

## **9 The colouring of textiles**

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### **9.1 The development of a scientific approach**

The dyeing, printing and decoration of textiles go back to the earliest times and, historically, have inspired craftspeople to remarkable levels of ingenuity as ways have been sought to exploit the colouring matters to be found in nature. The basis for most of the dyeing methods in use up until the nineteenth century was established by the ancient Egyptians, who developed the application of plant extracts often in association with mordanting (the pre-application of solutions of metal salts such as alum to the textile to give improved washing fastness and, in some cases, a specially desirable shade through the formation of complex compounds). For obvious reasons the plants and other materials used tended to be those indigenous to the region so that, for example, the production of scarlet shades from insects of the kermes family which originated in Persia did not feature in Egyptian dyeing practice. Similarly woad, later to be displaced by indigo, which was one of the most important colouring matters in use in ancient times, did not reach Egypt until about 300 BC. Another important ancient source of dyes was the molluscs used by the Phoenicians to produce the famous Tyrian Purple and related shades. It should not be forgotten that considerable experimentation and chemical expertise were required to make many of the developments which took place. The colouring matters derived from the indigo or woad plants and the molluscs used by the Phoenicians are chemically closely related, and to extract and use them requires several processes which could have come to be adopted only after much experimentation, which was carried out, let it be remembered, without any chemical knowledge that would be recognised today.

Prior to the sixteenth century dyeing was a secret and closely guarded technology. For example, the production in Turkey of the famous Adrianopolis or Turkey Red by the application of the extract of the madder root to cotton mordanted with alum was a secret which was retained for 250 years, in the pursuit of which many European industrial spies lost their lives. At a less dramatic level every dyer sought to retain secret methods. The fact that many of the 'secrets' were illusory and depended on some local factor, such as the presence of mineral traces in the water supply, or were based on totally spurious reasoning does not matter. However, with the expansion of trade and travel which accompanied the European renaissance and, more particularly,

the development of the printing press, there was an explosion of knowledge and information which exposed much of the mystery to the light of day. To the chagrin of the European woad growers, Marco Polo returned from India with details of the use of the much more effective indigo as a dye (prior to this it had been used in Europe only as a pigment in painting). Many works were published in that period detailing dyeing and colouring procedures for different textiles, largely for domestic use. Of special importance, in that it was directed towards the industrial dyer, was *The Plictho* of Giovanventura Rosetti, published in 1548, which records, in addition to many dyeing recipes and methods of preparing plant and other extracts, procedures for the preparation of important chemicals such as hydrochloric acid (Rosetti, 1548).

With the expansion of knowledge and great increases in the volume of production that followed this period came the demand for more reliable quality control, and as a consequence the demand for greater understanding and the beginnings of scientific investigation into the phenomena involved. Some hundred years after publication of Rosetti's work, Colbert in France established regulations to control dyeing quality (Colbert, 1671), and this was followed sixty years later by the appointment of the first Inspector General of the Dyeing Industry, Dufay de Cisternay, who must be regarded as the founder of modern dyeing theory. Dufay established systematic fastness testing and quality classification in dyeing to replace the established and not very reliable *grand teint*, *bon teint* and *petit teint* qualities. As a result of his studies Dufay published what may be described as the first truly scientific account of dyeing processes based on physical chemical ideas (Dufay, 1737). He was the first to advance the concept of specific sites for dye adsorption based on the different compositions of the various textile fibres, a remarkable insight considering the fact that there existed no knowledge at that time of organic chemical structure or polymers. Following Dufay came a succession of distinguished chemists who developed such ideas as were possible, given the chemical knowledge available to them at the time, to account for the properties of mordants and, remarkably, the conception that dyeing was a physical binding process on a molecular scale (Berthollet, 1791).

The succession of Inspectors General of the Dyeing Industry in France came to an end with the French revolution. However, it was the blockade of Napoleonic France by England that prompted the search for substitutes for dyes and other compounds imported from the East and also the Americas. Napoleon's Minister of the Interior was the chemist and dyer, Jean Antoine Chaptal, who gathered around him the greatest chemists of the time and also established the first academic department for the teaching of chemical technology at the University of Montpellier. Chaptal advanced ideas for the development of technological education involving an interaction between industry and academic centres, which were to some extent subverted by the defeat of Napoleon. However, they were taken up to great effect in Germany, and formed the basis for the system of *Technischen Hochschulen* which

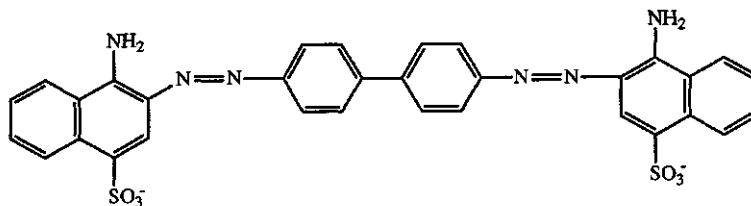
enabled Germany to take advantage of, and play its own important part in, the emergence of the dyestuffs industry in the second half of the nineteenth century.

As early as 1740, experiments had shown the possibility of synthesising dyes. Naturally occurring indigo was treated with concentrated sulphuric acid by Barth to produce a product which was marketed as Saxe Blue. Later, in 1776, Scheele found that by treating uric acid with nitric acid a reddish compound was obtained which coloured the skin red. It was thus named purpuric acid. In 1818, Proust made the ammonium derivative and showed its use as a dye for tin-mordanted wool, mercury-mordanted silk and lead-mordanted cotton. Under the name murexide, the dye was manufactured in Mulhouse and in Manchester as bulk supplies of uric acid became available from South America. However, such discoveries could have no systematic basis. Firstly, it was generally believed that only living organisms or God could prepare organic materials and, secondly, there was insufficient chemical knowledge on which to base anything other than random excursions into chemical synthesis. However, a major change took place after Wöhler prepared urea from inorganic materials and also observed that urea and the inorganic ammonium thiocyanate were isomeric. The development of analytical methods by Liebig and the development of the coal gas industry, with its production of coal tar as a by-product, laid the basis for the next step.

The German chemist W.H. Hofmann was appointed to head the newly established Royal School of Chemistry in 1845. This became a centre for the analysis and isolation of the multiple components of coal tar produced in great quantity by the new and flourishing coal gas industry. W.H. Perkin, who became a student under Hofmann in 1853, was concerned with the reactions of aniline and, carrying out work in his own laboratory, attempted to prepare quinine by the oxidation of allyl toluidine using acidic potassium dichromate. There being no such concept as structural organic chemistry at that time, for Perkin quinine was  $C_{20}H_{24}N_2O_2$ , and the proposed synthesis was perfectly reasonable. In the event, the dark brown product achieved was extracted with water to yield a purple solution that was clearly not quinine. Perkin showed that the new product could be used to produce a novel purple shade on silk, and following favourable comment from Pullar's dyeworks, Perkin & Sons Ltd went into manufacture of Aniline Purple. Not only was it necessary to develop methods for the manufacture of aniline on an industrial scale and suitable reactors for the process, a not inconsiderable achievement in its own right, but Perkin had also to devise dyeing methods for the application of his product. This was because it did not behave like any naturally occurring dye in commercial use, being what would now be termed a basic dye, i.e. a salt with a coloured cation. In the event, bulk supplies came on to the market in the first instance from France where, taking advantage of Perkin's failure to secure adequate patent protection and the more advanced state of chemical technology in that country, several

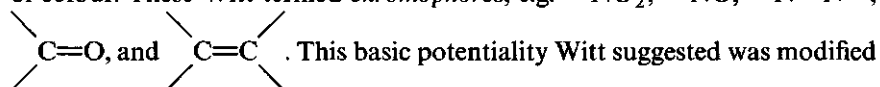
manufacturers were able rapidly to offer the dye. The name, Mauve, suggested by the French was more attractive commercially than Aniline Purple and eventually displaced Perkin's original name for the product. Following Perkin's discovery, an intensive period of experimentation began, to study many oxidative reactions of aniline and its derivatives to produce mostly new basic dyes. Another discovery which was to prove to be of major importance was made by another of Hofmann's assistants, Peter Griess, who, in 1858, found that by treating aniline and its derivatives with acidic sodium nitrite, compounds were formed which reacted with phenols and related compounds to produce brilliant yellows, reds, and other colours. This reaction proved to be one of the most important in colour chemistry. However, while the impact of these new colouring matters was considerable, progress was inevitably unsystematic. The development of structural organic chemistry following Kekulé's proposal for the ring structure of benzene seven years later in 1865 transformed research in the field from an empirical to a more systematic approach. Kekulé's ideas had little effect in England and France, but were taken up with enthusiasm in Germany, to which many of the emigrant chemists, including Hofmann, had returned in 1861. It should be said that despite their commercial success the dyes synthesised prior to 1865 were, in general, lacking in fastness to washing and to light. However, once it was realised that the important structural feature of organic compounds, particularly dyes, lay not in the ratio of the numbers of carbon, hydrogen, nitrogen and oxygen atoms but in their structural arrangement, it was possible to begin to look scientifically at dyes such as madder and indigo which, although derived from plants, were very stable. Commercial natural madder contained only 4% of the essential colouring matter, alizarin, but the establishment of the structure of alizarin and possible routes to its synthesis by Graebe and Liebermann in 1868 led rapidly to the availability of the highly concentrated synthetic product.

On the exploratory front it was possible to begin to relate the structure of dyes to dyeing behaviour and other properties. At that time it was possible to dye cotton only after the application of a mordant. By examining the dyeing behaviour of azo dyes of known structure formed using Griess's diazo reaction, Paul Böttiger found that linear dye molecules containing two azo groups (**1**) dyed cotton directly from a saline dyebath without mordants, and in 1884 he obtained a patent for the new dye, Congo Red (**1**). The C.I. Direct Red designation relates to the classification system in the Colour Index, discussed on p. 299. This was the first direct cotton dye, so called because of its direct applicability to cotton fibres. Congo Red is little more than an acid/base indicator, and the fact that it was regarded as a commercial proposition gives some indication of the prevailing standards of durability and fastness that obtained at that time. The opportunity presented by this development was seized upon by the German dyestuff manufacturers who never lost the impetus thus achieved.



(I) Congo Red (C.I. Direct Red 28)

As more and more dyes came to be prepared and the structures of natural colouring matters were elucidated, the beginnings of a theoretical connection between colour and chemical constitution began to emerge. The earliest proposal was put forward by Graebe and Liebermann, the elucidators of the structures of alizarin, who suggested that colour was associated with unsaturated carbon atoms. A rather more effective extension of this idea was proposed by Witt (1876), who postulated that all coloured compounds contained an unsaturated group or groups which conferred the potentiality of colour. These Witt termed *chromophores*, e.g.  $-\text{NO}_2$ ,  $-\text{NO}$ ,  $-\text{N}=\text{N}-$ ,



This basic potentiality Witt suggested was modified by other substituents in the molecule which he called *auxochromes*, e.g.  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{NHR}$ , and  $-\text{NR}_2$ . Auxochrome substituents did not in themselves give rise to strong colours but had a significant effect on the shades of chromophoric molecules. According to these ideas, there are present in the molecules of a coloured compound three sub-systems, a chromophore, an auxochrome and a system of conjugated double bonds linking the two. At the stage of development of organic chemistry in Witt's time his ideas were of little predictive value, but they provided a foundation upon which, with the development of quantum mechanics and molecular orbital theory, methods are available to the modern organic chemist that are far removed from the empiricism of the approach to dyestuff development characteristic of the latter part of the last century and the first half of this.

In contemporary terms chromophoric and auxochromic systems shift the principal absorption bands of the conjugated system to longer (visible) wavelengths. Griffiths (1976) has suggested a classification of chromophoric systems as follows:

- (i)  $n \rightarrow \pi^*$  chromogens
- (ii) donor-acceptor chromogens
- (iii) acyclic and polycyclic polyene chromogens
- (iv) cyanine type chromogens.

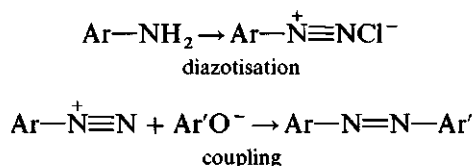
Griffiths uses the term chromogen to describe any reasonably well defined unsaturated system which either is coloured or becomes coloured as a result

of substitution by simple atoms or groups. He restricts his use of the term chromophore to any unsaturated group which is colourless. The donor-acceptor chromogens comprise the largest group and include the great majority of commercially useful dyes and pigments. Such systems contain an electron donor group possessing a lone pair of electrons which is connected directly to a conjugated system of  $\pi$  electrons. The whole thus contains a population of electrons which become excited by low energy radiation, i.e. visible light, and thus exhibit selective absorption and thus colour. The visible absorption band corresponds to the migration of electrons away from the donor into the general  $\pi$  system. When several atoms in the acceptor show an increase in electron density then the whole acceptor  $\pi$  system is best regarded as a complex acceptor. Commercial dyes and pigments for textile use generally fall into this category, while the simpler donor-acceptor systems have an important place in photoreprography and other areas where resistance to chemical attack is of less importance.

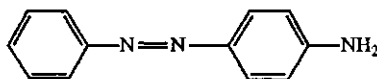
The effectiveness of a donor in the donor-acceptor chromogens is determined by the ease with which it releases its electrons. Thus the group  $-\text{N}(\text{CH}_3)_2$  is highly effective, followed (in order of reduced donor power) by  $-\text{NH}_2$ ,  $-\text{OCH}_3$ ,  $-\text{NHCOCH}_3$  and  $-\text{O} \cdot \text{COCH}_3$  groups. The presence of a hetero (i.e. non-carbon) atom is an obvious essential to provide the lone electron pair, but the ease with which the electrons are donated will depend on the hetero-atom substituents. If these increase the electronegativity of the hetero-atom by electron withdrawal as, for example, in the case of the acetyl group, then the donating power is reduced, while on the other hand alkyl groups will reduce the electronegativity of the hetero-atom, thus increasing its donor power. The presence of several donor groups will produce an increasing bathochromic shift, raising the wavelength of the principal absorption band from the ultraviolet into visible wavelengths. In a simple donor-acceptor chromogen, the donor and acceptor groups are linked by a conjugated system which provides the path for the electron migration. However, the acceptor system can be itself conjugated and may offer a relatively delocalised destination for the electrons. Such systems, termed by Griffiths (1976) complex acceptors, when present in dye or pigment molecules generally offer the most intense colours and are characteristic of commercial dyes.

Space does not permit a full account of the range of chromogens to be found among commercial dyes and pigments today. However, some of the more important examples can be considered. The most important are the azo dyes, the first examples of which were prepared using Griess's reaction to form a diazonium salt, which was then coupled with an aromatic amine or a phenolic compound. The reaction is based on the formation of a diazonium compound by reaction of nitrous acid on an aromatic amine. This leads to the formation of a diazonium salt, which can act as an electrophilic reagent in the formation of an azo compound. In this the diazonium salt is called the 'azo component' and the electrophilic reagent is called the 'coupling

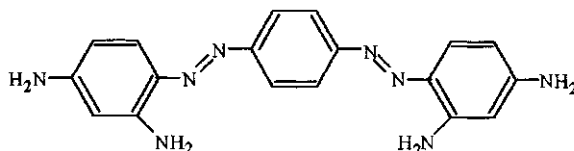
component'. Because of its weakness as an electrophile it can only work successfully with reasonably strong nucleophiles, and consequently only aromatic compounds bearing  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{NHR}$  and other electron-donating substituents. Typically, sodium nitrite is allowed to react under ice-cold conditions with the hydrochloride of the amine to form the diazonium salt, which is then added to an alkaline solution of the coupling component. A generalised reaction scheme is shown:



In 1861, Mène reacted aniline with nitric acid to form Aniline Yellow (2). This compound is not soluble in water and cannot be used directly in dyeing. Kekulé's ideas being very new and the mechanism outlined above being as yet not understood, the full structural implications of the formation of Aniline Yellow were not clear, but its formation showed that the amino group of aniline and related compounds could be transformed into a colour-forming group. The first water-soluble azo dye, Bismark Brown (3), was prepared by Martius in 1862.



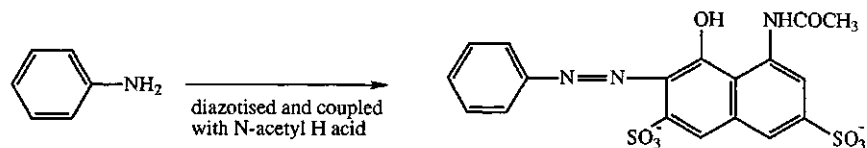
(2)



(3)

The easily performed diazo reaction offers the chemist almost limitless options in selecting dye structures for various end-uses. If the coupling component itself contains an amine group, the dye can then be diazotised again to form an even more complex system. Alternatively, there may be present in the original amine two diazotisable groups, so that a tetrazonium salt is formed, which can couple with two molecules of the same or different coupling systems. Examples (4, 5 and 6) of dyes of these three types are shown.

