CHAPTER 16

Dyeing

16.1 INTRODUCTION

Dyeing is one of the more important steps in leather making as it is usually the first property of the leather to be assessed by the consumer or customer. He or she will make judgements in a glance: colour, depth of shade, uniformity. Therefore, it is critical that the science and hence the technology of colouration is well understood. The origin of colour and its perception was reviewed by McLaren in a Procter Memorial Lecture for the SLTC.[1] Randall has explored colour as it applied to leather.[2] There, he reviewed the measurement of colour from surfaces, pointing out the difference between reflection from a relatively continuous surface, as is the case for grain leather, and the effects of reflection from the tips or the fibre of suede, resulting in a directional effect of colour perception. The standard system for measuring colour defines the coordinates in the CIELAB colour space: a* is the red-green component, b* is the blue-yellow component and L* is the black-white component from which the other parameters can be calculated, such as the hue angle and the chroma. These measurements are useful in comparing colour and for colour matching. Tysoe has reviewed the classification of dyes in the Colour Index and introduced the problem of colour matching for leather.[3] Colour match prediction is relatively straightforward when dealing with pigments, but when the dyestuff confers transparent colour to leather, the outcome is dependent on the following parameters:

- dyestuff chemistry and mechanism of fixation;
- relative affinities of the dyestuff and the substrate;
- nature of the substrate, including its colour;
- illumination of the leather: the perceived colour depends on the light source, an effect called ‘metamerism’.

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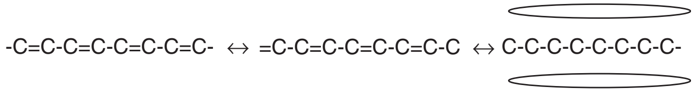


Figure 16.1 Formation of a molecular orbital from adjacent p orbitals.

The modern synthetic dyestuffs industry was initiated by the development of mauveine by Perkin in 1856: the primary markets were textiles, but the leather industry eventually took advantage half a century later, especially when it was realised that bright deep shades could be achieved with the new tannage with chromium(III).

All dyes work on the same principle. The colour is generated by the creation of a system of delocalised electrons, made possible by chemically synthesising molecules that contain a system of conjugated double bonds, *i.e.* alternate double and single bonds (Figure 16.1).

What this actually means is the π orbitals of the double bonds create a molecular orbital over the whole carbon chain. The system can include other delocalised groups, such as benzene rings or naphthalene rings, *etc.*, where molecular orbitals are already present above and below the plane of the ring. Note, dye structures are often presented in the form of the Kekulé structures of the aromatic rings, merely to emphasise the concept of conjugation over the molecule.

The groups with the delocalised electrons are called 'chromophores', because they are the primary sources of colour. Often the chromophores are linked by the azo group, N=N, which can contribute to the delocalisation of electrons over the chromophore system. The diazotisation reaction to create the azo group is conducted as follows. Acidification of sodium nitrite produces nitrous acid:

$$\mathrm{NaNO_2 + HCl \rightleftharpoons HO\text{-}N = O}$$

An aryl amine is reacted with nitrous acid under cold conditions, preferably close to 0 °C, to yield the diazonium salt:

$$\mathrm{Ar\text{-}NH_2 + HONO \rightleftharpoons Ar\text{-}N = N + Cl^-}$$

The diazonium salt then reacts with an active hydrogen on another aryl compound, to link the molecules *via* the diazo group:

$$\mathrm{Ar\text{-}N = N^+ + Ar\text{-}H \rightleftharpoons Ar\text{-}N = N\text{-}Ar + H^+}$$

Many aromatic amines have been used to make the so-called azo dyes, but are now known to be toxic, particularly carcinogenic. Because there is a possibility of regenerating the amine from the azo derivative they are now excluded from this application, notably benzidine (Figure 16.2) and its

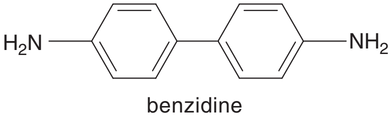


Figure 16.2 Benzidine.

derivatives. Other banned reagents include 4-aminodiphenyl, toluidine, 2-naphthylamine, dianisidine, cresidine, *etc.*

The delocalisation of electrons can be modified by the presence of substituents on the aromatic chromophores: these are called 'auxochromes'. They alter the distribution of electrons by electronegativity effects or hyperconjugation. By changing the energy of the molecular orbital, the energy to excite an electron is changed and consequently the energy of the quantum released when the electron falls back to its ground state is changed. If the effect of the structural change is to cause the colour to move to longer wavelength it is called a 'bathochromic shift'. Change to shorter wavelength is called a 'hypsochromic shift'.

Groups that donate electrons to the aromatic ring system (nucleophiles) include OH (phenolic), CH_3, OCH_3, NH_2, NHR and NR_2.

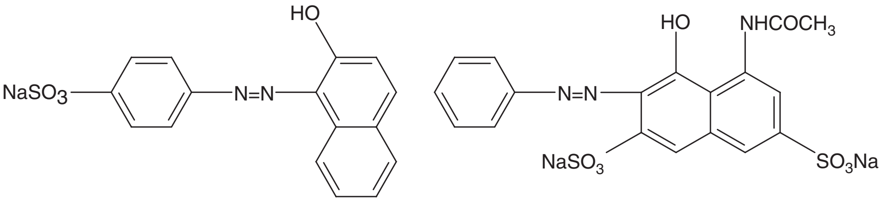
Groups that accept electrons (nucleophilic) include NO_2, COOH and SO_3^-.

Groups that contribute to the solubility of the dye include SO_3^-, CO_2^- and NH_3^+.

In a leather context, the auxochromes react with the collagenic substrate in various ways, to confer colour addition. In addition, the reaction can be considered a form of tanning: any chemical species that binds to the substrate alters the properties of the substrate, including contributing to the hydrothermal stability. This is not usually taken into account when considering the eventual outcome of wet processing.

