77).

In a typical application process, dyeing is commenced at 20-45°C under weakly acidic conditions (pH ~4.5 – 5.0), the dyebath temperature raised to 98°C and dyeing continued for 30 – 90 min; the dyeing is then washed-off using aqueous alkaline conditions (eg ~0.5 gl^{-1} non-ionic surfactant and 1 gl^{-1} Na_2CO_3) at 95°C for 20-30 min.

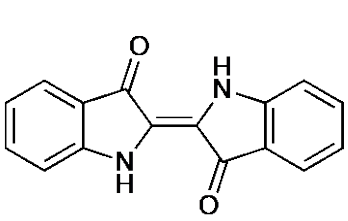
By using a modified PA 66 fibre of increased AEG content and commercial ranges of anionic reactive dyes intended for use on PA fibres, high wet fastness dyeings on microfibre PA fibres in full depths of shade can be achieved (77).

Disperse dyes

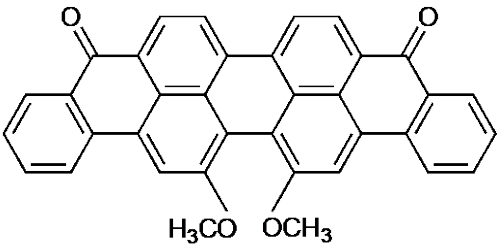
Disperse dyes can be applied to PA fibres, being insensitive to chemical variations; whereas low energy dyes cover physical irregularities well, dyes of larger molecular size display a greater sensitivity towards physical variations in the substrate. However, as disperse dyes tend to display only moderate fastness to wet treatments on PA substrates, they are mostly used in low depths of shade where fastness limitations do not pose problems (eg hosiery). Dyeing is carried out typically at or about the commercial boil in the presence of a dispersing agent (~0.5-2 gl^{-1}) at pH ~5 (CH_3COOH) for 30-60 min.

Vat dyes

A vat dye is *a water-insoluble dye, usually containing keto groups, which is normally applied to the fibre from an alkaline aqueous solution of the reduced enol (leuco) form, which is subsequently oxidised in the fibre to the insoluble form* (61). Vat dyes are used predominantly on both natural and man-made fibres.



C.I. Vat Blue 1



C.I. Vat Green 1

Although the insoluble vat dye displays little if any substantivity towards PA fibres, the dyes contain two or more *conjugated keto groups* (aka *carbonyl groups*), -C=O, as illustrated by two of the most famous vat dyes C.I. Vat Blue 1 (*indigo*) and C.I. Vat Green 1 (*Malachite Green*), which enables the dyes to be converted by reduction under alkaline conditions to the substantive, anionic, water-soluble *alkali leuco derivative*.

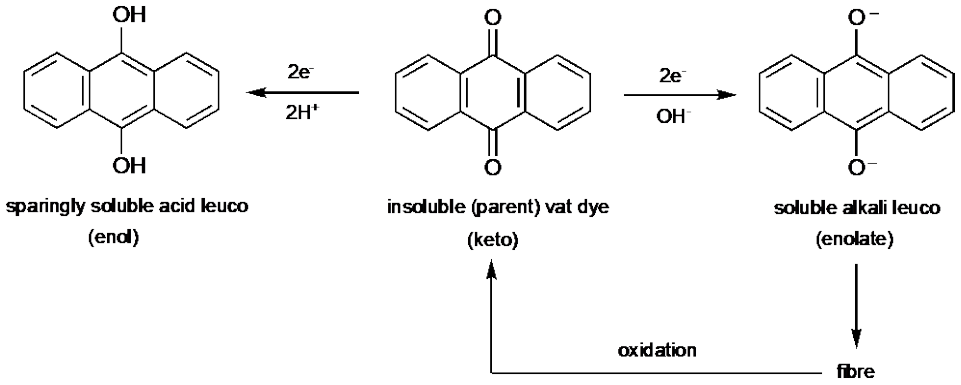
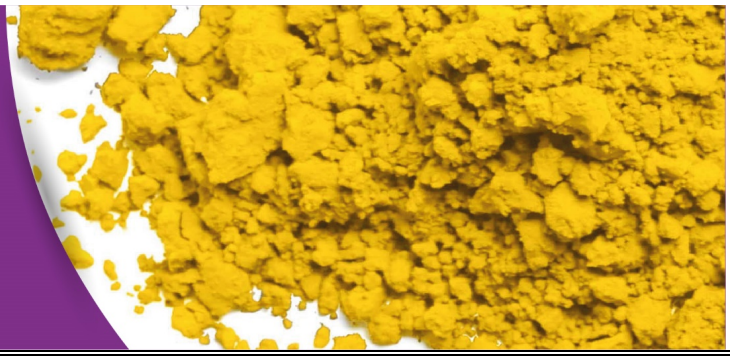


Figure 10 vat dye reduction and dyeing process

When reduction is undertaken under alkaline conditions, deprotonated *enolate groups*, -C-O$^-$, are produced and the ensuing water-soluble dye, or *alkali leuco derivative*, is applied to the substrate by exhaust methods (Figure 9). When the dye has been applied, subsequent oxidation converts the soluble leuco form of the dye to the parent, insoluble dye *in situ* within the fibre and generates the final hue of the dye (Figure 9).



The principal use of selected vat dyes is on PA blend materials (eg PA/cotton, etc.). In the case of solo PA fibres, selected vat dyes can display high fastness to light and also to wet treatments, especially when applied as the acid leuco variant (ie as the *enol* form) (78).