There is now available a variety of methods of forming diazonium compounds, and the azo chromogen has enormous flexibility. It is to be found in dyes ranging in shade from yellow through to black. An indication



(4) (C.I. Acid Red 1)

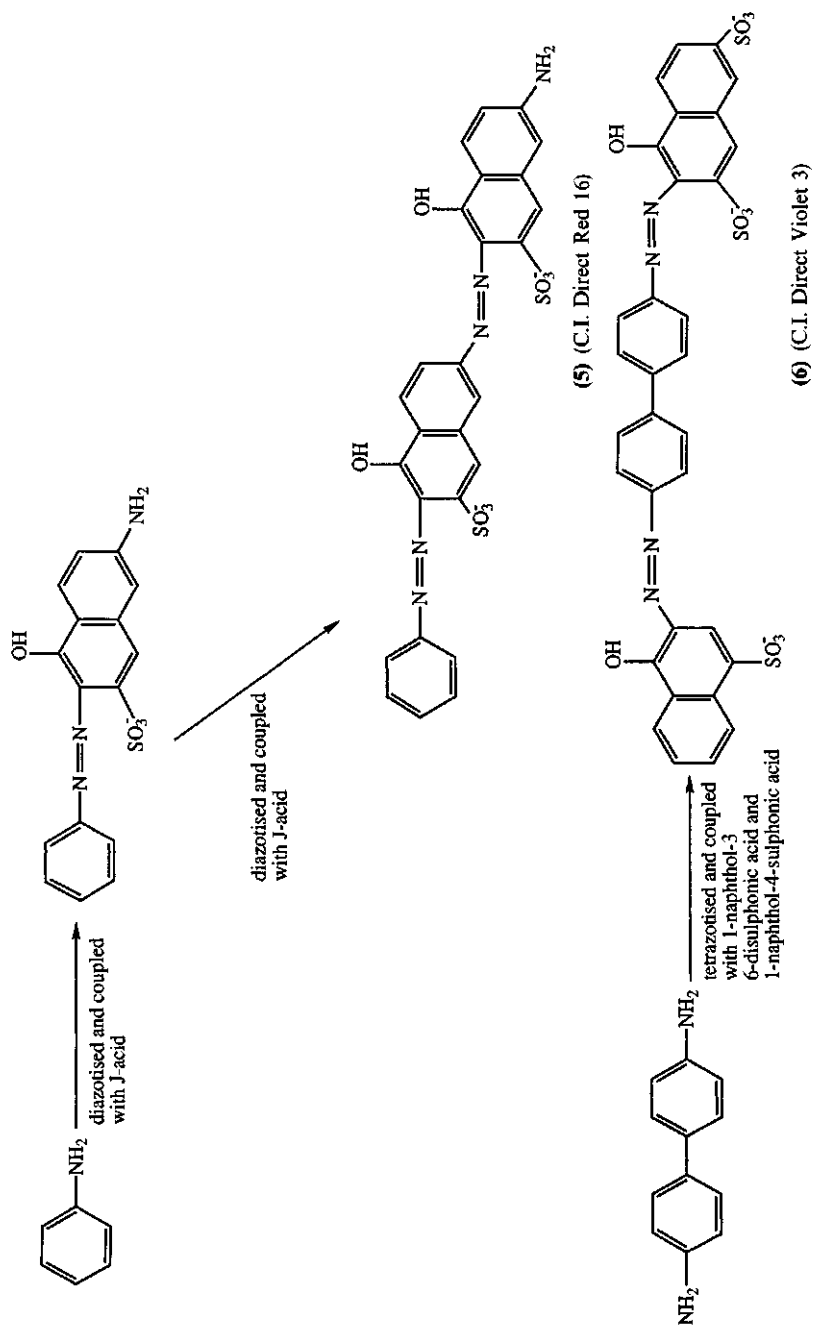
of the scope offered to the chemist by this chromogen is provided by the fact that upwards of 3 million speculative examples of dyes have been prepared in the 135 years since it was first made. Another important feature is their potential for the preparation of metal complex dyes. By selection of coupling and diazo components, dyes may be prepared containing *o,o'*-dihydroxy or *o*-hydroxy-*o'*-amino groups relative to the azo group. Such a configuration readily complexes with copper or chromium to give colouring systems that are very stable to light. The formation of the metal complex involves a considerable broadening of the principal absorption band to produce shades which, while often stronger than those obtained without complex formation, are usually duller. Initially, dyers applied the metal-free dyes to fibres and then developed the metal complexes *in situ* by after-treatment with a suitable copper or chromium salt. Such methods are very much less used today for a variety of health and ecological reasons and preformed complexes are the norm. Typical examples (7 and 8) are shown.

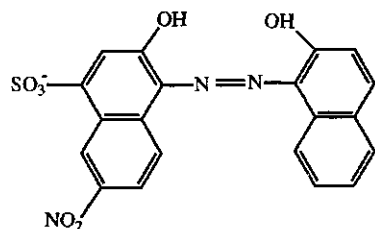
The second most important group of commercial chromogens is the donor-substituted quinones, which provide a complex conjugated acceptor system. A typical example is anthraquinone (9), which absorbs light principally in the near ultraviolet. However, when it is substituted with simple donors intense colours ranging through orange to red and blue can be obtained. Examples (10 and 11) are shown.

Quinonoid dyes do not offer as wide a range of shades as do the azo dyes, but they provide the basis for bright fast blues and green shades, whereas the strength of the azo dyes lies at shorter wavelengths. They are used extensively in applications for which azo dyes are unsuitable and for textile substrates for which the small molecular dimensions of many quinone chromogens are especially suitable (see p. 318). Additionally they provide the majority of the class of vat dyes (see p. 321), which are temporarily solubilised during application by alkaline reduction of the quinone system. In this case, complex condensed quinone systems such as (12) are used.

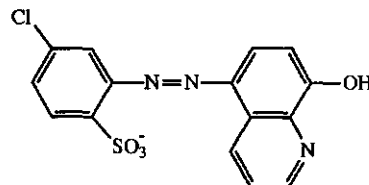
The first of the vat dyes, the blue pigment indigo, contains quite a different chromogen (13). Alkaline reduction converts the carbonyl groups to ionised hydroxyl groups and the pigment to a water-soluble dye. Following its analysis, several substituted indigo analogues with different shades were manufactured.



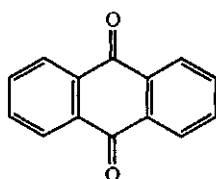




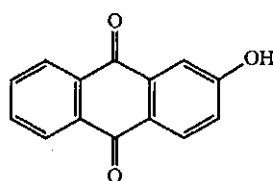
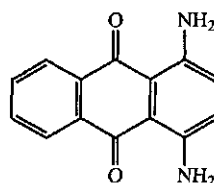
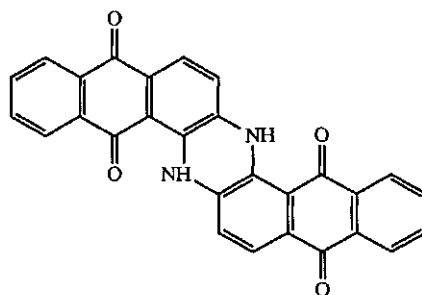
(7) (C.I. Mordant Black 1)



(8) (C.I. Mordant Orange 26)

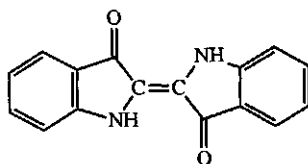


(9)

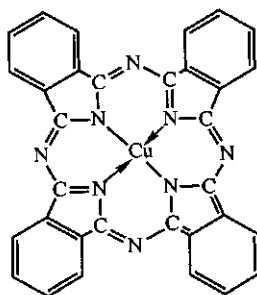
(10)  $\lambda_{\max} = 365 \text{ nm}$ (11)  $\lambda_{\max} = 550 \text{ nm}$ 

(12) (C.I. Pigment Blue 60)

Another extremely important but highly specialised chromogen which provides the basis of pigment blues and greens as well as soluble turquoise blue dyes for a variety of textile fibres is the phthalocyanine system (14). Substitution by sulphonic acid or quaternary onium groups provides solubility. In its unsubstituted form phthalocyanine provides very stable blue pigments.



(13)



(14)

The modern dye chemist, unlike those of even only 50 years ago, is able to target with a good degree of precision the structures which will provide not only the shade required but also the dyeing properties which are needed to make the product fit in with the existing dyes alongside which it will be used. A good understanding of dyeing as a chemical process as well as a technical operation has made this possible. Accordingly, before discussing the characteristics of the various dye classes, consideration will be given to the physical chemistry of the dyeing process.

## 9.2 The physical chemistry of coloration

Investigators have speculated about the reasons why dyeing occurs for many centuries, but the scientific investigation of the phenomenon is relatively recent. This was due to the difficulty of measuring dye concentrations in solution or on the fibre without the availability of spectrophotometers. Today such instrumentation is commonplace, but this is a situation which has come about only during the last 40–50 years. The essential basis for any discussion of the physical chemistry of dye adsorption is a consideration of the energy of the system. When a textile fibre is immersed in a dye solution, there is a spontaneous transfer of dye from the solution to the fibre phase resulting in a reduction in the concentration in solution. This is because the movement of dye between the phases results in the system reaching a *state of lower energy* or higher stability. In order to reverse the process, it follows that energy must be put into the system, and consequently the adsorbed dye can

be seen to behave as if it had formed bonds of some kind with the fibre or substrate that resist rupture. The adsorption does not normally lead to 100% uptake of dye and an apparent equilibrium is observed, which is characteristic of the formation of physical bonds. This is an essential feature of the adsorption of all dye classes on all textile fibres. In the case of acid, basic, direct and disperse dyes the whole dyeing process is essentially reversible. In the case of vat, reactive and azoic dyes, physical adsorption is an essential feature of the dyeing process, which is rendered irreversible at some stage by oxidation to form a vat pigment from the soluble leuco compound, reaction with the fibre or precipitation following reaction with a diazo component. Thus, from the physical chemical point of view, dyeing can be considered firstly as a single process covering all dye classes on all fibres, and secondly from the point of view of the special features of some of the particular methods employed to limit the reversibility of the adsorption process. The process can be analysed mechanistically with regard to the ways in which dye molecules become bound to substrates, or statistically with regard to the distribution of dye molecules in the dyebath and the kinetics of the dyeing process.

### 9.2.1 *Binding forces*

The two kinds of physical bonds which are involved are coulombic interactions between permanent (ionic) charge centres and dipolar or dispersion forces. It should be remembered that, since the adsorption generally occurs in the presence of water as a solvent, the interactions between all the components of the system have to be considered.

Coulombic interactions are involved wherever the adsorption of dye ions is involved. Thus, in all cases except that of disperse dyes, coulombic interactions are inevitably involved in some way in the dye adsorption process. Where the substrate is initially positively charged, dye anions will be attracted until the surface potential falls to zero. Further adsorption of any dye ions will lead to the development of a powerful electrical potential which will oppose further adsorption by ions of the same charge. Near to the charged surface there will be a distribution of ions such that oppositely charged ions are attracted to the surface and similarly charged ions repelled. Assuming a positively charged surface the concentrations  $C_+$  and  $C_-$  for the anions and cations respectively are given by:

$$C_+ = C_0 \exp(-z^+ e\psi/kT) \quad \text{and} \quad C_- = C_0 \exp(+z^- e\psi/kT)$$

in which  $C_0$  is the general concentration,  $z^+$  and  $z^-$  are the charges on the two ions,  $e$  is the electronic charge,  $\psi$  is the surface potential,  $k$  is Boltzmann's constant and  $T$  is the temperature. Where more than one kind of anion is present in the above case, both will be attracted, leading to competition between them for the negative charge centres in the surface. Clearly, to some extent the presence of co-ions associated with the dye ion or due to the

addition of another electrolyte will reduce the repulsive potential, but since the surface potentials involved are very high (several kV), little adsorption can take place when electrical saturation has been reached. It can be seen that a repulsive surface potential will act against the adsorption of dye ions by neutral or similarly charged surfaces.

Several theoretical models, notably those of Donnan, of Gouy and their numerous refinements, have been advanced to facilitate the calculation of the surface potentials of charged surfaces. The Donnan model has been used particularly effectively to calculate the pH inside fibres and to develop a quantitative theory of the physical chemistry of reactive dye fixation (Sumner and Taylor, 1967). However, coulombic interactions are quite nonspecific and are concerned only with charge centres. Consequently, it would not be expected that, if they were the only factor involved, dyes of the same charge would show much difference in behaviour or, for that matter, differ much from simple electrolytes. The fact that this is not the case shows that while coulombic interactions, both attractive and repulsive, may be of great importance influencing the way in which dye is distributed between the solution and fibre phases, they do not provide the strong bonding forces that are needed for a useful dye.

Unlike coulombic interactions, dipolar and dispersion forces are always attractive. Where two oppositely charged centres exist in a single molecule due to the presence of different permanent charge centres, as in a zwitterion, or a degree of charge separation exists due to the interaction of electrophilic groups, a molecule will operate as a dipole which is attracted by other dipoles or other molecules of the same kind. A dipolar molecule is capable also of inducing in a susceptible molecule a corresponding dipole and thus providing the basis for a useful binding force. This process of induction is carried further in dispersion forces, which are universal and very powerful.

Considering the simplest system of an atom consisting of an orbiting electron and a positive nucleus, it is clear that while it is not possible to be certain about the location and energy of the electron at any particular moment, an instantaneous dipole must exist. Since the relative positions of the electron and the nucleus are in constant flux even in their lowest energy states, the atom must exist as an oscillating dipole with a time-integrated dipole moment of zero. When two such atoms approach and the oscillations are in phase, then an input of energy will be needed if they are to be separated again. Consequently, it will appear as if an attractive force is operating to bring the two atoms together. The interaction between two equal permanent dipoles of moment  $d$  at a distance  $r$  is given by:

$$U = -2/3(d^4/r^6 kT)$$

That between a permanent dipole and an induced dipole is given by:

$$U = -(2\alpha d^2/r^6 kT)$$

where  $\alpha$  is the polarisability or the ease of induction of the dipole. Considering two mutually induced dipoles such as operate in the case of dispersion forces:

$$U = -3/2\{I_a I_b / (I_a + I_b)\} \{\alpha_a \beta_b / r^6\}$$

where  $I_a$  and  $I_b$  are the ionisation potentials of the two species. In each case  $I$  can be replaced by  $h\nu_0$  where  $h$  is Planck's constant and  $\nu_0$  is the characteristic frequency. For simple substances  $I$  and  $h\nu_0$  are almost identical, while for more complex substances such as dyes where the transitions are not in any sense ionisations,  $h\nu_0$  is the proper term. The  $r^{-6}$  dependence of the potential *energy* becomes an  $r^{-7}$  dependence when considering the attractive *force*. The further development of this theory to take in asymmetric molecules brings in terms in higher negative powers of  $r$ . It might be thought that forces which diminish so rapidly with distance might be unimportant in dye adsorption, were it not for some decisive complicating factors. Firstly, with regard to dye adsorption, it is an assemblage of atoms in both the dye and the substrate that has to be considered. Casimir has shown that, due to co-operative effects, this reduces the distance dependence to  $r^{-3}$ . It also increases the time taken for the full force to develop, although this is still very short. Secondly, it has to be remembered that dye adsorption takes place in an aqueous environment. A water molecule existing surrounded by other water molecules will not experience an attractive force in any particular direction, since the surrounding water molecules will be all the same. However, when an alien molecule, e.g. a dye molecule, is present, the dispersion force interaction with an adjacent water molecule will change it sufficiently for it to interact with another water molecule in an abnormal way. Thus the initial dye-water interaction can be transmitted to an extent depending on the different susceptibilities of the dye and water molecules between the adsorbing surface and the dye or between two dye molecules over significant distances, leading to an above random probability of the two molecules coming together. As the distances between the interacting species grow less, then the normal dispersion interactions become increasingly important.