Dyestuffs as supplied are typically not pure compounds. Owing to variations in synthesis, they may be formulated with other dyes to remain on shade. This can lead to problems in colour matching (see below). They are also typically marketed with a diluent. These can include sodium chloride, sodium carbonate, dextrin, sulfite cellulose, naphthalene sulfonate, sodium sulfite, *etc.* The reason is technologically sound: to allow the tannery operative to weigh quantities in kilograms, with little associated error. If the undiluted dyestuff were to be supplied, the quantities required for a pack would be grams; such weighings would have a large associated error, with consequent variations in dyeing consistency. It is the same argument that applied to formulations of enzymes, discussed in Chapter 8.

The following sections illustrate the structures of the different, commonly used dye types. Each has its name, usually indicating the dye chemistry, the colour and a designated number: each has a Chemical Index number, where it is categorised by its structure. Not all the dyes given as examples are designated particularly for leather applications: the structures are illustrative of the



Acid Orange 7 (CI 15510)

Acid Red 1 (CI 18050)

Figure 16.3 Mono azo acid dyes.

principles involved in creating dyes with different reaction characteristics and different degrees of applicability to leather.[4]

16.2 ACID DYES

Acid dyes are so called because they are fixed under acid conditions (Chapter 15). This class of dyes is the most commonly used in the leather industry, particularly for chrome tanned leather. Figure 16.3 illustrates the type of structure.

The properties can be summarised as follows:

1. Relatively small, typically hydrophilic molecules;
2. Used for penetrating dyeing, producing level shades;
3. Anionically charged, therefore high affinity for cationic leather;
4. Fixed by acidification, due to the presence of sulfonate groups (Chapter 15);
5. They react predominantly through electrostatic reaction between their sulfonate groups and the protonated amino groups of lysine;
6. Secondary reaction is *via* hydrogen bonding through auxochrome groups;
7. Some dyes may react with the bound chrome, using it as a mordant (see below);
8. Good fastness properties: less complex molecules offer fewer opportunities for structural changes by free radical mechanisms, as discussed in the context of condensed vegetable tannins;
9. Wide range of colours, offering bright deep shades.

16.3 BASIC DYES

The structures of basic dyes are essentially the same as the acid dyes, except they carry a net positive charge from the cationically charged amino substituents, even though they may also have anionic sites (Figure 16.4). Quaternary amino groups are less hydrophilic than sulfonate or carboxylate groups, so they are typically less water soluble than acid dyes.

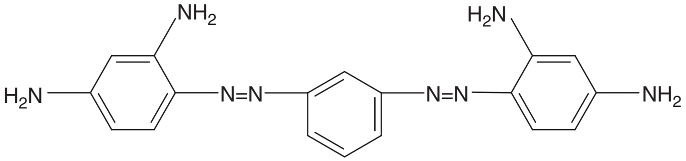


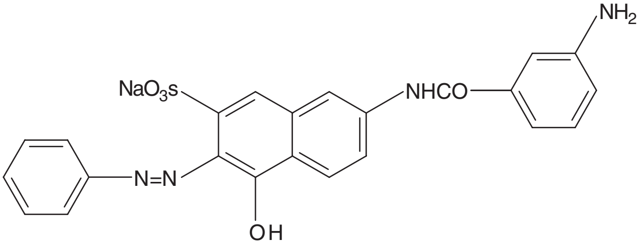
Figure 16.4 Disazo basic dye: Manchester Brown or Bismarck Brown.

The properties can be summarised as follows:

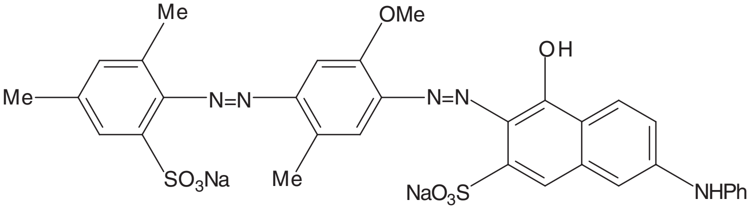
1. They produce strong, brilliant colours (red, orange, yellow, green, blue, indigo, violet and black);
2. They tend to be relatively hydrophobic, because they contain fewer solubilizing groups than the acid dyes; consequently, they are often soluble in oils and non-aqueous solvents.
3. They tend to bronze, *i.e.* produce a metallic sheen. This is due to surface reaction, when the dye molecules lie on top of one another, attracted by van der Waal's dispersion forces, allowing light to be reflected from the layered structure. This is a consequence of hydrophobicity, when the dyes have greater affinity for themselves than for the aqueous solution or the substrate.
4. Poor light fastness;
5. Good perspiration fastness, because they are not displaced by elevated pH;
6. High affinity for anionic leather, *e.g.* vegetable tanned, anionic retanned, acid dyed leathers. The latter property is exploited in 'sandwich dyeing': acid dye, then basic dye, possibly topped with more acid dye. The electrostatic attraction between the charged species creates deep shades, with good rub fastness.
7. Precipitated by hard water and anionic reagents;
8. Applied by mixing with acetic acid, then diluting with hot water;
9. They react electrostatically through their protonated amino groups and ionized carboxyl groups on collagen;
10. Secondary reaction is by hydrogen bonding;
11. Since they are typically more hydrophobic than acid dyes, some reaction will be *via* hydrophobic bonding.

16.4 DIRECT DYES

Direct dyes have the same sort of structural features as the acid and basic dyes, but with higher molecular weight. Figure 16.5 shows that direct dyes have obvious similarities to acid and basic dyes. There is an additional category of direct dyes, the developed direct dyes, which can be diazotised *in situ* and additional aromatic chromophores added to the dye as a route to black.



Direct Red 118 (CI 17780)



Direct Violet 51 (CI 27905)

Figure 16.5 Direct dyes.