Sulphur dyes

Sulphur dyes are complex macromolecular compounds of mostly unresolved structure that comprise mixtures of coloured oligomers and higher molar mass components linked by disulfide/polysulfide bonds (-S_n-), and which contain functional groups (eg =NH, etc.) that can be reduced under alkaline conditions to generate the *alkali leuco derivative* which is applied to natural and man-made cellulosic fibres (Figure 11).

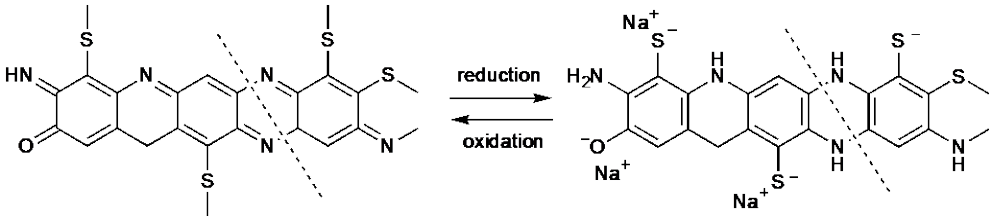
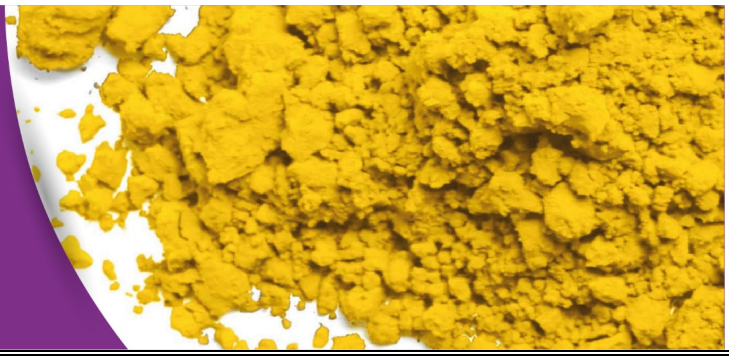


Figure 11 schematic representation of the reduction of C.I. Sulphur Black 1 (79)

The Colour Index lists four *application classes* of sulphur dye, namely *C.I. Sulphur dyes*, *C.I. Leuco Sulphur dyes*, *C.I. Solubilised Sulphur dyes* and *C.I. Condense Sulphur dyes*, though the latter type is no longer manufactured.

C.I. Sulphur Dyes

These contain '*sulphur both as an integral part of the chromophore and in attached polysulphide chains, normally applied in the alkali-soluble reduced (leuco) form from a sodium sulphide solution and subsequently oxidised to the insoluble form in the fibr*e' (52). Although the low-solubility (parent) sulphur dye displays little if any substantivity towards PA fibres, as the dye contains appropriate functional groups, it can be converted, by reduction under alkaline conditions, into the corresponding, anionic, water-soluble, substantive *leuco* derivative (*thiolate*) that is substantive (Figure 12).; after the *leuco form* of the sulphur dye has been applied, subsequent oxidation converts the soluble thiolate (leuco form) into a low solubility derivative *in situ* within the substrate.



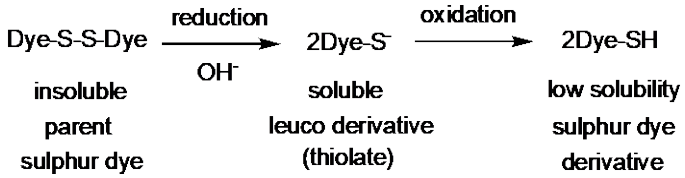


Figure 12 representation of dyeing process using C.I. Sulphur dyes

C.I. Leuco Sulphur Dyes

These are commercially produced, pre-reduced compositions of the *leuco derivative* of a (parent) C.I. Sulphur dye that contain a small excess of a reducing agent; C.I. Leuco Sulphur dyes possess the same *C.I. Constitution Number* (*CICN*) as the parent C.I. Sulphur dye (eg both C.I. Sulphur Black 1 and C.I. Leuco Sulphur Black 1: CICN 53185).

C.I. Solubilised Sulphur Dyes

These are a water-soluble, thiosulfuric acid derivatives of a (parent) C.I. Sulphur dye which are converted into the substantive, alkali-soluble *leuco form* during dyeing; C.I. Solubilised Sulphur dyes possess a different CICN to the parent C.I. Sulphur dye (eg C.I. Solubilised Sulphur Black 1: CICN 53186; C.I. Sulphur Black 1: CICN 53185).

The principal use of selected sulphur dyes is on PA blend materials (eg PA/cotton, etc.). When applied to solo PA fibres, deep dyeings can be obtained that display very good fastness to repeated washing, which can be improved by an aftertreatment with a proprietary *cationic fixing agent* [see (1)], but poor fastness to light (80); maximum colour yield is obtained when dyeing was carried out at pH 7 (81). Interestingly, the adsorption of both C.I. Sulphur dyes and C.I. Solubilised Sulphur dyes is unaffected by the nature of the PA fibre variant used (ie namely deep-dyeable, standard-dyeable as well as cationic-dyeable which implies that dye-fibre substantivity can be attributed to H-bonding, dispersion forces and polar van der Waals' forces of interaction (82).

Azoic colorants

The main use of azoic colorants on PA fibres is for the production of deep, economical, high fastness, black shades that are produced using diazotised and developed black disperse dyes [see section 9.4.2].