As an active dipolar molecule present in large excess, water is an active participant in the whole adsorption process. Water molecules readily form hydrogen bonds both with other water molecules and with appropriate groups in dye molecules or adsorbing surfaces. It is due to its powerful hydrogen bonding capacity and the resultant development of a complex structure in liquid water that it is relatively nonvolatile rather than a gas with a boiling point of  $-161^\circ\text{C}$ . As a result of its structure and bonding behaviour, water plays a role in dye adsorption in two ways additional to those already discussed.

Due to their involvement in hydrogen bonding, water molecules compete with other bonding forces, leading to disruption of cohesive forces in textile fibres, with resultant swelling and opening of the physical structure to allow large dye molecules to penetrate the polymer matrix. They can also compete with dye molecules for adsorbing centres in the fibre. The latter effect is

readily detected in the adsorption of nonionic disperse dyes by cellulose acetate or poly(ethylene terephthalate), since these dyes can be applied from the vapour phase in the absence of water as well as from aqueous dyebaths. Although both of these textile substrates are regarded generally as being hydrophobic and do not swell significantly when immersed in water, they do take it up to at least as great an extent in molecular terms as they do dye molecules (a 5% uptake of a dye with relative molecular mass 450 is equivalent to only a 0.2% water uptake in molar terms). It is found that, in the absence of water, these textile substrates adsorb far more dye than they do from an aqueous bath. Moreover, fibres dyed to heavy shades from the vapour phase desorb dye rapidly when they are exposed to an atmosphere containing water. It is not possible to make the same comparison with natural fibres, since they have to be dyed from aqueous baths, but there is no reason to suppose that the situation in these cases differs fundamentally from that operating with disperse dyes.

The second effect arises from the extensive structure of liquid water. When a large molecule is dissolved in water its presence results in extensive disruption of the structure with a consequent rupture of hydrogen bonds. Thus the free-energy gain which results from the dissolution is partially offset by the energy consumed in breaking up the water structure. The presence of ionic centres in the solute causes polarisation of the water molecules, thus favouring interactions between oppositely charged centres which can result in the release of water molecules. Of significance also is the effect of nonpolar molecules or substituents of molecules. These cause extensive structuring of the water to an extent which has led some writers to use the term 'iceberg' to describe the state of the water in the vicinity of the solute. The structuring arises from the combined effects of hydrogen bonding in the water and dispersion force interactions between the water and the nonpolar moiety of the solute, which lead to fully bonded water molecules similar to those in ice in a solvent envelope around the solute. The loss of entropy which results provides a driving force which can lead to a reorganisation of the system to minimise the amount of water disrupted, and this can be achieved by including two or more solute molecules within one 'envelope'. Thus, the system behaves as if the nonpolar moieties were bonding together. This phenomenon which is readily observed with detergents is called a hydrophobic interaction.

From this brief consideration of binding forces it should be clear that in devising a dyeing process the extent of assistance or impedance which can be expected from coulombic interactions has to be taken into account and the molecule designed to develop dispersion and dipolar binding forces to the degree required. This process is considerably assisted because a dye derives its colour from the fact that electrons in the molecular orbital are easily raised to an excited state by low energy radiation, namely visible light. Thus the same electrons are very readily perturbed in a dispersion force interaction. Thus, dyes with extended conjugation and high molecular mass would be

expected to show high affinity for fibres as well as a tendency to form aggregates in solution due to self-bonding. The presence and the position of sulphonic acid groups in such molecules would also be expected to be important in modifying these bonding characteristics.

### 9.2.2 Dyeing equilibria and kinetics

After a material has been immersed in a dye solution, adsorption takes place until a steady state or equilibrium has been reached. At this point the percentage of the total dye present which has been adsorbed is termed the percentage exhaustion of the dyebath. The experimental values of the corresponding concentrations of the dye in the solution ( $D_s$ ) expressed in appropriate mass units per litre and in the substrate ( $D_f$ ) expressed in the same units per kilogram may be recorded in terms of an isotherm or an isostere. An isotherm expresses the relationship between  $D_f$  and  $D_s$  at a fixed temperature, while an isostere relates  $D_s$  to temperature at a fixed  $D_f$ . In practice, three isothermal relationships are observed, which can be expressed mathematically:

$$\text{Partition isotherms} \quad D_f = k(D_s)$$

$$\text{Langmuir isotherms} \quad (D_f)^{-1} = k(D_s)^{-1} + k_1$$

$$\text{Freundlich isotherms} \quad D_f = k_1(D_s)^n \text{ (where } n < 1)$$

Partition isotherms are observed with nonionic disperse dyes both on the relatively hydrophobic substrates to which they are normally applied, viz. polyesters, cellulose acetates and polyamides, and on natural fibres on which they are relatively weakly adsorbed. The partition isotherm is observed also in the case of ideal gases but this should not be taken to suggest that disperse dyes exist in ideal solutions, there being other more likely explanations.

The Langmuir isotherm was derived theoretically and shown to fit situations in which the adsorbate is taken up by a restricted number of fixed sites on the adsorbent. If the concentration of fixed sites is expressed as  $S$  with the adsorption and desorption processes treated as first order reactions:

$$\text{The rate of adsorption} = k_a(D_s)(S - D_f) \quad (9.1)$$

$$\text{The rate of desorption} = k_d(D_f) \quad (9.2)$$

In the steady state of equilibrium the two rates are equal so that:

$$\begin{aligned} k_a(D_s)(S - D_f) &= k_d(D_f) \\ (D_f)^{-1} &= (k_d/k_a S)(D_s)^{-1} + (S)^{-1} \end{aligned} \quad (9.3)$$

The normal test for the operation of a Langmuir isotherm is a plot of  $(D_f)^{-1}$  against  $(D_s)^{-1}$ . If a rectilinear relationship is observed, the line may be extrapolated to determine  $(D_f)^{-1}$  at  $(D_s)^{-1} = 0$ , which gives the value of



$(S)^{-1}$ , allowing the site concentration or saturation value to be calculated. It should be noted that reciprocal plots are not sensitive to actual curvature in the relationship and this, combined with the normal scatter of even good experimental results, may imply applicability of the isotherm when strictly speaking it does not exist. Consequently, the apparent applicability of the Langmuir isotherm should not be taken as proving that the adsorption is a simple case involving dye taken up by identifiable single sites. On the other hand, the reciprocal plot method can provide a good method of estimating saturation values. Acid and basic dyes of low relative molecular mass and showing little or no tendency to aggregation in solution, as well as simple inorganic acids, have been shown to follow the Langmuir isotherm relationship when adsorbed on amphoteric fibres such as wool or polyamides or, in the case of basic dyes, on acrylic fibres.

The Freundlich isotherm is an empirical relationship which has been found to apply in many adsorption situations. The normal test is to plot  $\log(D_s)$  against  $\log(D_f)$  giving values of  $k_f$  and  $n$ . Again, it should be remembered that log/log plots are very insensitive to curvature, and theoretical conclusions should be drawn with care. The main point regarding the Freundlich isotherm is that although the plot of  $(D_f)$  against  $(D_s)$  shows negative curvature, it does not predict any saturation value. Thus, this isotherm is generally taken to imply that the adsorbate has a tendency to aggregate on the adsorbing surface, building up multilayers. This situation is considered theoretically in another important isothermal relationship, the BET (Brunauer, Emmett and Teller) family of isotherms. However, due to the strong tendency of the direct dyes to aggregate in solution to a degree which is very difficult to determine, such refinements as applying the BET equations to such dyebath equilibria are not justifiable.

The observation of the applicability of the Langmuir isotherm to the uptake of simple acids by wool encouraged Rideal, Vickerstaff and others to apply classical thermodynamic concepts to dyebath equilibria. This leads to the following relationships,

$$\mu_s = \mu_s^0 + RT \ln a_s \quad (9.4)$$

$$\mu_f = \mu_f^0 + RT \ln a_f \quad (9.5)$$

where the  $\mu$  terms are the chemical potentials of the dye in the solution and fibre phases respectively, the  $\mu^0$  terms are the corresponding standard-state chemical potentials and the  $a$  terms are the corresponding activities. At equilibrium the chemical potentials in the two phases become equal, so that:

$$\mu_s^0 + RT \ln a_s = \mu_f^0 + RT \ln a_f \quad (9.6)$$

$$\mu_s^0 - \mu_f^0 = -\Delta\mu^0 = RT \ln a_f/a_s \quad (9.7)$$

The term  $-\Delta\mu^0$  is the change in standard chemical potential or standard molal free energy resulting from the transfer of dye from the solution to the fibre surface and is the *affinity* of the dye for the substrate under the relevant

conditions. Equating concentrations with activities, it can be seen that  $a_f/a_s$  equals  $k_a/k_d$  in the Langmuir isotherm equation, so that

$$\Delta\mu^0 = RT \ln D_f(D_s(S - D_f))^{-1} \quad (9.8)$$

Further to this, from the standard thermodynamic relationship,

$$\Delta\mu = \Delta H - T\Delta S \quad (9.9)$$

$$\ln a_s = -(\Delta H/R)(1/T) + \Delta S/R + \ln a_f \quad (9.10)$$

Again, equating activities and concentrations,  $\ln D_s$  may be plotted against  $1/T$  at a constant  $D_f$  to give a value for the enthalpy of the adsorption. In fact, the underlying assumption is more justified in this case than in equation (9.8), since the error involved in the case of equation (9.10) appears as a constant log function with  $\ln D_f$ . The information needed to calculate a value for  $H$  is easily derived from a set of isotherms.

There are many reasons why the application of classical thermodynamics to dyebath equilibria may be regarded as being optimistic. The textile substrates are rarely sufficiently chemically stable to avoid the presence of dissolved degradation products in the dyebath, thus distorting the equilibrium. The dyes frequently aggregate both in solution and the adsorbed state. A combination of mechanisms of adsorption may well be involved, as has been discussed, and this may itself vary with adsorbed concentration. However, providing that mechanistic theories of adsorption are not based too much on reliance on thermodynamical analysis, these points are of less importance than the fact that by using the thermodynamic approach experimental data can be summarised extremely conveniently in two parameters,  $\Delta\mu^0$  and  $\Delta H$ , and the behaviour of different dyes can be compared systematically providing that their structures, in particular the extent of their conjugation, do not differ too much. It is clearly not possible to compare meaningfully affinities, etc., on different substrates.

There are several approaches to the subject of dye adsorption kinetics. The elementary processes involved are as follows:

- (i) Mass transport of dye to the adsorbing surface
- (ii) Material transport across the fibre/dyebath interface
- (iii) Diffusion of dye molecules in the textile material
- (iv) Interaction of the dye with binding centres.

Each of these four processes can, depending on conditions, become rate-determining. They are governed by different mechanisms. Process (i) is totally governed by the fluid mechanics of the system. Process (ii) is governed by a combination of fluid mechanics, the mechanisms of adsorption and diffusion, and the fabric or yarn structure. Processes (iii) and (iv) behave similarly to a chemical reaction in that they are governed by the temperature, concentrations, etc., as well as the polymer structure.

The approaches to stages (i) and (ii) are essentially phenomenological and

are concerned more with the relationships between the environmental parameters of the system than with its chemistry. Thus, chemical engineering concepts, the thermodynamics of irreversible processes (TIP) and network thermodynamics have each been brought to bear on the problem with, in some cases, important results. However, these topics lie outside the scope of the present treatment, which has to be confined to stages (iii) and (iv). The diffusion of dyes in fibres is, in thermodynamic terms, an entropy-driven situation. It is governed by the same kind of linear relationship as are very many spontaneous processes, in this case Fick's equation,

$$J = -D \text{grad } C \quad (9.11)$$

which relates the flux,  $J$ , to the gradient of concentration through a constant, the diffusion coefficient  $D$ . For the particular case of one-dimensional material transport, using cartesian coordinates,

$$J = -D(dC/dx) \quad (9.12)$$

which is usually termed Fick's Law. Since the dimensions of  $J$  are  $\text{m}^{-2} \text{t}^{-1} \text{m}^{-2}$  and those of the concentration gradient are  $\text{ml}^{-4}$ , it can be seen that the diffusion coefficient has the dimensions  $\text{m}^2 \text{t}^{-1}$ .

In the experimental determination of diffusion coefficients in textile substrates two problems arise. Firstly, conditions have to be established such that dye molecules are supplied to the surface at a rate which exceeds the rate at which they diffuse into the polymer. This is less easy than it seems, because the rate of flow of a liquid past a fixed surface varies from zero to the general velocity with distance away from the surface. Thus, the situation readily arises in which the surface layers of solution become depleted. The layer in which depletion occurs is termed the diffusional boundary layer, and unless it is reduced to a minimum thickness the diffusion coefficients calculated from the experimental data are dependent on the circulation rate. This restricts investigations to studies on single fibres or sheets, as all other forms prevent effective circulation near the surface. The second problem arises from the fact that the diffusion coefficients of dye and other ions in fibres are concentration-dependent, due to potential and other effects, and so vary down the concentration gradient. Such effects can be offset by calculating a diffusion coefficient relative to some arbitrary standard state or by studying trace atom-labelled dye molecules in a system without a chemical potential gradient. Another factor which does not arise often, but has to be remembered, is the possibility that the adsorption process leads to physical changes in the substrate such as fibre swelling, with obvious implications for the observed diffusion coefficient. The mathematics of the solution of Fick's equation in the case of a concentration-dependent diffusion coefficient are complex, and generally analytical solutions are employed (Jost, 1952; Crank, 1956). Of these the simplest is that due to Boltzmann (1894), who derived an expression for the diffusion coefficient at concentration  $c$ ,  $D_c$ ,

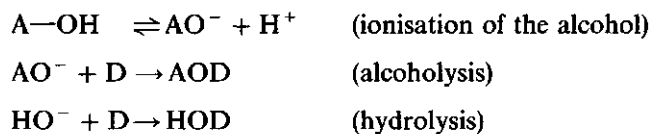
$$D_c = \frac{1}{2t} \left[ \frac{dx}{dc} \right] \int x dc \quad (9.12)$$

which can be solved by numerical methods.

Tracer diffusion studies are based on the use of dyes labelled using, for example,  $^{35}\text{S}$  or  $^{14}\text{C}$  mixed with unlabelled dye. This allows the diffusion to be studied effectively without mass transfer, and with a potentially constant diffusion coefficient. Using this method it has been shown that for the chloride ion in nylon fibres the diffusion coefficient is a harmonic average of two coefficients reflecting site-bound chloride ions and chloride ions migrating in free entrained water (Chantrey and Rattee, 1969). It has also been shown that polyamide fibres have a previously unsuspected surface layer which is relatively resistant to the diffusion of dyes (Coates *et al.*, 1980). The thickness of this layer is dependent on spinning conditions and its presence affects dyeing behaviour. Similar effects have been shown to arise in wool dyeing.

Diffusion studies have their greatest value in relation to the dyeing properties of the polymer rather than the dye, and the migration of dye molecules through the polymer matrix provides information which it is not possible to obtain by other means. Below a certain characteristic temperature  $T_g$ , the glass transition temperature, amorphous polymers exist as a rigid glass, while above the  $T_g$  they become rubbery and behave like a highly viscous fluid. Useful textile polymers have a  $T_g$  below normally encountered temperatures, otherwise they would be unwearable under cold conditions. It has been shown that, below  $T_g$ , dyes can move only through solvent-filled defects in the polymer structure, while above  $T_g$  these do not exist and the dye must move through the *free volume* of the polymer (Murayama *et al.*, 1968). This represents that fraction of the total volume which is not occupied by the polymer itself. It exists in the form of voids appearing and disappearing in the polymer matrix. Clearly, only those voids which are big enough to accommodate the diffusing dye molecule will be involved in the diffusion process, and consequently a diffusional free volume must be defined which relates to the size of the dye in question and is in any case less than the polymer free volume.

Reactive dyes present a quite different picture from that of reversibly adsorbed dyes due to the need to take into account the influence of the reaction on the uptake and kinetics of dyeing. These matters are dealt with extensively elsewhere and only a brief introductory account is necessary here (Rattee, 1978). Considering first the reaction between a reactive dye and an alcohol in solution, three reactions are involved:



The respective rates of alcoholysis and hydrolysis are given by:

$$df/dt = k_f[D]_t[AO^-]_t \quad \text{and} \quad dh/dt = k_h[D]_t[HO^-]_t \quad (9.13)$$

where  $k_f$  and  $k_h$  are the bimolecular rate constants of fixation and hydrolysis, and time equals  $t$ .