The properties of this type of dye can be summarised as follows:

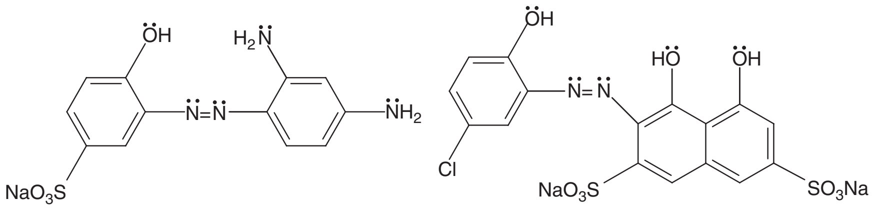
1. They are larger molecules than typical acid or basic dyes.
2. Used for surface dyeing, with consequent likelihood of uneven colouring.
3. Acid is not needed for fixation, because they are more reactive, due to the higher number of reactive sites on the molecule and the hydrophobicity of the overall structure.
4. Fastness properties average to good;
5. Usually dark colours;
6. Have the same sort of structures as acid and basic dyes, although typically with lower charge, resulting in lesser importance of electrostatic bonding.
7. High molecular weight means more direct reaction, not requiring fixation by pH adjustment.
8. Relies more on hydrogen bonding from larger number of auxochromes per molecule, similar to the relative astringencies of vegetable tanning agents, and more emphasis on hydrophobic bonding.

16.5 MORDANT DYES

The original mordant dyes were typically plant extracts, which produced relatively dull and pale shades and fixed poorly to textiles when used alone: to fix the colouring agent to a substrate, it was necessary to provide an additional fixing mechanism, by applying metal salt either before or with the dye. Modern mordant dyes are similar to acid dyes, but usually with less anionic charge (Figure 16.6). They generally have poor affinity for collagen, but rely on the presence of a metal ion with which they can complex, so that the metal acts as the link between the leather and the mordant dye.

Suitable metal salts include chromium(III), which of course may already be bound to collagen. Other metals that can be used are aluminium(III) and iron(III), *etc*. The formation of metal complexes means that the final colour struck by the dye depends on the metal mordant. This is illustrated by alizarin (Figure 16.7 and Table 16.1).

The technology is to apply the mordant to the leather, then treat with the dye. A common option used to be to treat the leather with a chromium(VI) salt, usually as dichromate, and reduce it to chromium(III) *in situ*, in a process



Mordant Brown 13

Mordant Blue 13

Figure 16.6 Mordant dye structures: lone pair sites for possible complexation are indicated.

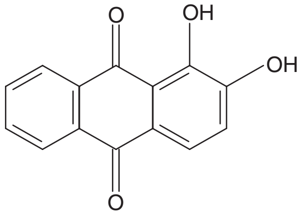


Figure 16.7 Structure of alizarin, mordant dye.

Table 16.1 Effect of metal mordant on the colouring of alizarin dyeing.

Metal ion	*Colour*
Al(III)	Red
Sn(IV)	Pink
Fe(III)	Brown
Cr(III)	Puce-brown
Cu(II)	Yellow-brown

analogous to two-bath chrome tanning. This is no longer used in the leather industry for two reasons:

1. The environmental impact of Cr(VI) is too high and discharges are strictly regulated.
2. The availability of premetallised dyes has simplified the process (see below).

The mechanisms of fixation are the same as for acid dyes, with the additional mechanism of covalent complexation:

- They have low affinity for collagen, typically having fewer sulfonate groups, particularly if they are natural dyes, and few hydrogen bonding groups.
- Reliance on creating complexes with metal ions (mordants) previously fixed to collagen.
- Binding to mordant metals will vary in the degree of electrostatic and covalent character, depending on the metal, *e.g.* Al(III), Cr(III).

16.6 PREMETALLISED DYES

16.6.1 1:1 Premetallised Dyes

The concept of premetallising dyes is to avoid the two-step process of mordanting then dyeing, by preparing the complex of dye and metal salt in advance. In this way, this is an example of a compact process, a concept introduced in Chapter 14. Figure 16.8 illustrates this principle, with a chromium(III) complexed dye, showing how the availability of lone pairs of electrons can be used to create dative bonds in a complex. Other metal ions that are used in premetallised dyes include cobalt, iron and copper.

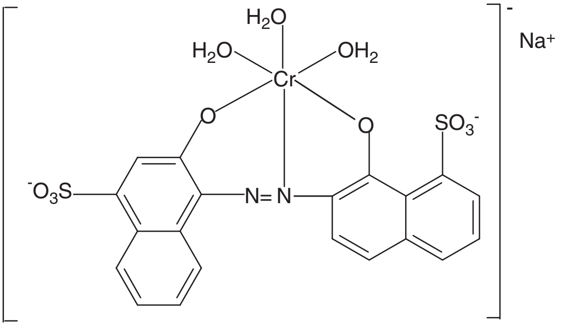


Figure 16.8 A 1:1 chromium(III) premetallised dye, Acid Blue 158 (CI 14880).

The mechanisms of fixation are the same as summarised for mordant dyes. The dyes exhibit the following properties:

1. They have lower anionic charge than the corresponding anionic uncomplexed dye.
2. Penetration and levelness of colouring are good;
3. They include pale, dull and pastel shades.
4. Fastness properties are good to very good;
5. They tend to be expensive, so are used for premium leathers, *e.g.* gloving, clothing, suede, nubuck, aniline.
6. They may be formed from either mordant dyes or conventional acid dyes precomplexed to a mordant metal ion, in the ratio of one dye molecule to one atom of metal.
7. Primary fixation mechanism is through reaction between the metal ion and collagen carboxyl groups, which can vary in covalent character.
8. Secondary reactions may be electrostatic and hydrogen bonding, depending on whether the dye is derived from mordant or acid dye precursor.

16.6.2 1 : 2 Premetallised Dyes

From Figure 16.8, further complexation can, obviously, occur in 1 : 1 complexes, because there are complexing sites remaining on the metal ion (Figure 16.9). Note, the second complexing dye species does not have to be the same as the first. They are referred to either as 1 : 2 or as 2 : 1 premetallised dyes.

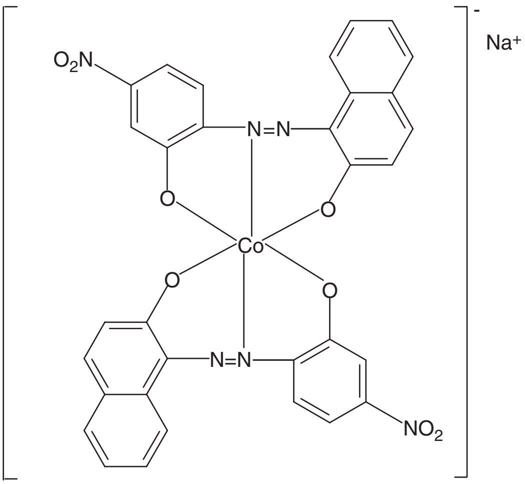


Figure 16.9 A 1 : 2 premetallised dye: Perlon Fast Violet BT (CI 12196).