Generally experimental conditions may be selected to give a large excess of the alcohol so that  $[AO^-]$  and  $[HO^-]$  are constants. This means that first-order kinetics apply and the total rate of disappearance of reactive dye is given by:

$$-dD/dt = df/dt + dh/dt = \{k_f[AO^-] + k_h[HO^-]\}[D]_t \quad (9.14)$$

so that

$$k_{tot} = k_f + k_h = k_f[AO^-] + k_h[HO^-] = 1/t \ln[D]_0/[D]_t \quad (9.15)$$

where  $k_f$  and  $k_h$  are the first-order rate constants of alcoholysis and hydrolysis. However, the ionisation of the alcohol is pH-dependent with an equilibrium constant  $K_a$  given by:

$$K_a = [AO^-]K_w/[AOH][HO^-] \quad (9.16)$$

where  $K_w$  is the dissociation constant of water. Since alcohols are weak acids, the degree of ionisation is small at any pH used for reactive dye fixation, so that effectively  $[AOH]$  is independent of  $[AO^-]$  and  $[H^+]$ , and the value of  $[AOH]$  used may be the gross concentration. Therefore:

$$k_{tot} = k_f[K_a/K_w][AOH][HO^-] + k_h[HO^-] = 1/t \ln[D]_0/[D]_t \quad (9.17)$$

Consequently, the reaction behaves as a first-order reaction if  $[OH^-]$  is kept constant, and there is an apparent bimolecular rate constant given by:

$$k_{tot}/[HO^-] = k_f[K_a/K_w][AOH] + k_h \quad (9.18)$$

Equation (9.18) may be simplified by combining the dissociation constants of the alcohol and water so that:

$$K_a[AOH]/K_w = K_0 \quad (9.19)$$

$$k_{tot}/[HO^-] = k_f K_0 + k_h \quad (9.20)$$

and the ratio of reactivities is

$$k_f/k_h = K_0 \{k_{tot}/(k_h[HO^-]) - 1\} = R \quad (9.21)$$

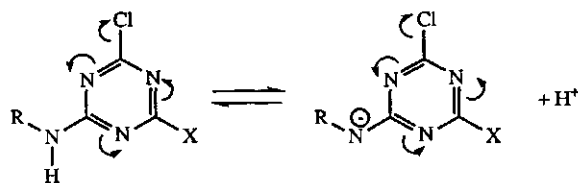
It can be seen from equation (9.21) taken with equation (9.18) that the reactivity ratio is a pH-independent constant varying with  $k_h$  and the properties and the concentration of the alcohol.

The efficiency of the reaction with the alcohol is given by the ratio of the reaction rates  $d_f/d_h$ , i.e.:

$$d_f/d_h = k_f[AO^-]/k_h[HO^-] = k_f K_0/k_h \quad (9.22)$$

when the ionisation of the alcohol is proportionally small. It can be seen that the properties of the alcohol are important, and in comparing reactivity towards different alcohols this must not be neglected.

Many of the reactive dyes based on heterocyclic systems, particularly the *s*-triazinyl and 2,4-diazinyl systems, exhibit reaction rate constants which vary with pH. Horrabin (1963) has suggested this is due to an acid-base equilibrium:



in which the deprotonated molecule is less reactive than the normal form. Some doubt has been cast on this hypothesis, since it has been shown that the way in which the reactivity varied with pH and temperature together did not conform to what would be expected of an acid-base equilibrium (Murthy and Rattee, 1969). It was considered that changes in the solution state may be the cause of the effect. Further to this, Rys and Zollinger (1966) have shown the existence of tautomeric forms of the dye with different reactivities due to changes in ring conjugation.

Dyeing cotton with reactive dyes involves a heterogeneous system requiring consideration of dye diffusion with simultaneous reaction. The rules governing the reaction are the same as those applying to alcohols in solution, but allowance must be made for the rate at which the dye is delivered to the reaction sites. The diffusion equations have been solved for a variety of conditions including chemical reaction, and it has been shown (Sumner and Weston, 1963) that:

$$Q_t = [D_f](t + 1/2k_f)(Dk_f)^{1/2} \quad (9.23)$$

where  $Q$  is the quantity of dye reacting in time  $t$  and  $D$  is the diffusion coefficient. The rate of fixation is given by:

$$dQ/dt = [D_f](Dk_f)^{1/2} \quad (9.24)$$

and the efficiency of fixation,  $E$ , after allowing for the negative surface potential of the cellulose and the consequent differences between internal and external phases is given by:

$$E = \frac{[D_f]}{[D_s]} \left[ \frac{DRK}{k_h[\text{HO}_s^-]} \frac{\exp(e\psi/kT)}{(1 + \exp(2e\psi/kT)^2)} \right] \quad (9.25)$$

in which  $\psi$  is the surface potential of the cotton due to the ionisation of

hydroxyl groups. Thus, the main factors governing the efficiency of fixation can be seen to be the substantivity ratio,  $[D_f]/[D_s]$ , and the surface potential factor. The value of the electrical potential function falls with  $\psi$  when it is more negative than 14 mV, as it always is with cellulose. Thus, factors which minimise the influence of the substantivity ratio or optimise its value are of primary practical importance. Fixation at heavy shade depths will be less than at paler depths due to the higher value of  $\psi$  which is brought about by the higher concentration of negative charges. Efficiency will also decrease with increasing pH due to the reduction of  $[D_f]$  and a fall in the substantivity ratio as a consequence of the increased negative potential of the surface.

The behaviour of dyes in solution is of great importance. A dye molecule capable of participating in hydrophobic interactions with a textile fibre or which has been designed to develop strong perturbational effects must be capable of participating in analogous dye-dye interactions. At the theoretical level, interactions which lead to thermodynamically nonideal behaviour clearly have to be taken into account. At the practical level, grosser effects leading to association in solution or the formation of aggregates can affect dyeing processes. The determination of the activity coefficients of dyes in solution is difficult, partly because of the very dilute nature of dye solutions used in practice ( $10^{-3}$ – $10^{-6}$  molar) but also because of their strong tendency to interact with any available surface, including those of the apparatus being used to contain or examine the solution. For example, even the simple matter of determining the pH of an aqueous solution of a dye acid can in many cases be complicated by dye adsorption on to glass electrodes. Nevertheless, studies using vapour pressure measurements (Chadwick and Neale, 1958; Friedrich and Stammach, 1968) have demonstrated that dye-dye association is common even with very simple dyes.

The aggregation of dyes is more easily studied, although the results frequently serve only to show how complex a dye solution can be. Two methods have been used. The first is based on the measurement of the diffusion coefficient of a dye in solution through a glass sinter. The diffusion coefficient can be related to the aggregate radius via the Stokes-Einstein relation:

$$D = RT(6\pi\eta Nr)^{-1} \quad (9.26)$$

in which  $\eta$  is the viscosity,  $N$  is Avogadro's number and  $r$  is the radius of the diffusing species. With dye ions there is a problem that the co-ions, e.g.  $\text{Na}^+$ , diffuse more rapidly than do the dye ions, and they set up a diffusion potential which accelerates their flux across the interface. Theoretical treatments allowing for corrections to be applied using ion-mobility data from conductivity measurements may be applied, and by using this technique the very marked aggregation of some direct cotton dyes has been demonstrated (Robinson and Moilliet, 1934). Diffusion coefficients in solution have been measured also by polarography (Hillson and McKay, 1965) to provide similar results. The second approach to the study of aggregation is to utilise the fact

that the dye–substrate interaction involves the same electronic orbitals as absorb light and create the colour. Thus, aggregation produces a shift in the absorption spectrum of dye solutions, which can be used to calculate association constants, subject to the assumption that only dimers are formed. The temperature jump-relaxation technique has also been used to measure extremely small spectral shifts. C.I. Acid Red 66 has been shown by this technique to be 66% dimerised at 20°C even at a concentration as low as  $3 \times 10^{-5}$  molar (Hague *et al.*, 1971).

Dyes in solution are, of course, able to interact with other solutes which may be present, and this has been put to use in the development of surfactants which, added to dyebaths, complex with the dye present to modify dyeing behaviour. Such interactions have been studied extensively (Rattee, 1953; Craven and Datyner, 1967). The practical application of this approach is discussed later in connection with particular situations.

### 9.3 Classes of colorants and their applications

Dyes and pigments may be classified by their chromogenic systems, and this has been achieved in the Colour Index (C.I.) published jointly by the Society of Dyers and Colourists and the American Association of Textile Chemists and Colorists. The Colour Index is the most comprehensive and authoritative reference work in the field. Technical information relating to fastness properties and methods of synthesis is provided. The classification in which dyes are identified by C.I. structure numbers according to chromogen cross-refers to a further classification in which the dyes are collected into groups according to use. For convenience the treatment which follows is based on the latter.

There are four main methods of colouring textiles.

- (a) The direct adsorption and attachment of water-soluble dyes. This category includes:
  - (i) Acid dyes
  - (ii) Direct cotton dyes
  - (iii) Basic dyes
  - (iv) Reactive dyes
  - (v) Disperse dyes
- (b) The adsorption of temporarily solubilised dyes converted to an insoluble form by an after-treatment. This category covers:
  - (vi) Vat dyes
  - (vii) Sulphur dyes
- (c) The adsorption by the fibre of components which react to form an insoluble pigment within the fibre. The main dye class behaving in this



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- (c) The adsorption by the fibre of components which react to form an insoluble pigment within the fibre. The main dye class behaving in this

way is:

(viii) Azoic dyes

(d) The pigmentation of fibres by either mass pigmentation or the attachment of pigmented resins. These processes do not involve dyes and necessitate consideration of a ninth class of colouring matter, i.e.:

(ix) Pigments

These nine groups are now considered in detail.

### 9.3.1 Acid dyes

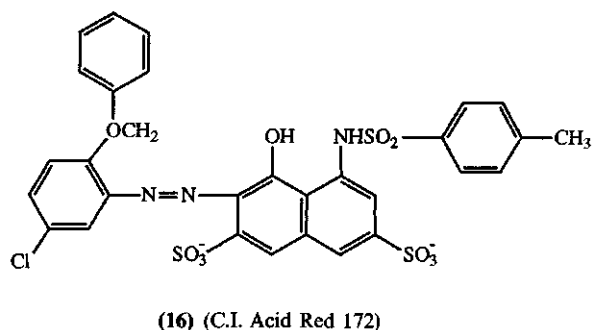
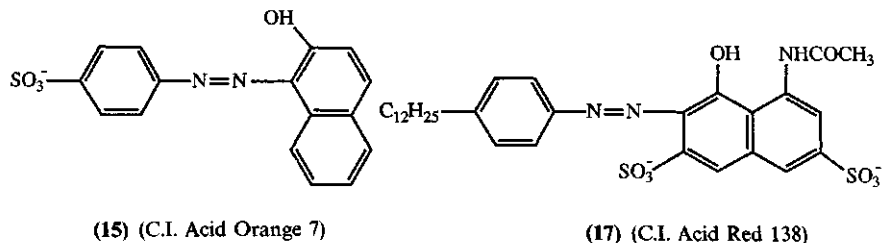
Substituting the chromogen with a sulphonic acid group produces an anionic dye. The adsorption of such dyes by a textile fibre introduces on to the adsorbing surface a strong negative potential which can prevent further dye adsorption. However, wool, silk and nylon fibres are amphoteric in character, containing carboxyl and protonated amino groups. Under acid conditions the carboxyl groups can be back-titrated, leaving a net positive charge which enables dye anions to be adsorbed.

Wool is a polypeptide of complex physical structure consisting of some 18 condensed  $\alpha$ -amino acids in polypeptide chains. While the characteristics of wool fibres depend on the presence and arrangement of all the amino acids, of major importance are the amino acid cystine, which provides disulphide cross links between polypeptide chains, the amino acids lysine and arginine, which supply side-chain amino groups, and the amino acids aspartic acid and glutamic acid, which provide carboxylic acid side groups. Silk contains most of the same amino acids, albeit in a different arrangement, but contains no cystine. Polyamide fibres are prepared by the condensation of a dicarboxylic acid and a diamine or by the self-condensation of an  $\varepsilon$ -amino acid to give a synthetic polymer with terminal amino and carboxylic acid groups. For example, nylon 6.6 is prepared by the condensation of hexamethylene diamine and adipic acid, while nylon 6 is prepared by the self-condensation of  $\varepsilon$ -amino caproic acid. The adsorption of acid dyes by amphoteric fibres has sometimes been discussed as if the charge centres were the driving force for the adsorption. However, if this were all, acid dyes would have much the same behaviour as, and would differ little from, simple anions. It is now understood that the role of the positive surface potential which exists under acid dyebath conditions is to enable adsorption to proceed without building up a potential barrier against the dye molecules. The driving force for the adsorption comes from other forces, as already discussed. Thus, the dyeing process is governed by the relative strengths of the two influences, coulombic forces which assist or oppose adsorption depending on pH conditions, and perturbational forces which are always attractive. With a simple acid *levelling* dye, e.g. (15), the coulombic repulsion can be dominant, so that a high concentration of positive charges has to be built up by dyeing at a fairly low

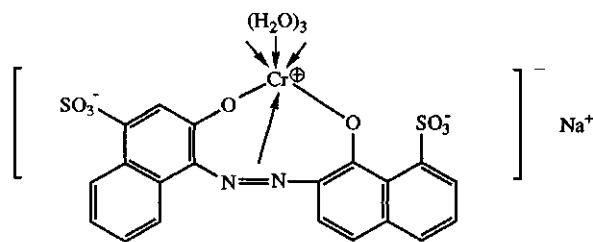
pH of 2.5–3.0. To control the rate of adsorption and assist uniform dyeing, an inorganic salt is usually added to provide colourless competing anions which increase the frequency of the adsorption–desorption process. Sulphate ions have relatively little affinity compared with acid dyes, but their ability to reduce the positive surface potential so that they have to be displaced by the dye anions creates a kind of competition.

By increasing the number of dipolar substituents or by incorporating large nonpolar substituents it is possible to make the dye less susceptible to electrostatic repulsion. More complex dyes such as (16) and (17), for example, show good exhaustion at a dyebath pH as high as 5–6, when the back-titration of carboxyl groups present is very much less. In these cases strong bonding forces supply the energy needed to overcome the potential barrier, with the process being assisted by the uptake of sodium ions present as co-ions. In the case of (17), the affinity is enough to allow wool to be dyed from neutral or even alkaline dyebaths, providing that a fairly high salt concentration is used. The increased molecular complexity of dyes such as (16) and (17) also reduces the ease with which the dye molecules can diffuse through the polymer structure. Consequently, the dye is more resistant to desorption processes such as washing or other wet treatments, particularly alkaline treatments, and acid dyes of this type are termed *neutral dyeing acid* or *acid milling dyes*. (Milling is a severe alkaline finishing process applied to certain types of wool cloth.) An interesting feature of (17) and similar structures is their marked tendency to develop hydrophobic interactions with soap or surfactants. This means that if any dye is desorbed during alkaline washing it complexes with the detergent and is prevented from dyeing back on to adjacent white material. The same tendency can be employed usefully to control the adsorption process in the dyeing operation, and this can be important, since the relative lack of influence of coulombic forces means that small anions cannot be used to control adsorption, as is the case with simple acid dyes.

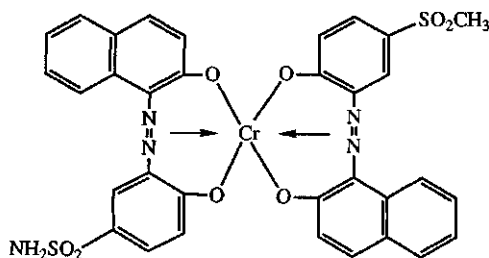
Using selected dye intermediates it is easy to produce acid dyes containing *o,o'*-dihydroxyazo functionalities or similar configurations which are able to form complexes with chromium. Such dyes are normally classified separately as *mordant dyes*, but they may be considered as a subgroup of the acid dyes. Dyes of this kind were first applied to wool previously mordanted by boiling the material in a dilute potassium dichromate solution. The latter reacted with reducing groups in the wool resulting from the hydrolysis of disulphide bonds, leaving the fibre containing chromic ions. Application of the appropriate dye to the mordanted fibre produces a 1:1 chromium-dye complex which is extremely fast to washing due to the chelation of the metal atom with both dye and fibre. This method fell into disuse when it was shown that a more reliable and rapid procedure was to apply the dye as a regular acid dye and then after-treat the dyed fibre with the dichromate in the after-chrome process. This method gives dyeings of very high washing-fastness combined with high



lightfastness, resulting from the stabilisation of the azo group to light through chelation, without the harshness of handle produced by premordanting the wool. Another version of the procedure, the metachrome process, which as the name implies involves simultaneous application of the dye and the dichromate, was introduced in 1900. Dyes suitable for metachrome application had to be stable to the oxidative action of the dichromate in the dyebath, and the method was more restricted than the after-chrome method. Both the after-chrome and the metachrome methods continued to be used extensively until relatively recently, when environmental legislation seriously discouraged dyers from discharging spent dye liquors containing chromium. However, in 1920 the preformed 1:1 chromium complex dyes appeared, e.g. (18).



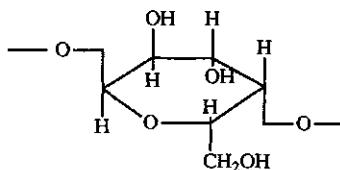
Because they were preformed complexes and no treatment of the wool with chromium salts was necessary, reliable production of shades was facilitated. However, it was not easy to produce level results because the dyes were very strongly adsorbed at normal acid dyebath pH values. By lowering the dyebath pH to 1.2–1.5 the tendency of the chromium atoms in the dye to chelate with the fibre was reduced, and this enabled dye adsorption to be controlled, albeit at the expense of fabric handle. Better methods were later developed which allowed a higher dyebath pH to be used, utilising the principle of temporarily complexing the dye molecules in solution with polyethanoxo surfactants (Valko, 1972). A much more satisfactory solution to the problem presented itself when it was found that the 1:1 chrome complexes could be reacted with a second complexing dye molecule under alkaline or weakly acidic conditions to form a 1:2 chrome complex, exemplified by (19). Such complexes formed from sulphonated dye intermediates were found to be very difficult to apply evenly, but a detailed study of the relationship of the ionic charge on the dye molecule and dyeing behaviour showed that sufficient solubility was conferred on dyes using even such weakly acidic groups as *N*-substituted or unsubstituted sulphonamido groups. Such dyes gave readily controlled dyeing rates in weakly acidic dyebaths. The development of level dyeing assistants that were either weakly cationic or nonionic surfactants capable of complexing with the dye and forming coacervates in the dyebath resulted in the very successful introduction of the Irgalan dyes by Geigy in 1949 (Schetty, 1955). In addition to the 1:2 chrome complexes which comprise the overwhelming majority of dyes of this type, some 1:2 cobalt complexes were also introduced to enhance the shade gamut. Due to the fact that in the 1:2 metal complex dyes all the coordination valencies of the metal atom are occupied within the dye molecule, no further complexing with groups in the fibre is possible. Consequently, the 1:2 metal complex dyes do not exhibit the very high fastness to alkaline treatments that is shown by the after-chrome dyes. Their advantage lies rather in their high lightfastness, their excellent compatibility of dyeing behaviour and the excellent appearance of the dyeings they produce.



(19) (C.I. Acid Violet 78)

9.3.2 *Direct cotton dyes*

Cotton and other cellulosic fibres such as the various forms of viscose rayon consist of a polymer of 1,4-anhydroglucoside units (20).



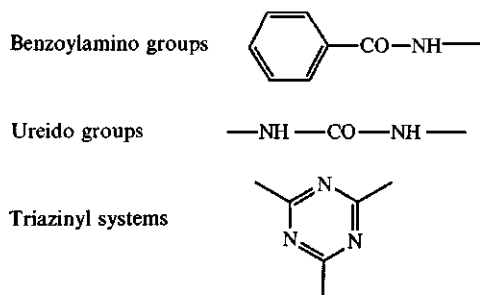
(20)

As a result of natural oxidation occurring during growth or subsequent processing, some of the pendant methylol groups are oxidised to carboxylic groups. There are no crosslinks between polymer chains and the polymer structure is strongly hydrophilic. Due to the high chain length and extensive hydrogen bonding between the chains, cotton cellulose is not water-soluble as is the case with many similar but smaller molecules. Due to the presence of the small number of carboxylic groups along the polymer chain, cellulose has a weak negative charge in dyebaths with a pH higher than 4. If the dyebath pH is raised above 8, some of the hydroxyl groups present on the methylol side chains ionise, increasing the negative charge significantly. The charge repulsion between polymer chains which results causes fibre swelling to occur. If the pH is raised further some of the other hydroxyl groups begin to ionise, and extensive swelling with polymer chain rearrangement can occur. Such extreme conditions are not normally encountered in dyeing situations.

The negative charge on the adsorbing surface of cellulose clearly creates a very unfavourable situation for the adsorption of anions. Although empirically based, the work of Böttiger and of Griess leading to the introduction of the direct cotton dyes pursued exactly the line of thought which would be suggested by our present understanding. By building up the molecular complexity of the acid dye and incorporating dipolar and similar substituents, sufficient dye-fibre bonding capacity can be introduced to offset the charge repulsion effect. This meant extending the length of the molecule by preparing bis- and tris-azo dyes. Furthermore, by applying the dye in the presence of an electrolyte such as sodium chloride, a high concentration of cations is made available to accompany the adsorbed dye molecules and nullify the negative surface charge. In essence, this is the way in which direct cotton dyes are applied.

Apart from the azo groups present which make a major contribution to dye affinity and other substituents normally present in acid dyes to modify

the colour the main substituents employed to enhance direct dyeing behaviour are:



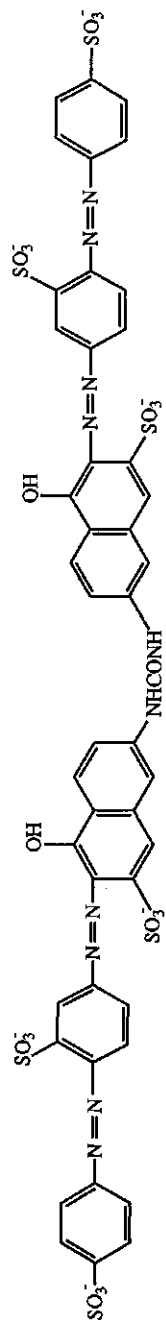
The second group is found in direct cotton dyes as a link between two chromogens, and the dyes can be produced by condensation of two molecules containing free amino groups with phosgene, e.g. (21).

The triazinyl systems, which are especially effective in conferring affinity on the dyes, are used in a similar way, but because it is possible to build the bridge in a stepwise manner, dyes can be made by bridging different chromogens, e.g. (22).

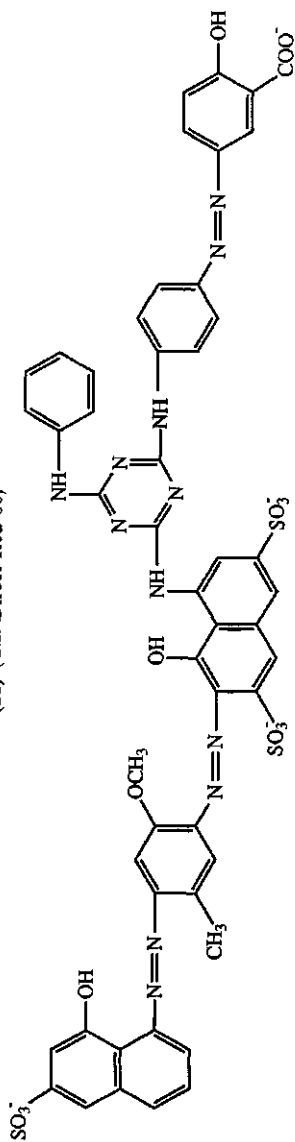
The way in which the substituents are introduced into the dye molecule is important. The normal configurations of an unsubstituted polyazo system is planar, and this allows optimum development of the molecular orbital. If a substituent is introduced that distorts the planarity of the molecule, the colour strength and the dye affinity, both of which depend upon the delocalised electron system in the molecule, are reduced significantly.

The direct cotton dyes have been subclassified in accordance with their relative needs for salt in the dyebath. Clearly, as the dye complexity is built up, the need for the addition of salt becomes less. The simplest of the direct cotton dyes require high concentrations of salt (Class A dyes), and the most complex exhaust with relatively little salt requirement (Class C dyes), while between the two are found the Class B dyes. Normally, dyes from the different subclasses would not be applied together.

Since the adsorption of the direct cotton dyes from the dyebath is promoted by the presence of salt, it follows that, after the dyeing is completed and the dyed goods are washed off, a major factor causing the dye to remain adsorbed has been removed. Therefore, it is not surprising that direct cotton dyeings do not possess good fastness to washing and other wet treatments. However, most washing treatments are of short duration, and providing that they are carried out at a low temperature at which desorption is slow the amount of dye lost is acceptable for certain end-uses. By carrying out dyeing at (typically) 85°C for 45 min, a satisfactory dyeing rate is achieved, while washing instructions would normally specify hand washing at 40°C. More serious than the loss of colour strength during wet treatment is the tendency of



(21) (C.I. Direct Red 80)



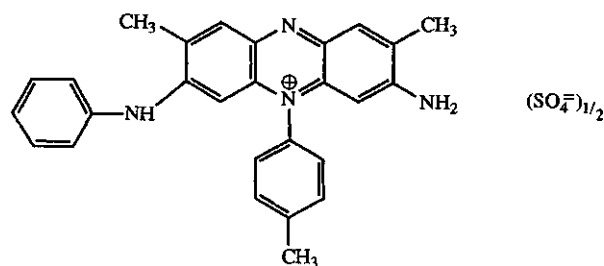
(22) (C.I. Direct Green 26)



desorbed dye to stain adjacent cellulosic materials. So far as can be determined, no attempt has been made to exploit dye-detergent interactions in a manner comparable with that described for acid milling and 1:2 chrome complex dyes. There have been many attempts to devise methods of after-treating direct cotton dyeings to produce a final dyeing of good fastness. Technically the most successful, although not all that widely adopted commercially, has been the use of direct cotton dyes carrying substituents with replaceable hydrogen atoms, for example amino, alkylamino, etc., which can be reacted with a so-called bridging compound to bond the dye chemically to the fibre. Such treatments are inevitably accompanied by a shade change, and any small proportion of the dye molecules escaping modification are available to produce a stain on adjacent material. Another form of after-treatment which has been used is to after-treat the dyeing with a high molecular weight cation, e.g. cetyl pyridinium bromide, to produce an insoluble salt. This is quite effective in improving fastness to perspiration and does assist washing-fastness. However, in a great many cases the lightfastness is significantly reduced by such treatments. With direct cotton dyes that have the capability of forming a stable copper complex due to the presence of an *o,o'*-hydroxyazo configuration it is possible to combine after-treatment with a cationic salt, and after coppering to obtain good lightfastness with improved washing-fastness.

### 9.3.3 Basic dyes

An alternative name for this application class is the cationic dyes. This indicates clearly that they mirror the acid dyes in that they are water-soluble with a coloured cation. In a sense the basic dyes represent, as far as synthetic dyes are concerned, the oldest dye class, as Perkin's Mauveine (23) was a basic dye.



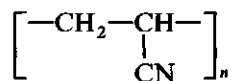
(23)

The same rules apply to basic as to acid dyes but in the opposite sense. Their adsorption on to wool and silk is promoted by using alkaline dyebath conditions, which develop a negative charge on the fibre, and is reduced in

acid dyebaths. They are weakly adsorbed on to cellulosic fibres, and when first introduced were applied to mordanted material.

With the acid and direct cotton dyes, the sulphonic acid groups providing solubility are substituents and not an intrinsic part of the chromogen. Therefore, it is possible to modify the structure and the dyeing behaviour relatively independently of the dye charge. However, most basic dyes resemble Perkin's Mauve in that the charge on the cation which renders the dye water-soluble is an integral part of the chromogen. Modifying the dyeing behaviour is consequently less easy than it is with acid dyes.

The brilliant shades offered by many basic dyes makes them attractive as textile dyes from the point of view of the consumer and the designer, but their poor fastness to washing and to light rapidly limited their use and eventually led to their decline as far as textiles were concerned. For many years basic dyes were encountered mainly in nontextile applications. This situation was changed dramatically with the introduction of fibres derived from polyacrylonitrile in 1948. These are straight polymers with the structure:



where  $n$  has a value between 600 and 2000. Various modified or modacrylic fibres are also available, which are made by copolymerising acrylonitrile with other monomers. As a group the acrylic fibres have aesthetic qualities similar to wool. In order to catalyse the polymerisation, redox catalysts are used (sodium bisulphite/potassium persulphate) and this results in the presence of terminal sulphonato- and sulphato-groups. In addition, carboxylic groups may be present in copolymerised systems. Consequently, the acrylic fibres readily adsorb basic dyes. The technical importance of this arises from the fact that many basic dyes have considerably greater lightfastness on acrylic fibres than they do on any other textile substrate. Thus, the introduction of these fibres led to a resurgence of interest in basic dyes for textiles and an extension of the chromogens employed to produce coloured cations to include azo and anthraquinonoid systems. Many examples are now available in which the positive charge centre is isolated from the chromogen by a saturated carbon link.

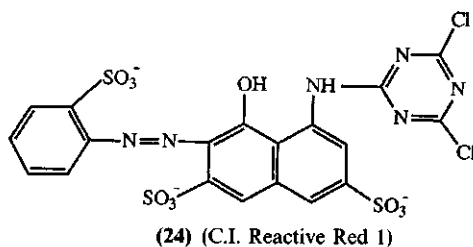
#### 9.3.4 *Reactive dyes*

In the discussion of acid, basic and direct cotton dyes it has been made clear that control over both colour and dyeing behaviour normally involves modifications to the chromogen. Since the more complex the chromogen the broader, in general, is the principal absorption band of the dye, it follows that the production of a direct cotton dye involves using chromogen systems that offer duller shades than are achievable with the simpler acid dyes. It

was realised at an early stage that a valuable solution to this problem would be to develop dyes that achieved fastness by the formation of a covalent link between chromogen and fibre. However, the principal realisation of this idea, the fibre reactive dyes, took over sixty years. Chemical reaction as a means of producing fast dyeings has attractions also for the dyeing of wool, silk and polyamide fibres, although the problem here is not the production of fast bright shades so much as the relative difficulty in devising reliable level dyeing methods with the structures which confer fastness by virtue of their high molecular weight and slow diffusion in the fibre.

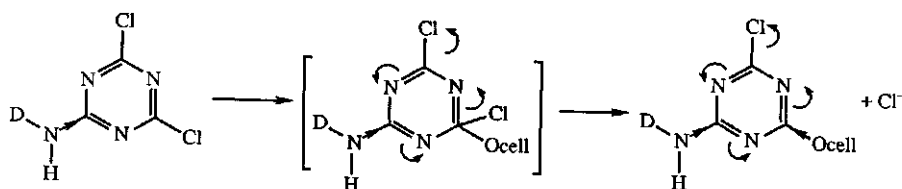
Early investigations of the chemistry of cellulose demonstrated that cellulose treated with strong sodium hydroxide solution to ionise the primary and some of the other hydroxyl groups may be benzoylated (Cross and Bevan, 1895). Starting with *p*-nitrobenzoyl chloride they prepared a cellulose derivative bearing a pendant nitro group, which they then reduced to amino. This was then diazotised and coupled to a phenol to give a coloured cellulose derivative in which the dye was covalently bonded to the fibre. While this early exercise showed that this kind of dye-fibre was possible, the means of its achievement did not provide a practical dyeing system. This had to await the work of Stephen and Rattee almost 60 years later, which resulted in the efficient reaction of chlorotriazinyl amino dyes to cellulosic fibres under mild conditions of alkalinity and temperature in practical dyeing times (Zeneca, 1954; Vicherstaff, 1957).

The first commercial reactive dyes for cellulose were effectively simple acid dyes bearing a chlorotriazinyl amino group, exemplified by (24). The successful



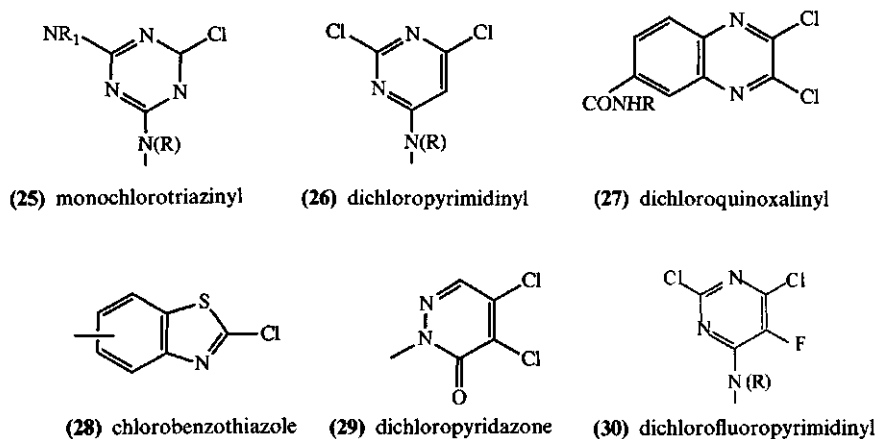
production and use of this type of dye depended on two observations. Firstly, it was shown that these very reactive compounds can be isolated and marketed as stable dye powders by preparing the final press cake (i.e. the filtered precipitated dye prior to drying and standardisation) at a buffered pH of 6.5, under which conditions the hydrolysis rate is at a minimum. Additionally, by incorporating in the dye powder suitable buffers, it was possible to prevent the pH from falling if any of the dye powder hydrolysed in the atmosphere to generate hydrochloric acid. Secondly, it was demonstrated that these dyes, while reacting with cellulose and with water at much the same rate at a pH of around 10, reacted preferentially with the cellulose if dyeing conditions

were selected that caused the dye to be concentrated in the cellulose rather than the water phase. The physical chemical aspects of this situation have been discussed (section 9.2). The mechanism of the formation of the cellulose derivative in the case of the chlorotriazinyl dyes involves the nucleophilic substitution of the chlorotriazinyl ring by the ionised group in the cellulose as shown in Scheme 9.1.