The difference between 1 : 1 and 1 : 2 premetallised dyes is that the fully coordinated dyes are more anionic and can exhibit a wider range of reaction properties. For leather applications, there are three designated types. These designations and their consequences for reaction can be understood from the HHB/HLB [hydrophilic–hydrophobic (HHB) or hydrophilic–lipophilic (HLB) balance] mechanism of reactions, set out above.

Type 1: Water insoluble, soluble in alcohols, glycols, *etc*. Used for spray dyeing and finishing aniline and semi-aniline leathers. High covering power, with high tinctoral power. Good fastness properties to water spotting, wet rub, light.

Type 2: Low water solubility, more soluble in non-aqueous solvents. Fastness properties inferior to Type 1.

Type 3: Higher water solubility. Used for dyeing woolskins; to colour the leather but not the wool.

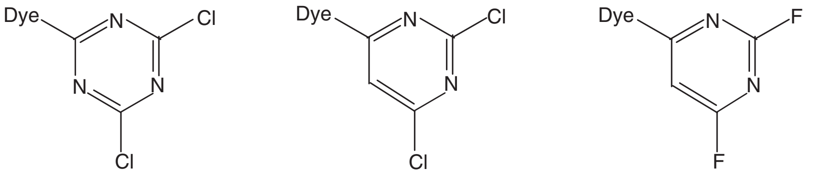
In addition:

- Composition is similar to the 1 : 1 complexes, except for the ratio of dye to metal, therefore reaction between the metal and collagen is not part of the fixation mechanism.
- Fixation is less dependent on electrostatic and hydrogen bonding than acid dyes and 1 : 1 complexes.
- The fixation mechanism is similar to direct dyes, therefore there are hydrophobic interactions.
- They may function more like pigments than dyes, with high covering power.

16.7 REACTIVE DYES

Reactive dyes are typically acid dyes that have been covalently bound to a reactive group, capable of reacting covalently with collagen or leather. The principle behind this technology is that a covalently bound dye will be fast to chemical removal. This is especially useful in applications when the leather may be subjected to washing, dry cleaning or perspiration damage, *e.g*. clothing and especially gloving leathers. The original dyes in this class were called Procion, based on triazine chemistry, developed by ICI, and others followed, illustrated in Figure 16.10, where the originating company is indicated. In Figure 16.10 shows other examples of nitrogen heterocycle chemistries, but the principles are the same. Note, the nitrogen heterocycle may contain a second dye species that is not identical to the first:

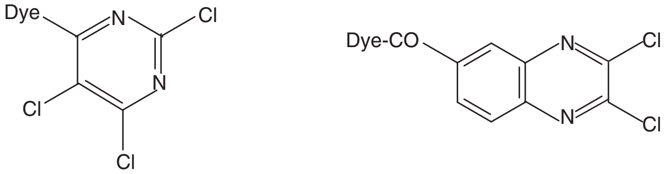
1. The heterocyclic ring system can react with available amino groups on collagen or leather.
2. The reaction is conducted under alkaline conditions, to ensure the availability of uncharged amino groups, by reacting with the acid produced by the reaction.



Dichlorotriazine
(Procion ex ICI)

2,4-dichloropyrimidyl
(ex ICI)

2,4-difluoropyrimidyl
(Drimalan F ex Sandoz)



2,4,5-trichloropyrimidyl
(ex Ciba-Geigy, Sandoz)

2,3-dichloroquinoxaline
(Levafix ex Bayer)

Figure 16.10 Reactive dye chemistry based on aromatic nitrogen heterocycles.

3. The reaction is driven by the addition of sodium chloride. This is an example of exploiting the stepwise mechanism of binding a solute to a substrate. Changing the affinity of the solute for the solvent, by making the solvent more hydrophilic due to the charged ionic content, decreases its affinity for the dye molecules and drives them into a more hydrophobic substrate.
4. There is competition between the reaction sites on the substrate and the hydrolysing effect of the solvent. The reactive dye is hydrolysed by water to the hydroxy derivative: the degree to which this happens depends on the specific chemistry of the reactive dye, but it always happens to some extent. In circumstances like this, it is important to remember that water usually has a competitive advantage over other reactants, because it is present at a concentration of 55.5 molal. Because the resulting aromatic hydroxy group is much less labile than the chloride, the reactive part of the molecule essentially becomes deactivated. In effect, hydrolysis turns the reactive dye back to a conventional acid dye.
5. The tanner is then faced with a dilemma. Fixing the acid dye under typical conditions for that type of dye will maximise the depth of shade from the dyeing, but the fastness properties will be compromised. Removing the acid dye will reduce the depth of shade, but the fastness properties will be maximised. This is a commercial decision.

An alternative approach was later developed by Hoechst, namely, the Remazol series of dyes based on vinyl sulfone chemistry (Figure 16.11).

The principle of the mechanism of fixation is the production of the vinyl sulfone group *in situ*, because sulfate is a good leaving group. The presence of the sulfone group also activates the vinyl group, allowing it to react with other

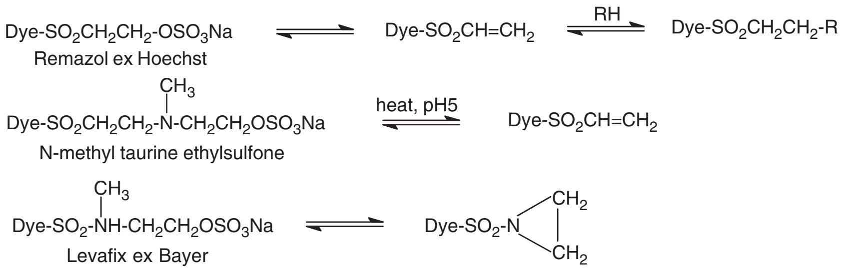


Figure 16.11 Reactive dye chemistry based on vinyl sulfones.