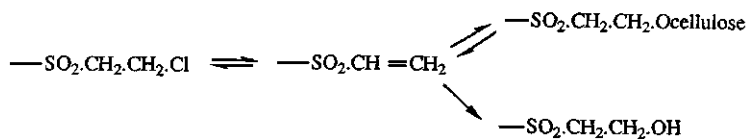


Scheme 9.1

Following the introduction of the dichlorotriazinylamino dyes a number of other halogenoheterocyclic systems were introduced for application by the same general methods, such as (25)–(30).



An alternative approach was taken in the development of the chloroethylsulphonyl reactive system. The mechanism of reaction with this system involves nucleophilic *addition* following a general base catalysed elimination of HCl:



The reactive dyes established themselves very rapidly as a major dye class for cellulosic fibres due to their ease of application, broader shade gamut than could be obtained with other dyes from cellulose, and excellent fastness properties. With their introduction came new and simple application methods which offered continuous and semicontinuous dyeing methods at low capital initiation costs such as pad-dry-wash and pad-batch-wash. Very reliable printing methods also came to be established. A summary of the principle application methods is given.

- (i) Exhaustion from an aqueous dyebath by salt addition followed by the addition of alkali to promote dye fixation. Using the most highly reactive dyes, the initial exhaustion stage is completed before the alkali is added in order to minimise hydrolysis of the dye in the dyebath. When dyes of lower reactivity and higher affinity are being applied the salt and alkali may be added together. Since the addition of alkali causes some ionisation of cellulose hydroxyl groups and the negative charge repels the dye anions, it is necessary to keep the dyebath pH as low as possible consistent with completing the reactions within a practical time. In practice this means a dyebath pH of 9–10 and the use of sodium carbonate rather than stronger alkalis. Depending on the properties of the fabric to be dyed, the reactivity of the dyes used and their affinity for the fibre, the dyeing temperature may lie between ambient temperatures and 85–90°C. At the end of the dyeing process the goods are rinsed and finally washed with successive treatments until all unfixed exhausted dye has been removed.
- (ii) Semi-continuous application (pad-batch) by impregnating the fabric with an alkaline dye solution using a padding mangle and storing or batching the wet material for the reactions to proceed at the ambient temperature. Under these conditions fabric contains no more than 70% of its own weight of dye liquor, whereas in exhaustion dyeing there is 5–10 times as much solution as fabric. These so-called 'short' liquor to goods ratios lead to high levels of dyebath exhaustion, and salt addition is not needed to achieve efficient fixation, because the fixation efficiency shows very little dependence on the substantivity ratio,  $S = D_f/D_s$  (cf. equation 9.25). The reason for this is as follows. The total amount of dye present,  $D$  is given by

$$D = D_f W + D_s V \quad (9.27)$$

The liquor to fabric ratio,  $L$ , is  $V/W$  so that

$$D = S D_s V L + D_s V \quad (9.28)$$

$$D = D_s V (S + L)/L \quad (9.29)$$

Therefore

$$D_s V/D = L/(S + L) \quad (9.30)$$

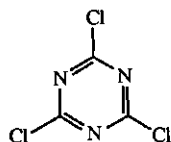
Since  $S$  is generally more than 20 when  $L$  is small, the proportion of the total dye which is in the liquor is small and its influence on the overall efficiency is minimised. Dyes of higher reactivity are not stable in alkaline solution and special methods have been devised to produce continuous mixing of dye and alkali and minimise the time available for hydrolysis. The batching time depends on the pH of the padding liquor and the reactivity of the dye used. At pH 8 ( $\text{NaHCO}_3$  used as alkali) with a dichlorotriazinyl dye, 24 h is required to complete fixation; at pH 12 ( $\text{NaOH}$  used as alkali) fixation is complete in 2–3 h with a dichlorotriazinyl dye or 48 h with a dichloropyrimidinyl dye. At the end of the batching time unfixed dye is removed by circulating hot water through the batch or by using a washing range. The method is very convenient for woven and knitted fabrics, as the equipment required, apart from the padding mangle, is cheap and simple. It is also very effective when dyes of lower affinity have to be applied, and is widely used for the application of the chloroethylsulphonyl dyes.

- (iii) Continuous applications, all of which involve padding fabrics where the fabric passes in a continuous web through the full sequence of impregnation, fixation, washing off and drying. The first continuous reactive dyeing sequence was pad(dye)–dry–pad ( $\text{NaOH}$  + salt)–steam–wash–dry. This complex sequence required expensive and elaborate machinery and is little used now. Later, simpler variations such as pad(dye +  $\text{NaHCO}_3$  or  $\text{Na}_2\text{CO}_3$ )–dry–steam–wash–dry were more adopted, although current market conditions lead to smaller batches which are not appropriate for continuous applications. One very interesting variant of this application sequence arose from the observation that, when the dye carried a dichlorotriazinyl system, the decomposition of  $\text{NaHCO}_3$  to  $\text{Na}_2\text{CO}_3$  during drying caused a sufficiently increased pH to bring about fixation of pale to medium shade depths without the need to steam. A corresponding method for less reactive dyes, e.g. monochlorotriazinyl dyes, was developed which used  $\text{Na}_2\text{CO}_3$  and a pad liquor containing 20% urea followed by drying and baking. The urea was believed to act a secondary solvent, i.e. fixation was thought to take place in the molten urea. In view of the chemistry of urea there is some doubt about this idea, as urea decomposes quite rapidly at 110–115°C to biuret which, in turn, melts at 190°C and is unlikely to provide a molten medium for reaction. No research has been carried out in this area and the subject is open for speculation.

With the passage of time two reactive systems have come to dominate the reactive dye market. The chloroethylsulphonyl dyes are the cheapest and

simplest to manufacture of the reactive dyes for cellulose. The reactive system (usually called the vinyl sulphone system) contributes little to the affinity of the dyes for the fibre, and consequently their main outlets have been in those areas where dye affinity is of lesser importance, i.e. textile printing and semicontinuous dyeing processes such as pad-batch-wash. They have established themselves as predominant in the production of goods for discharge printing, which is discussed in detail later. The preparation of vinyl sulphonyl dyes with greater affinity for cellulose is governed by the same principles as apply to the preparation of direct cotton dyes, and with the same limitations restricting the brightness of shade of the more complex dye structures. Nevertheless, the problems have been overcome to enable black and dark blue dyes, which are a vital feature of any commercial range of dyes, to be produced.

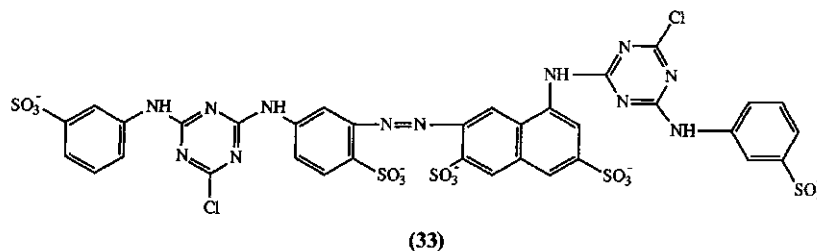
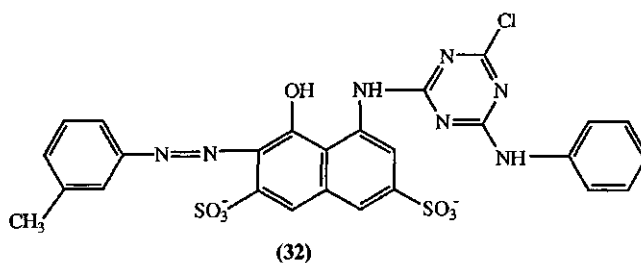
The heterocyclic reactive systems offer the chemist greater flexibility, especially when the reactive component is multifunctional e.g. 1,3,5-trichloro-2,4,6-triazine (31). The important characteristic of (31), which has been a



(31)

major factor in making it the most widely used of the heterocyclic reactive intermediates, is the fact that the chlorine atoms are mutually activating. Thus, replacement of one chlorine atom leads to a deactivation of the remaining two, and the replacement of the second chlorine leads to a further deactivation of the third. It is possible, therefore, to replace the chlorine atoms in an exactly stepwise fashion. This feature was used in the direct cotton dyes incorporating a triazinyl bridge (see 22), and some of the dyes which were marketed actually contained a residual chlorine atom which could be reacted with cotton under the right conditions. However, in preparing reactive dyes the retention of unreacted chlorines is deliberate and essential. The most reactive triazinyl dyes are those containing two residual chlorine atoms, and these are prepared by condensation of the trichlorotriazine with either an intermediate containing a primary or secondary amino group or the dye molecule similarly substituted. The dye is then isolated by precipitation from a buffered solution using salt, filtration, drying and final standardisation using an appropriate buffer to optimise storage stability. The main difference between dyes prepared using primary and secondary amines lies in their solubility and affinity for cellulose. The triazine ring is the most powerful physical bonding system in the molecule and an *N*-alkyl group sterically hinders the ability of the ring to participate both in the formation

of aggregates and in physical bonding with the cellulose. This option is of great value when the dye formed using a primary amine has inadequate solubility or too great a tendency to stain adjacent materials in washing. However, while very widely applicable and providing the basis for new dyeing methods, the dichlorotriazinylamino dyes proved too unstable for some applications, notably printing, which requires stable print pastes that can be stored for some weeks, and also exhaustion methods employing higher temperatures, which are frequently needed to ensure levelness and fabric penetration. For such applications, the second chlorine atom can be substituted to give a less reactive dye suitable for the more severe conditions of application and offering solution stability when required. By selecting the second nonreactive substituent with care it is possible to fine-tune affinity, solubility and even reactivity to provide dyes designed for particular application methods with a precision previously unattainable. In addition, it was found possible to produce dyes designed for textile printing which contained more than one monochlorotriazinyl group to optimise reaction potential and at the same time to provide extra solubilisation to assist print paste preparation and the removal of any unfixed dye at the end of the printing process, e.g. (32) and (33). Simple monochlorotriazinyl dyes with structures such as (32) are valuable for exhaustion dyeing processes from warm dyebaths. The inert substituent may be selected to enhance affinity or solubility, the rules being the same as those applying to the design of direct cotton dyes. Dyes with a binary reactive system exemplified by (33) offer many opportunities for modifying the solubility and reactivity, including, as will be discussed below, the use of two reactive systems of different kinds.





Dyes designed for high-temperature exhaustion applications have a structure exemplified by (33). The similarity to direct cotton dyes incorporating a triazinyl bridge, e.g. (22), will be noted. The difference in practice lies in the knowledge the modern dye chemist has when it comes to the design of the dye molecules for specific end-uses, which allows a high fixation efficiency to be achieved.

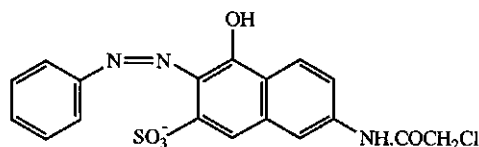
Other heterocyclic systems, e.g. (26)–(30), are not dissimilar but do not offer the same degree of flexibility as the triazinyl system. The most extensively explored of the alternative heterocyclic ring systems has been that based on pyrimidine (26) or 1,3-diazine. Due to the fact that the ring contains two instead of three nitrogen atoms as in the triazine ring, there is less ring activation, and although there is some mutual activation by the chlorine atoms in the dichloropyrimidinyl dyes the two chlorines are not equivalent due to the asymmetry of the system, the chlorine atom in the 2-position being more reactive than that in the 4-position. In practice, only the more reactive of the two can be used to form a bond with the fibre. In order to complete a reaction in a reasonable time the application pH has to be fairly high, to provide a high concentration of ionised sites in the cellulose for the nucleophilic substitution. This makes it more difficult to achieve exhaustion, due to the charge repulsion of the dye anions. Since the pyrimidine ring, in any case, does not contribute very much affinity to the dye, the net result is a limitation on the value of the system in dyeing processes depending on exhaustion. Compensation for this can be obtained by careful selection of chromogens with good affinity, but this approach imposes limitations which do not apply as strongly with a more reactive system. It is possible to increase reactivity in the diazine ring by suitable substitution in the 5-position. A 5-chloro substituent increases reactivity slightly but usefully, and this has been used commercially. A 5-fluoro substituent (30) has a greater activating effect and, although relatively expensive, has been used. An instructive but technically useless example of activation is provided by the 2,4-dichloro-5-nitropyrimidinyl dyes. The nitro group has a very powerful activating effect and the dyes can be reacted with cellulose under quite mild conditions. However, the nitro group remains on the reacted dye molecules and continues to activate the dye–cellulose condensation product, which is only marginally less readily hydrolysed than the original reactive dye. Consequently, the dye–fibre bonds are broken down by the alkali present to induce the fixation at a rate which is just a little slower than the fixation itself. This example provides a valuable reminder that reactive systems used in dyes generally possess both permanent and temporary activation, but that the most effective reactive systems are those which depend on the latter rather than the former.

The dichloroquinoxaliny system (27) uses the 1,4-diazinyl ring in a condensed ring system. The chlorine atoms in the 2- and 3-positions are mutually activating, and if one of them is lost the system is relatively inactive. Consequently, in order to attach the group to a chromogenic system a  $\text{—COCl}$

group is introduced in the 6-position, which can be reacted readily with a chromogen bearing a free amino or methylamino group. The dyes are very effective as reactive dyes for cellulose, but the amide bridge linking the reactive system to the chromogen is less stable to acid hydrolysis than the imido bridge found with other reactive systems, and this leads to a lack of fastness to acid conditions.

A number of reactive dyes for cellulose have been introduced which incorporate both a halogenoheterocyclic and a vinyl sulphonyl reactive system. The underlying concept is that not only is the probability of fixation rather than hydrolysis increased by having two systems, but also that the two systems, having different reactivity characteristics, can be brought into play separately during the dyeing process, giving the dyer greater control.

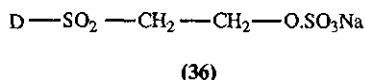
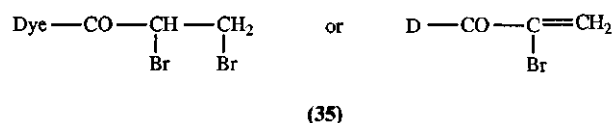
Wool, silk and polyamide fibres all have available amino groups with which reaction under mildly acid conditions is easily achieved. However, it was not until the mid 1930s that dyes were marketed that depended to some degree on dye-fibre reaction for their fastness. These were the chloroacetyl amino dyes, the chlorine atom of which is readily substituted by an amino or thiol group, both of which are available in wool. A typical structure (34) is shown.



(34) (C.I. Acid Orange 30)

It should be noted that the capacity of these dyes for reaction with the fibre was not realised or demonstrated until the mid-1950s, in the course of work that ultimately led to the introduction of reactive dyes for cellulose. The problems arising in the development of reactive dyes for protein and polyamide fibres are not the same as in the case of such dyes for cellulose. With the latter, unreacted or hydrolysed dye does not exhaust strongly on to the fibre and is, in any case, fairly readily removed. In addition, cellulosic fibres are relatively pure and take up dyes uniformly under fairly mild conditions. However, dyes diffuse relatively slowly in wool, silk and polyamide fibres, and temperatures at or approaching the boil are generally needed to complete dyeing processes within acceptable times. Further to this, it is found that there are variations between one wool fibre and the next, which gives rise to non-uniform dyeing characteristics, and uniformity of shade requires either prolonged dyeing at high temperatures to equalise dye distribution or specially selected dye structures and assistants to obtain uniform initial 'strike'. These considerations mean that the conditions that exhaust an acid dye on to wool and the other similar fibres also cause strong exhaustion of nonreacting dye. This is then removed from the fibre only with difficulty,

and by methods which easily lead to fibre damage. In addition, wool itself hydrolyses during the dyeing process to produce dissolved protein in the dye bath, and this is able to react with some of the dye to give a product which then exhausts back on to the fibre. Consequently, an ideal reactive dye for these fibres needs to have a reactive substituent that is resistant to hydrolysis under fairly severe aqueous dyeing conditions and a hydrolysed form that has low affinity for the fibre. No reactive system for these fibres has been developed which fully meets these criteria. However, two systems have been developed that possess a balance of properties which provides a sufficiently good level of behaviour for practical purposes. These are (35) and (36). Dyes of both types are applied to the fibre under mildly acidic conditions



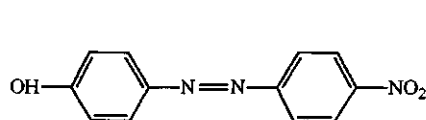
with appropriate level dyeing assistants. Under these conditions reaction with the fibre is not significant until the dyeing temperature approaches the boil, when a condensation reaction involving nucleophilic addition begins with available amino groups. In wool an additional side reaction takes place with thiol groups present due to hydrolysis of the disulphide bond of cystine. The product of this reaction is not very stable to alkali and can give rise to washing-fastness problems. The amount of hydrolysed dye adsorbed by the fibre is small if dyeing conditions are correctly chosen, but is sufficient to cause problems if the highest standards of fastness are demanded. Consequently, dyeings may be after-treated in a mildly alkaline bath to give the fibre a weakly negative charge leading to the ready desorption of unwanted dye anions.

### 9.3.5 Disperse dyes

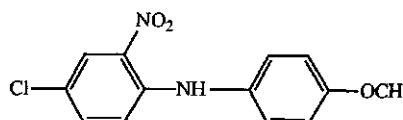
The dyes so far discussed have all been water-soluble salts in which the coloured moiety is an anion or a cation. It was found in the 1920s, when cellulose acetate was first introduced as a textile fibre, 'artificial silk', that dyes of this type had very little affinity for the new fibre and that a new type of dye would have to be developed if cellulose acetate fibres were to become economically viable as a textile. The problem is that cellulose acetate is relatively hydrophobic and takes up very little water as compared with natural fibres such as cotton or wool. This greatly increases the electrical repulsion effects which are a very important factor when dye ions are adsorbed, as has

been discussed already. In addition, the low water uptake reflects low swelling of the fibres and consequently they are permeable with difficulty and by only small dye molecules. The solution to the problem was found in the use of small dye molecules of low polarity and consequently very sparing aqueous solubility, which are present in the dyebath initially as a dispersion. In the early stages of development of this class of dyes various ideas were advanced to explain their mode of action, which were based mostly on the somewhat dubious concept of a process of direct transfer from the dye in the solid state to a 'solid solution' in the fibre which was regarded as a 'solid colloid'. This concept received apparent support from the fact that cellulose acetate could take up dye by direct contact with the warmed dye powder and also by transfer from the vapour phase under certain circumstances. It was not until the 1950s as a result of a series of studies led by C. L. Bird (Bird, 1954; Bird *et al.*, 1954; Bird and Harris, 1957; Bird and Firth, 1960; Bird and Rhyner, 1961), that a true picture began to emerge of the mechanism whereby these dyes were being taken up.

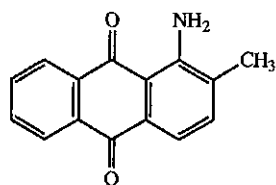
The lack of an accurate theory of the mechanism of the adsorption of the disperse dyes did not, however, seriously impede the development of the dyes in the early years, since an empirical approach was adequate to deal with such problems as arose and, in any case, cellulose acetate remained the only synthetic or man-made textile fibre until the much later appearance of the polyamide and polyester fibres. The first dyes developed were based on azobenzene, which was substituted with a variety of substituents in the 4,4'-positions, and on diphenylamine, as exemplified by (37) and (38). Such dyes gave a shade gamut largely restricted to yellow, orange and red shades, although in recent years this has been considerably extended. The overwhelming majority of early blue disperse dyes were based on simple substituted anthraquinones, which provided excellent bluish reds, violets and blues to give a full shade coverage, e.g. (39), (40) and (41).



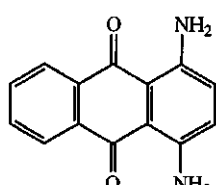
(37)



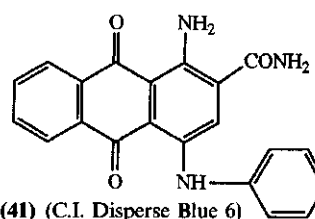
(38)



(39) (C.I. Disperse Orange 11)

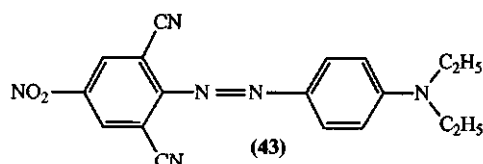
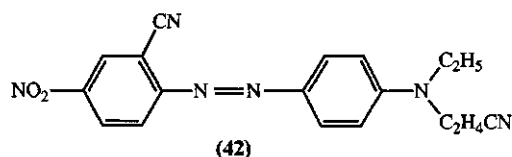


(40) (C.I. Disperse Violet 1)



(41) (C.I. Disperse Blue 6)

With the appearance of polyamide and polyester fibres the importance of the man-made textile fibres extended rapidly, seriously eroding the dominant position of cotton in the world textile market. The demand for disperse dyes grew considerably and supported extensive research leading to the development of dyes of higher fastness. Of particular importance have been advances in the chemistry of azo dyes, which have led to an extension of their colour gamut to cover most of the visible range, through the development of 2-cyano-4-nitroaniline as a diazo component, and bluish reds, e.g. (42), and bright blues, e.g. (43), are possible.



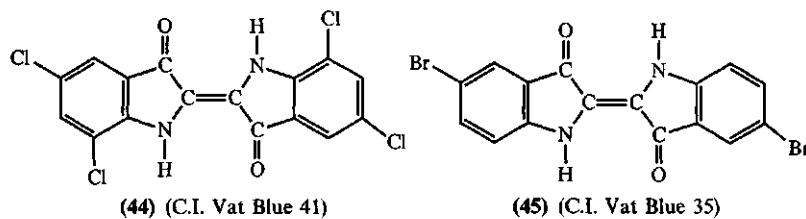
An important feature of the post-polyester developments has been the growth in the number of disperse dyes of higher molecular weight and lower vapour pressure. These have higher fastness, particularly to heat processing, than the earlier disperse dyes, but the effect of these factors is to reduce the aqueous solubility at normal dyeing temperatures to very low levels and to reduce the rate of diffusion of these larger molecules through the fibre, so that the higher dyeing temperatures are needed to complete the dyeing process in commercially acceptable times. Thus were developed high-temperature dyeing procedures carried out under pressure at temperatures of 130–140°C. It is interesting to note that at these temperatures and at dyebath concentrations the dyes are in solution for most of the dyeing time and the term disperse dyes, in a sense, no longer strictly applies.

It is a characteristic of textile coloration developments that a serious disadvantage in relation to one application can be turned to a positive advantage in another. In the case of the disperse dyes, the relatively high vapour pressure of many of these dyes has been put to good use in the development of sublimation transfer printing for polyester fabrics (de Plasse, 1972). This process had its beginnings in the early development of disperse dyes by Ellis and his colleagues in the 1930s, who observed that certain disperse dyes could be transferred by heat from a printed paper to cellulose acetate. This observation was of little practical value at the time, but particularly with the widespread introduction of knitted polyester fabrics the basis was created for the development of the early results into a fully-fledged

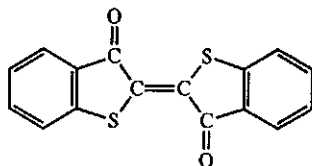
production process. In essence, a transfer printing paper is produced by printing a design on a suitable selected paper using a specially formulated ink, in which the colouring matter is a disperse dye selected for its volatility under high-temperature conditions. The paper is then brought into close contact with a polyester fabric under light pressure at 200–220°C for 20–30 s in a specially designed calender unit. When the paper is peeled off the fabric, the bulk of the dye is found to have transferred on to the fabric, which is thus decorated with the initial design in reverse. The available disperse dyes have been classified according to their degree of volatility as Class A, B, C and D dyes, and it is the dyes of Classes B and C which are useful for this application. Dyes of Class A are so volatile that it is difficult to preserve the integrity of the design during the transfer, while dyes of Class D have insufficient volatility for significant transfer. Although its use has declined since the polyester 'boom' of the 1960s, transfer printing remains a significant coloration process for polyester fabrics. While a limited number of new disperse dyes has been developed to fill in gaps in the range of dyes available for transfer printing, the great majority of new disperse dye developments have fallen into Class D.

### 9.3.6 Vat dyes

The vat dyes owe their name to their ancient origins in the application of indigo. It was discovered in the Bronze Age that by grinding the leaves of the woad or indigo plants in water and then leaving the paste to ferment, and adding an alkali (at that time derived from fermented urine, lime water or wood ash), a weakly coloured solution was obtained which could be used to dye textile materials. When the dyed fabric is exposed to air a durable blue colour develops. This is not the place to speculate by what ingenious chain of thought this complex path to a dyed fabric was discovered. Later, the blue colour, indigo, was isolated and became a marketable product after it was shown that the blue insoluble pigment could be solubilised by treating it in an alkaline reducing bath or vat to convert it to its soluble form, called the leuco form due to its pale colour (Greek leucos = white). Indigo remained the sole member of the class of vat dyes until its structure (13) had been elucidated. Following this, numerous indigo derivatives were prepared by halogenation, for example (44) and (45).



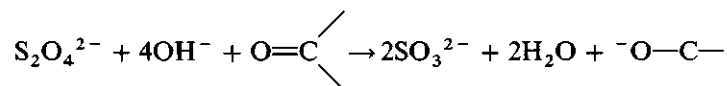
Later the thioindigoid vat dyes were prepared, in which the two —NH— groups are replaced by sulphur atoms, for example (46).



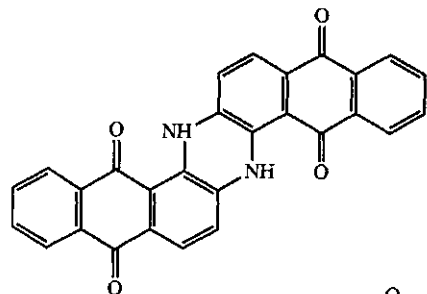
(46) (C.I. Vat Red 41)

However, after the production of synthetic indigo, the most important development in the vat dyes was the synthesis of the anthraquinonoid vat dyes in 1901 by R. Bohn. As with many important dyestuff discoveries, their first synthesis resulted from a failed attempt to produce something else. In this case it was Bohn's attempt to produce an analogue of indigo by the caustic fusion of 2-anthraquinonylglycine. Instead of indigo, what was formed was the blue vat dye with the structure (47). Over the next decades this important dye, which demonstrated the superiority of the polycyclic quinones over the indigoid dyes, was joined by anthraquinone derivatives, e.g. (48), anthrimides, e.g. (49), anthanthrones, e.g. (50), pyranthrones, e.g. (51), and dibenzanthrones, e.g. (52), as well as other condensed aromatic ring systems.

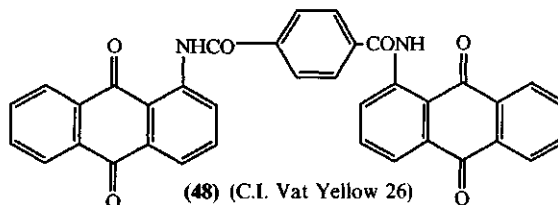
These chemical developments would have been largely academic if there had not been also great advances, made during the last thirty years of the nineteenth century, in the chemistry of vating. Up until that time, vat dye reductions had been obtained by treating the pigment by taking advantage of the reducing action provoked by the micro-organisms on fermentable sugars, fruit, etc., or latterly the reducing action of zinc in aqueous alkaline solution. In 1869, hydrosulphurous acid solution was first prepared and shown to be highly effective in reducing indigo when made alkaline. Dyeworks wishing to take advantage of this discovery had to prepare the substance themselves, but in 1898 solid sodium hydrosulphite, more correctly termed today sodium dithionite,  $\text{Na}_2\text{S}_2\text{O}_4$ , was manufactured. This reacts readily under alkaline conditions with the keto groups of vat dyes to form the leuco compound:



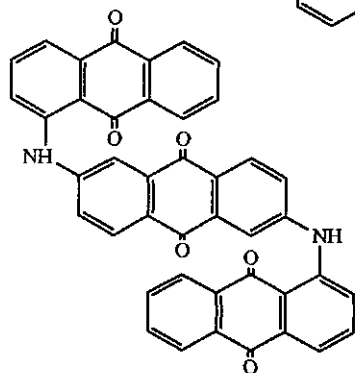
The vating reaction is heterogeneous, taking place at the surface of the vat dye pigment particles, and has not been fully elucidated. It is thought that the electron donor in the reduction is the  $\text{SO}_2$  radical. The vat dyeing process involves adding sodium dithionite to a suspension of the vat dye pigment and allowing the reduction to proceed before adding the leuco solution to



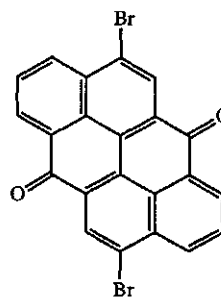
(47) (C.I. Pigment Blue 60)



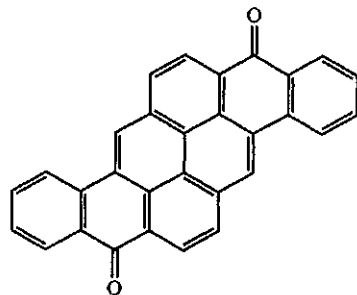
(48) (C.I. Vat Yellow 26)



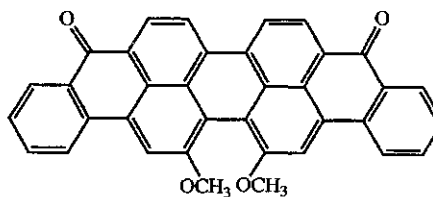
(49) (C.I. Vat Red 48)



(50) (C.I. Vat Orange 3)



(51) (C.I. Vat Orange 9)



(52) (C.I. Vat Green 1)

the main dyebath in which dyeing proceeds. It can be seen from the reaction scheme above that the reduction liberates acid, which slowly neutralises the alkali present. When, as is usual, the dyebath is exposed to the atmosphere, the reduction of the vat dye and the maintenance of the leuco solution compete with oxidation, so that careful supervision of the condition of the dyebath is needed.



The reduction reaction is normally accompanied by a large colour change, due to the extensive change in conjugation which accompanies reduction. In the indigoid series the shift is hypsochromic, while in the anthraquinonoid and condensed aromatic systems the shift is bathochromic. The conjugation can impose a planarity on the large molecule which is not present in the quinonoid form, and this can be a significant factor in the colour change occurring as a result of re-oxidation. This part of the vat dyeing process is no longer left to the slow action of atmospheric oxygen but is achieved rapidly using potassium dichromate, peroxides, etc. More than just the regeneration of the carbonyl form is involved in oxidation, however. The adsorption of the leuco planar molecule by the fibre involves extensive interaction of the molecular orbital of the dye with the polymer molecule, as will be considered in more detail later. Thus, oxidation may give rise to an isomorph of the dye which, though oxidised, is stabilised in a planar configuration by dye-fibre bonding. As a result the shade may be unstable to hot washing processes, as these will supply the necessary energy for the breaking of the dye-fibre bonds and complete reversion to the more stable non-planar form. When this occurs it is accompanied by a shade change. Additionally, the freshly oxidised dye will be in a state approximating to molecular dispersion, in which state the dye will have an unusually high solubility. Hot wet treatments lead to the growth of vat pigment microcrystals which have very low solubility, and this process also includes a shade change due to the change in the optical properties of the pigment dispersion in the fibre. In order to produce a dyeing or a print with a stable colour it is necessary to subject the coloured fabric to a hot washing or 'soaping' process.