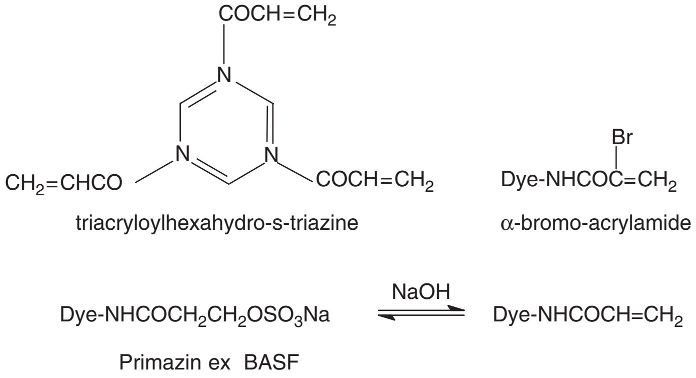


Figure 16.12 Reactive dye chemistry based on acryloyl derivatives.

groups that have an active hydrogen, *e.g.* hydroxyl, amino, *etc*. Figure 16.11 also shows another approach – the formation of an ethylene imine derivative: the heterocycle ring is readily opened to react with groups with an active hydrogen. In all cases, hydrolysis is still a competitive reaction.

Figure 16.12 illustrates an alternative approach, using the acryloyl group. The presence of the carbonyl group activates the system in the same way as the sulfone group does in the same position in the molecule. The acryloyl group may be present from the start or it can be created from the sulfate derivative (Figure 16.12).

Within the variations of chemistries of reactive dyes, some properties are common:

- very good fastness to washing, dry cleaning, perspiration;
- good light fastness;
- limited range of colours: pale and medium shades;
- expensive;
- health hazard, due to their reactivity towards organic substrates, therefore stricter COSHH regulations (Control of Substances Hazardous to Health) apply to their use.

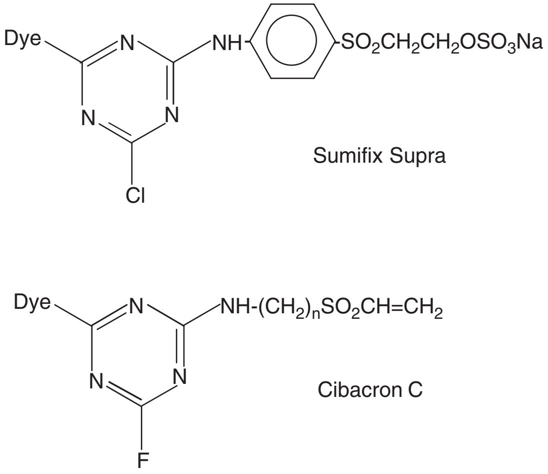


Figure 16.13 Reactive dye chemistry based on combinations of fixing mechanisms.

It is not necessary to rely on a single chemistry in reactive dyes. Figure 16.13 gives examples of mixed fixing systems.

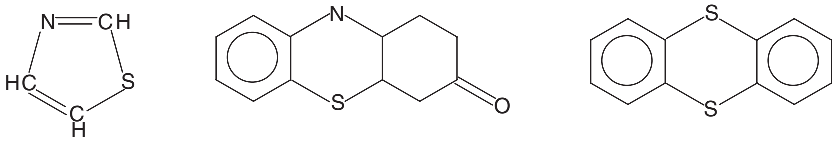
16.8 SULFUR DYES

Clearly from the descriptions of the dye types presented above, the dyes discussed so far are all chemically related. Sulfur dyes originate from 1893; they form a class of colourants that is different in chemistry and fixation mechanism. Like syntans, the structures of sulfur dyes are so complicated, because of the way they are prepared, that the structures are largely unknown. Consistency of colour therefore depends on consistency of production conditions.

Sulfur dyes are made by heating together aromatic compounds containing amino and hydroxy groups with a source of sulfur, in the following ways:

- Sulfur bake: the organic compound is heated with elemental sulfur to 160–320 °C.
- As for sulfur bake, but using polysulfide salt.
- Polysulfide melt: the reagents are heated with water, under reflux or in a pressure vessel.
- Solvent thionation or melt: as for polysulfide melt, but the solvent is butanol, dioxitol, *etc.*

Excess sodium bisulfite may be used to incorporate thiosulfate groups, *e.g.* $-S_2O_3^-$, to enhance water solubility. In this way the preparation is cheap, although somewhat variable. The product often has low water insolubility, due to its structure: Figure 16.14 illustrates a few of the identified chromophores, typically linked by disulfide bonds, as already encountered in cystine.



thiazole thiazone thianthrene

Figure 16.14 Chromophores in sulfur dyes.

In the technology of applying these dyes, they must be solubilised. This can be achieved using the chemistry already familiar in sulfide-based hair burning. The effect of sulfide ion, a reducing nucleophile, on the insoluble dye is to break the disulfide links, creating the soluble, leuco (white) form. Subsequent oxidation reforms the insoluble dye on and in the substrate leather:

$$\text{Dye-S-S-Dye(insoluble)} \underset{[\mathrm{O}]}{\overset{\mathrm{S}^{2-}}{\rightleftharpoons}} \text{2Dye-S}^{-}\text{(soluble, leuco form)}$$

The properties of sulfur dyes can be summarised as follows:

- They are suitable only for leathers that can resist the high pH necessary for dye reaction, *e.g.* aldehyde or oil tanned. Note, chromium(III) and vegetable tanned leathers are severely damaged at pH 12–13: in each case the tanning is reversed.
- Good perspiration and wash fastness; insoluble in dry cleaning solvents.
- Generally dull shades, with a limited range of colours – a true red shade is not available.
- They have little or no affinity for wool.
- They exhibit little reactivity of the kinds set out for the other dyes; therefore, there is primary reliance on hydrophobic interactions.

16.9 DYE REACTIVITY AND FIXATION

Dye fixation is subject to the principles of reaction from solution onto a substrate, as set out in Chapter 15. The reactions are dependent on the following conditions:

1. Status of the substrate, including the impact of prior processes;
2. pH of the substrate and solution;
3. HHB/HLB values of the dyes.

The trichromatic theory of colour is based on the observation that all colours of light can be created by a mixture of red, blue and yellow lights. By analogy, it is common for tanners to use a mixture of dyes, particularly for brown. However, if there are differences in the chemical properties of the components of the

Table 16.2 Dye fixation mechanisms: ✓✓ = primary mechanism, ✓ = secondary mechanism.

Dye type	*Electrostatic*	*Covalent*	*H-bonded*	*Hydrophobic*
Acid	✓✓		✓	
Basic	✓		✓	✓
Mordant	✓	✓		
Direct	✓		✓✓	
1 : 1 Premetallized	✓	✓✓		
1 : 2 Premetallized	✓		✓	✓
Reactive	✓	✓✓	✓	
Sulfur				✓✓

mixture, they will react independently. This often happens if the HHB/HLB values are not matched, so that the surface reactions and penetration will not be the same, so the cross section may be a different colour to the surface, leading to problems if the leather is scuffed or cut surfaces are visible in leather articles. This problem has been addressed in the Sellaset dyes, where the HHB values of the dyes are matched and the mixture behaves as though it were a single dye.

For comparison, Table 16.2 summarises dye fixation mechanisms.

16.10 ROLE OF THE SUBSTRATE

16.10.1 Chrome Tanned Leather

One of the many advantages of chrome tanning is the minimum change to the collagen structure, particularly with regard to occupation of the sidechains and lack of inhibition of consequent reactions. There is a degree of cationic character, which is useful in fixing acid dyes. Also, the colour conferred to the leather is pale, hence there is little background colour to interfere with the colour struck by dyes.

The one area in which chrome has a major impact on dyeing is when there is too much surface reaction. Chapter 11 shows that chrome fixes to a small degree at the peptide links. Ordinarily, the small amount and uniform distribution do not affect dyeing, but at high concentration it does interfere. This can be at two levels of effect:

1. If the effect is shadowing, causing uneven colour, dyeing is likely to be uneven, due to the variation in base colour of the substrate.
2. If the effect is staining, reaction sites for dye fixation can be all taken up by the chrome, resulting in dye resist. Therefore, the fault of staining cannot be covered up by dyeing.

In each case, the fault cannot be remedied. The commonly used tannery option of 'put it into black' may work for chrome shadowing, but does not work for chrome staining. There the only solution is pigment colouring in finishing.

Chrome tanning is very lightfast, so any effect of light on the leather is due to the light fastness of the dyes themselves.

16.10.2 Vegetable Tanned Leather

The chemical basis of vegetable tanning is completely different to chrome tanning. The tanning agent is usually present at much higher concentration within the leather, it interacts with both charged sidechains and peptide links and confers colour. In this way, all vegetable tannins block most of the dye fixation sites and produce colour themselves, which can be intense.

The consequences are as follows:

- The dye will have to bind to the polyphenol molecules, at least in part, so the colour will be affected.
- The base colour will usually affect the overall colour of the dyes leather: this can vary from very pale cream, in the case of tara, to the very dark brown, in the case of chestnut.
- The overall outcome is a marked dulling of the shade in comparison with the effect on chrome tanned leather: this is referred to as ‘saddening’ the colour.
- Plant polyphenols may be susceptible to light damage, particularly the condensed tannins, which are likely to redden, although occasionally bleaching is observed with hydrolysable tannins such as tara. Change in base colour after dyeing will affect the perceived colour of the dyed leather.

16.10.3 Other Tannages

Syntan tannage will have a similar effect to vegetable tanning, especially if a replacement syntan is used. Aldehydic tannage deprives the substrate of sites for reaction by dyes relying on sulfonate fixation.

16.11 DYEING AUXILIARIES: LEVELLING AND PENETRATING AGENTS

16.11.1 Anionic Auxiliaries

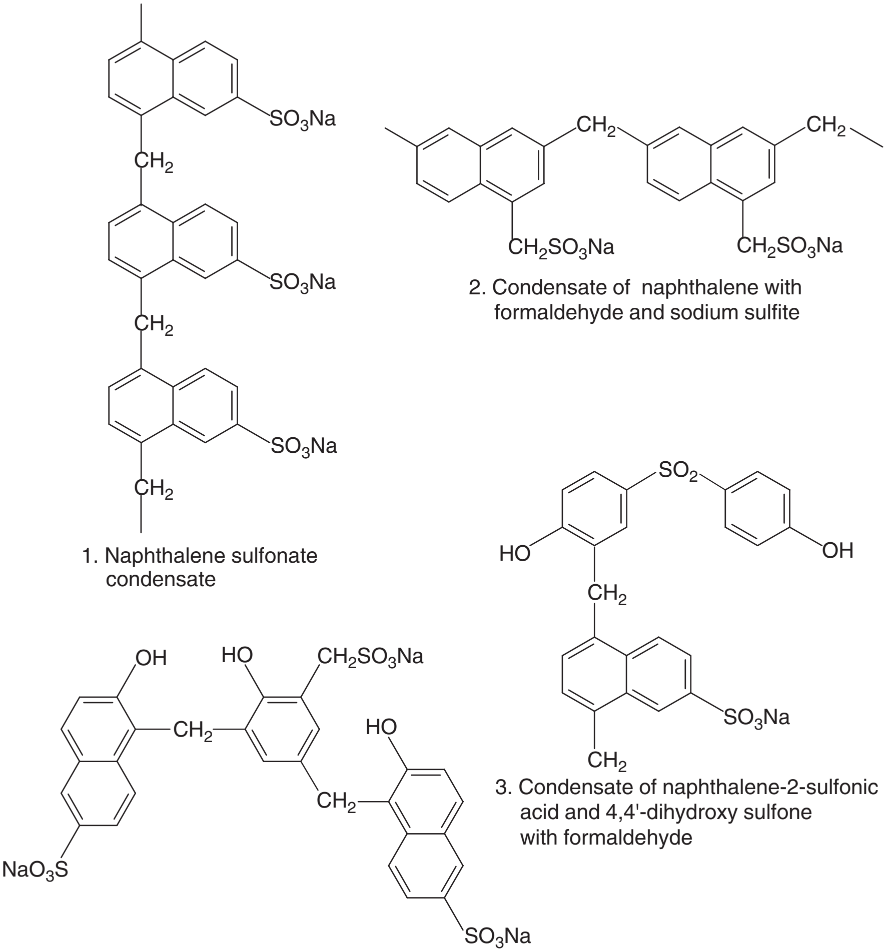
This class of levelling agents is based on low molecular weight, aromatic sulfonate condensates (Chapter 14): some structures are illustrated in Figure 16.13. They function by competing with dyestuff for binding sites or occupy those sites by prior treatment. In either case, if the kinetics might be expressed as follows:

$$\text{Rate} = k[\text{dye}]^{a}[\text{collagen sites}]^{b}$$

Therefore, any reduction in availability of reaction sites reduces the rate of interaction with substrate, making it more uniform. Note, the presence of the auxiliary may also modify the HHB/HLB and the charge of the substrate, to contribute to the effect. Controlling dye concentration is an option, like vegetable tanning, but it is not used as a technological strategy.

In Figure 16.15, structure 1 is a naphthalene-2-sulfonate condensate: for levelling, the degree of polymerisation may be 2–10. Modifying the structure of the condensate by using an alternative crosslinker, such as a sulfone derivative, improves the light fastness of the auxiliary, as illustrated in structure 3.

An alternative approach is to use a byproduct of the Kraft process for paper making, as introduced in Chapter 14. Since the structure of lignin, which is the basis of the material, is a non-uniform polymer, the structure can only be illustrated in the notional form presented in Figure 16.16. The similarity to the



1. Naphthalene sulfonate condensate

2. Condensate of naphthalene with formaldehyde and sodium sulfite

3. Condensate of naphthalene-2-sulfonic acid and 4,4'-dihydroxy sulfone with formaldehyde

4. Condensate of naphthol-2-sulfonic acid and cresol with formaldehyde

Figure 16.15 Structures of some dye levelling agents.

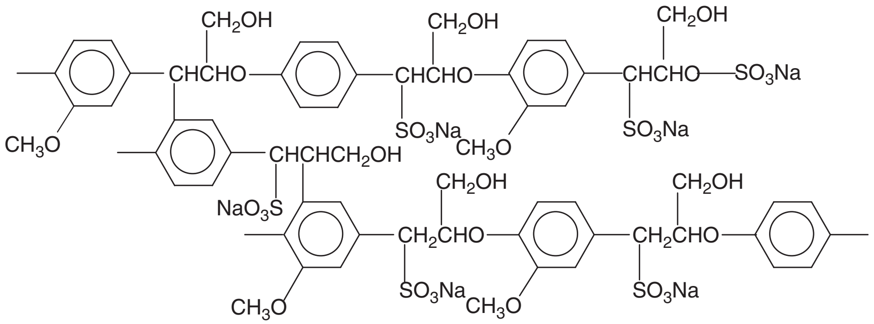


Figure 16.16 Illustrative structure of lignin sulfonic acid.

other synthetic reagents is clear. Such byproducts have only weak affinity for collagen or leather (Chapter 14): in this case, there is no disadvantage, since what is required is for the reagent to interfere with dye fixation, to slow down the reaction, not necessarily to prevent it.

In all cases, if the auxiliary is added before the dye, the colour intensity may be reduced by up to one-third of what would be obtained on untreated leather. If it is added with the dye, there is less effect on the colour, but the levelling effect is slightly reduced. Conditions that favour penetration of the levelling agent, such as short float, increase surface colour intensity and reduce levelness. The effect of the auxiliary is enhanced at higher temperature, *e.g.* 70 °C is better than 20 °C.

16.11.2 Auxiliaries that Complex with Dyestuff

These auxiliaries change the HHB/HLB properties and reduce the anionic charge. Examples include polyglycol ethers with weakly cationic amino groups. These will form strong complexes with high affinity dyes, to improve penetration and levelness. They form weak complexes with low affinity dyes – consequently with little useful effect.

16.11.3 Auxiliaries that have Affinity for both Leather and Dye

Examples include poly(ethylene oxide) chains with strong cationic groups. These agents cannot be used with premetallised dyes containing anionic dispersing agents. They tend to produce very pale colours when offered at low levels. At higher offers, colour intensity can be increased or enhanced.

16.11.4 Intensifying Agents

The purpose of colour intensifying agents is to allow dyes to accumulate at higher concentration on the surface of the leather. In this way, deeper shades are obtained, but the fastness properties of the leather, particularly to rub or crock (see below), are not compromised as they would be by merely precipitating the dye on the leather surface by pH manipulation. These auxiliaries may also be referred to as dye fixing agents, since their function is to create additional sites at which dye molecules can be chemically bound to the leather, rather than physically bound to it.

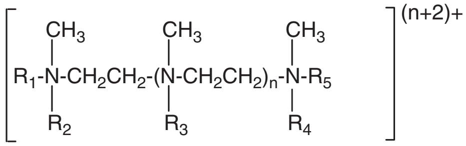
16.11.5 Cationic Tannages

The presence of cationic centres from the tanning reaction provides addition sites with which anionic dye can react. Such tannages include Al(III) chloride or sulfate, Zr(IV) sulfate, polyurethane and dicyandiamide retanning resins.

16.11.6 Cationic Auxiliaries

This class of auxiliaries includes cationic polyamine compounds with nonionic ethylene oxide chains (Figure 16.17). Short chains of this type increase dyeing intensity, but levelness is reduced. The opposite applies to longer chains.

Other fixing agents are based on polyamines, such as dicyandiamide derivatives (Figure 16.18).



$$\left[R_1\text{-}\overset{CH_3}{\underset{R_2}{N}}\text{-}CH_2CH_2\text{-}(\overset{CH_3}{\underset{R_3}{N}}\text{-}CH_2CH_2)_n\text{-}\overset{CH_3}{\underset{R_4}{N}}\text{-}R_5 \right]^{(n+2)+}$$

R_1 is higher alkyl radical

$R_{2\text{-}5}$ are $-(OCH_2CH_2)_nOH$, where n=10-20

Figure 16.17 Cationic polyamines.

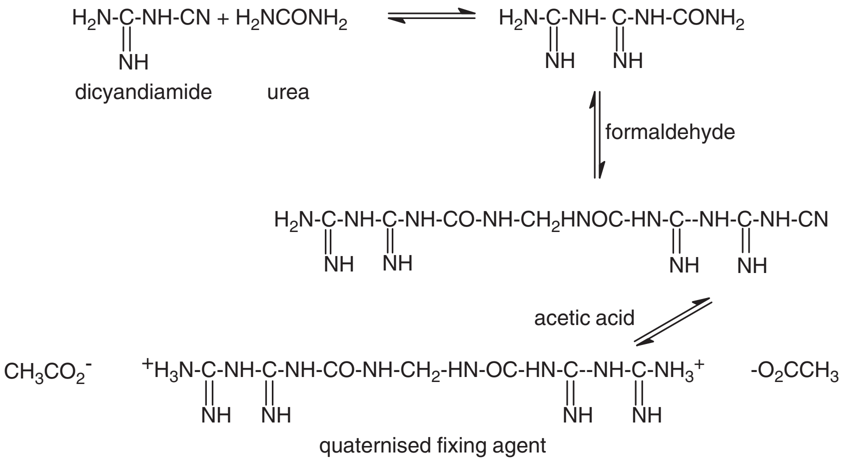


Figure 16.18 Dicyandiamide quaternary fixing agents.

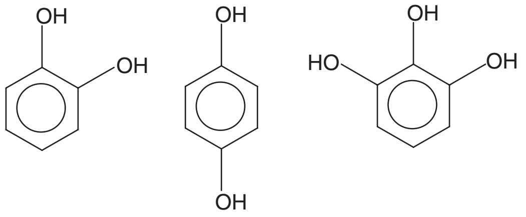
Typically this type of treatment is applied in a separate short float at low temperature before dyeing. It is followed by thorough washing, otherwise dyeing is likely to be unlevel. Leather treated in this way usually has slightly poorer rub fastness properties, compared to untreated leather.

16.12 ALTERNATIVE COLOURING METHODS

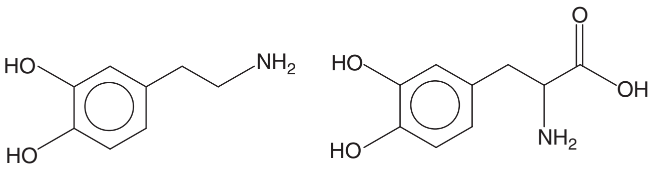
Chapter 2 introduces the chemistry and biochemistry of the mammalian pigments, the melanins (Section 2.3.6). A potential route to colouring leather is to harness those reactions, to create colour *in situ* and possibly obtain some stabilisation of the collagen through the formation of quinoid species by polymerising phenols with enzymes. Laccase (benzenediol:oxygen oxidoreductase, E.C. 1.10.3.2) is a copper-containing polyphenol oxidase that catalyses the oxidation of electron-rich substrates such as phenols.[5–7] It is produced by some fungi basidiomycetes that cause white rot of wood[8] and certain reaction products of laccase-mediated oxidation and polymerisation of phenolic compounds can give coloured products, such as melanins.[9,10] Besides producing colour, polymerisation products of phenolic compounds may produce tanning properties, causing the coloured products to stabilise the collagen whilst at the same time binding covalently and thereby making the colour fast to washing.[11]

Some phenolic compounds (Figure 16.19) give tanning effects with laccase (Table 16.3). The effects are relatively small, certainly in comparison with similar chemical reactions,[12,13] although the outcome is not unexpected.

Table 16.4 gives the kinetic parameters, K_M and V_{max}, from the Michaelis–Menten equation. Based on the K_M values, the order of affinity of laccase



catechol hydroquinone pyrogallol



3-hydroxytyramine

L-DOPA
3,4-dihydroxy-L-phenylalanine

Figure 16.19 Phenols used with laccase in colouring studies.

Table 16.3 Shrinkage temperature (°C) of hide powder dyed with phenolic compounds and laccase.

Phenol	*Phenol + laccase*	*Phenol alone*
Catechol	71	61
Hydroquinone	74	61
Pyrogallol	59	60
L-DOPA	59	57
3-Hydroxytyramine	57	56

Table 16.4 Kinetic parameters for laccase reaction with phenols at 30 °C and pH 6.0.

Substrate	K_M (mM)	V_{max} ($U\,min^{-1}\,ml^{-1}$)
Catechol	0.50	76.9
Hydroquinone	0.21	100.0
Pyrogallol	0.19	70.9
L-DOPA	0.89	91.7
3-Hydroxytyramine	0.82	73.5

Figure 16.20 Colours created on chrome tanned leather by phenol oxidation by laccase.

with phenolic compounds is pyrogallol > hydroquinone > catechol > 3-hydroxytyramine > L-DOPA.

Figure 16.20 shows the effects of laccase-mediated polymerisation in the presence of chrome tanned pelt. L-DOPA is oxidised to L-dopaquinone by laccase in an oxygen environment and *in vivo* is polymerised to produce the final product melanin.[9,10] Hydroquinone is oxidised to *para*-benzoquinone by laccase under aerobic conditions[14] and the outcome is a weak a purple colour conferred to the pelt. Catechol is oxidised by laccase to *ortho*-benzoquinone and this results in the deepest shade achieved in these tests, a dark brown-black colour. In this context, the colour struck on the leather is a reflection of the interaction between the phenol and the enzyme: the deeper shades resulted from higher affinity, but not the degree of blackness.

The principle of colouring without dyes and achieving simultaneous covalent tanning appears to be feasible, although clearly it is not easy to transfer the biochemistry of melanin production into a biomimetic technology. The target in these trials was deep jet black, but the best colour achieved was a dark brown-black. However, although the principle was not proved completely, the approach to new compact processing is sufficiently interesting to warrant further study.

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