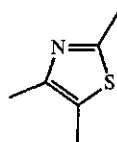
### 9.3.7 Sulphur dyes

Like the vat dyes, the sulphur dyes comprise water-insoluble coloured compounds that are solubilised by reduction. In the reduced state they are used to dye cellulosic fabrics, and after the dyeing stage is complete they are oxidised once again to the insoluble pigment form. The dyes are relatively cheap to produce and easy to apply. They were first prepared by entirely empirical methods using unknown starting materials of animal or vegetable origin. Sulphur dyes based on starting materials of known structure were introduced towards the end of the last century, but since the methods of preparation lead to complex mixtures of reproducible but uncertain composition, the structures and the chemistry of the sulphur dyes have not been evaluated as yet and their classification is based on their method of manufacture rather than their chemical structure. Three main methods are used in their preparation:

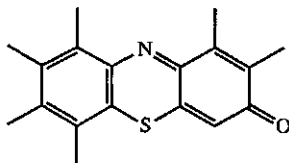
1. *Sulphur or polysulphide baking*, in which the starting materials are heated to temperatures in the range 160–320°C with sulphur or sodium polysulphide.

2. *Polysulphide melting or refluxing*, which involves heating the starting materials with aqueous sodium polysulphide under reflux or under pressure in a closed vessel.
3. *Solvent melting*, whereby the water in the melt process is replaced wholly or largely by a solvent such as 2-ethoxyethanol, butandiol or dioxitol.

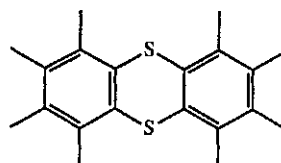
The dyes prepared by the baking method using sulphur are usually based on aromatic amines, mono- and di-amines, and their alkyl or acyl derivatives. Other compounds, for example, may be added to produce shade-modifying byproducts. The colour produced, generally yellow, orange or brown, is thought to be due to the presence of the thiazole (53), thiazone (54) or thianthrene (55) in the numerous coloured products formed. The dyes formed



(53)



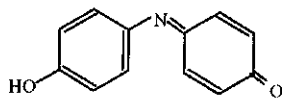
(54)



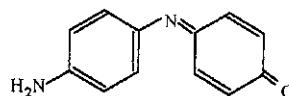
(55)

are polymeric in nature with disulphide bonds linking the individual coloured polymer units. In the presence of aqueous sodium sulphide these are reduced to ionised mercaptan ( $-S^-$ ) groups which solubilise the dye during the dye application. The baking with polysulphide method produces a slightly different range of compounds. It can be used with nitro and polynitro intermediates more safely than straight sulphur. The shades produced are usually brown or olive.

The melting on reflux process can be used to provide a much wider range of shades than the baking processes. Starting with 2,4-nitrophenol, a black dye is produced, C.I. 53185, which it has been suggested (Rys and Zollinger, 1972) is probably the most important single dye in production "amounting to 10% by weight of world production". Violet and bluish-green as well as black dyes can be made by starting with indophenols (56), and indamines (57) can be used as a basis for bordeaux and red-browns.



(56)



(57)

### 9.3.8 Azoic dyes

The azoic dyes are actually azo pigments synthesised inside cellulosic fibres in the course of the dyeing process rather than ready-formed colouring matters. The concept of colouring cotton by this method was developed in 1880 when T. and R. Holliday impregnated the fibres with an alkaline solution of  $\beta$ -naphthol and then with a diazo solution obtained from aniline and other primary aromatic amines, so that an azo pigment was formed within the interstices of the fibres. It was applied to the dyeing and the printing of the cotton a few years later (Kunert, 1912; Kunert and Acker, 1914). Although  $\beta$ -naphthol was extensively used in the early stages it has many disadvantages due to its very low affinity for cellulose, especially under the alkaline conditions needed to produce the water-soluble sodium salt. In addition, the azoic pigments formed from  $\beta$ -naphthol do not have good fastness to light. Despite this, the process was attractive because of the intense shades that could be produced, sufficiently attractive in fact to sustain interest during the twenty years it took before a naphthol with affinity, 3-hydroxy-2-naphthoic acid anilide, was developed. Prior to this development, fabrics impregnated with naphthol had to be dried before treatment with the diazonium salt solution in order to obtain an acceptable result. 3-Hydroxy-2-naphthoic acid anilide was marketed under the name Naphtol AS, and its use made it possible to dye cotton at 30°C and treat with the diazonium solution directly. A series of new coupling components with behaviour similar to that of Naphtol AS was rapidly developed. It should be noted that despite the use of the term Naphtol only a minority of the compounds developed contained a hydroxyl group. Initially the shades produced were orange, scarlet and red, but as new naphthols and also new diazotisable amines were developed an almost complete range of shades became possible. The original Naphtol AS remained, however, the dominant coupling component in cotton dyeing by this method, and an indication of the range of shades which could be produced using it is given in Table 9.1. The method adopted for the production of azoic prints involved preimpregnation and drying the fabric and then printing it with a thickened paste containing the diazotized amine. This left unchanged coupling component in the unprinted areas, and this had to be washed out.

**Table 9.1** The variety of shades produced with Naphtol AS using different diazo components

Diazo component	Shade
<i>o</i> -Nitroaniline	Orange
2,5-Dichloroaniline	Scarlet
<i>p</i> -Nitroaniline	Red
2-Methoxy-4-nitroaniline	Bluish red
Dianisidine	Reddish blue

The advantageous affinity which had been built into many of the new Naphtols developed for dyeing thus became a liability, although Naphtol AS itself and selected other coupling components could be used. The 3-hydroxy-2-naphthoic arylamides could not be used for the production of yellow shades and a new series of compounds, the acylacetic arylamides, was developed.

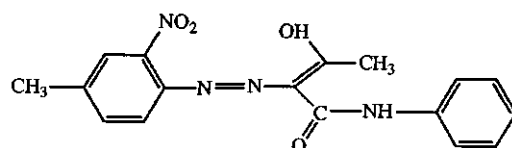
The production of an azoic pigment in the interstices of the fibre leaves a certain amount of surface pigmentation which must be removed to give a dyeing which does not have poor rubbing-fastness properties. In addition, the trapped pigment is in a very highly dispersed state which is not physically stable. Consequently azoic dyeings (and prints) need to be washed at the boil to remove surface pigmentation and also to enable the pigment particles to grow to a size with minimum solubility. In this state their lightfastness is maximised and their shade is stable to further washing treatments.

The extent to which azoic dyes are used has declined considerably due to two factors. Firstly, the appearance of reactive dyes for cellulose has made a full range of fast bright shades covering the whole colour gamut available to dyers, making the contribution of azoic dyes much less important. Secondly, the textile printing designs for which azoic dyes proved highly suitable for many years are now produced using resin bonded pigments or reactive dyes.

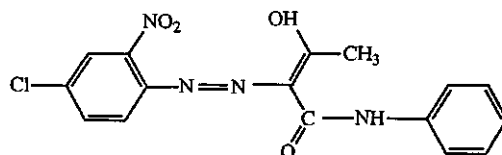
### 9.3.9 *Pigments*

The distinction between dyes and pigments is not as clear cut as might be supposed. Dictionary definitions are of little help. Chambers English Dictionary (1988) defines a dyestuff as 'a material used in dyeing' while a pigment is 'any substance used for colouring or that which gives colour to animal and vegetable tissues'. In the textile as well as the coatings field, pigments are regarded as insoluble colorants while a dye is a soluble colorant at least during some essential stage of application. Thus vat and azoic dyes, while colouring textiles by pigmentation, are applied from solution like other dyes, including the sparingly-soluble disperse dyes. Pigments are used in two ways to colour textiles. For the most part they are used together with binding resins to produce a surface coloration, primarily in printing applications, but also to some extent in so called 'pigment dyeing' processes. A second more limited application is in the mass coloration of man-made textile fibres during the spinning stage of manufacture. The main uses of pigments are in the production of paints, inks and mass-coloured plastic fabrications, and in these fields both inorganic and organic pigments are to be found. Their use in textile applications makes demands of a special kind on the stability of the pigments to hot alkaline washing, bleaching, etc., and consequently, apart from the black (carbon black) and white (titanium dioxide) pigments extensively used in textile printing, the pigments employed in textile coloration are synthetic organic materials.

The chromogens used in the production of organic pigments are the same as those used in making dyes. Early synthetic pigments were frequently the insoluble calcium, barium and magnesium salts of soluble acid dyes or the phosphotungstomolybdic acid salts of soluble basic dyes, both known generically as lakes. These are still in use in printing of ephemera but are of little value for textile applications due to their frequently poor light fastness and solubility in alkali. The majority of textile pigments are based on the azo chromogen which provides yellow, orange, red and brown materials. Yellows are generally derived from acetoarylamides, typical examples being (58) and (59).



(58) (C.I. Pigment Yellow 1)



(59) (C.I. Pigment Yellow 3)

Yellows based on tetrazotised benzidine were in use for some years but have been generally superseded on health and safety grounds. Red pigments for textile use are normally based on the naphthoic arylamides used in relation to the azoic dyes. Blue pigments are completely dominated by copper phthalocyanine and its derivatives.

The way in which pigments produce their coloured effect differs from that of dyes, and this has very important repercussions with regard to their manufacture. Dyes generally behave as if they were in solution, selectively absorbing incident radiation passing through an essentially transparent medium. Pigments, on the other hand, produce colour due to selective absorption of light reflected at the pigment particle surface and light penetrating the particle which is subject to multiple internal refraction before emerging. The refractive index of the pigment particle relative to that of the medium in which it is embedded is of great importance, because this will affect the degree of light-scattering and transparency of the coloration. The relative contributions of these factors to the final colour depends on the particle size and the production of a useful pigment involves finishing the

raw pigment to optimise colour strength and covering power. Some pigments immediately following their synthesis have very little colour strength and exhibit a very dull shade, both of which change dramatically when the particle size has been optimised. At the same time the surfaces of the pigment particles may also be modified by coating with dispersants and resins to enhance the dispersibility and the dispersion stability of the pigment in the medium in which it is to be used. Some pigment products contain as little as 50% of the colouring matter but have nonetheless enhanced colour strength. Covering power or the ability to hide the substrate is of great importance in many printing applications, since many of the fabrics printed may be strongly coloured.

Suitable pigment dispersions can be 'exhausted' on to textile by controlled destabilisation to deposit the pigment on the fabric surface. This was used extensively at one time to apply vat dyes to yarn packages by the Abbot-Cox process, now little used. However, ecological pressures on dyeing operations may lead to some revival of this approach, by using regular pigments and binders, because pigments potentially offer the advantages of high exhaustion efficiency and low effluent colour levels. Pigment dyeing is normally carried out by impregnating cotton fabrics with an aqueous dispersion of pigment and binder, drying and curing to polymerise the binder. No post-washing is needed and fixation is 100%. Achieving drying without migration of the pigment requires careful control. The binders used are generally acrylic- or polyurethane-based and of the same types as are used in pigment printing. Since pigment printing is the major textile use for these colouring matters, pigment binders are discussed in greater detail in the following section.

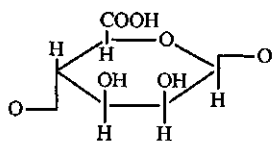
#### 9.4 Textile printing

In effect, textile printing involves localised dyeing processes in which a dye or pigment solution or dispersion is applied to the fabric in a design, and dyeing proceeds from the printed 'dyebaths'. Thus, the general principles and colouring matters involved are the same as those already discussed. However, the production of the printed design introduces new considerations as compared with general exhaustion processes, in particular the questions of thickeners, binders and procedural modifications made necessary by printing conditions.

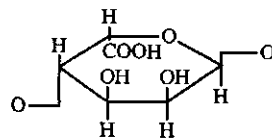
Textile printing is carried out using gravure rollers or more usually with rotary or flat screens. In the first method the ink is delivered to an engraved roller and excess is removed to leave ink only in the engraved indentations using a doctor blade. The roller is contacted with the fabric so that the ink is drawn from the engraved areas to produce the printed design. In screen printing a polyester or metal mesh is partially sealed to leave the design as an open area. The ink is delivered to the screen and then forced through the mesh using a metal or synthetic resin squeegee on to the fabric. A thickener

is necessary to ensure that the printed design is precisely located with clean defined edges. The flow properties of the ink have to be such that the ink can flow in and out of the engraving in the case of gravure printing or through the screen in a controllable manner in the case of screen printing. In the latter method the shear forces on the ink as it passes through the screen are very high and the high fluidity produced has to be lost through thixotropic behaviour rapidly enough to retain definition. Several other characteristics are essential in a successful thickener, not the least of which is ready release of the dye. The characteristics of print-paste rheology are too extensive for the present chapter and are covered elsewhere (Miles, 1995).

Numerous polysaccharides derived from starch-containing plants, seaweeds yielding alginates, plant gums, and cellulose derivatives, particularly cellulose ethers, are used as thickeners in textile printing. The alginates are of particular importance in the printing of reactive dyes, since they do not react with the dyes. This is due to the D-mannuronic acid (60) and L-glucuronic acid (61) monomer units, which not only lack the primary carbinol groups which react readily with the dyes, but also supply ionised carboxylic acid groups, which prevent the physical interaction with the anionic reactive dye molecules which is a necessary precursor to reaction.



(60) D-mannuronic acid



(61) L-glucuronic acid

It is also possible to make a print paste using an emulsion of white spirit in water. Normally a combination of emulsion and chemical thickening is used, because the thickener also performs the function of temporarily holding the dye and dyeing auxiliaries such as alkali, reducing agents, etc., *in situ* pending dye adsorption and fixation by steaming.

A combination of safety factors and ecological legislation has greatly eroded the popularity of white-spirit emulsions, which have become increasingly replaced by synthetic thickeners based on poly(acrylic acid) derivatives. Copolymers of methacrylic acid and ethyl acrylate dispersed in water under neutral or weakly acid conditions produce no viscous effect. Under these conditions the polymer chains are coiled randomly, but when the pH is raised the carboxylic acid groups along the polymer chains ionise, causing strong charge repulsion effects which straighten out the polymer chains and develop a structure in solution in which the distance between the chains is maximised. The resistance of this structure to deformation creates the viscosity required. The development of viscosity with this simple system has a very sharp end-point and its sensitivity to pH is too great for practical use. By using a

bifunctional monomer crosslinking is developed, which prevents the polymer from going into solution and a more satisfactory product is obtained. Since the thickening effect is produced almost entirely by coulombic intersections, the effect is always sensitive to the electrolyte concentration. This can create difficulties when thickening dye solutions, especially where the dye is a polyelectrolyte, for example a reactive dye. However, because of their marked effect at low solids levels, acrylic thickeners are very suitable for pigment printing, which in any case is the basis for 60% of textile printing world wide.

Pigment printing involves the application of a thickened dispersion of pigment containing a polyacrylic or polyurethane binder, which condenses during a baking treatment after printing and drying. Its great attraction, apart from simplicity, is the fact that prints do not need to be washed off and dried, fixation being 100%. Acrylic thickeners are available which combine to form part of the binding system. The binders, like the synthetic thickeners, are generally acrylic copolymers produced by emulsion polymerisation. According to this technique the unsaturated monomers are dispersed in water using appropriate surfactants and then caused to polymerise using free-radical initiators, e.g. potassium persulphate/sodium bisulphite. The polymer chains grow to a high molecular weight, which can be controlled by the addition of monofunctional blocking compounds. The polymer is produced in the form of an emulsion containing 40–45% solids, the surfactant controlling the dispersion size to 120–300 nm. When the emulsion is dried, flocculation takes place followed by coalescence to form a film. The film formation is a vital part of the development of a pigment print. The binders used are capable of forming a film at room temperature. It is necessary for the film, when cured, to have a strong adhesion to the textile, be resistant to abrasion and possess a high degree of flexibility. Copolymers of butyl acrylate and acrylonitrile have many of the required properties, although the resistance to solvents (e.g. dry cleaning) is reduced if too much butyl acrylate is used. Emulsion polymers based on butadiene are also used, as well as the reaction products of mono- and di-carboxylic acids with polyols. Emulsion polymers of polyurethanes have also been used. Binders and thickeners now available enable printers to produce very fast soft prints with a soft handle, and the simplicity and economy of application has led to pigment printing dominating textile printing world wide.

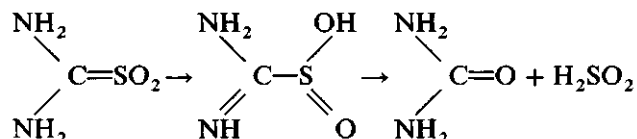
Of less importance than the printing of continuous-web fabrics but nevertheless of considerable importance is the printing of precut garment panels. These have to be printed by dry processing, but as approximately 40% of panels to be printed are predyed simple pigment printing cannot be used as this would not cover the ground shade adequately. Two processes are used instead. Firstly, an adaptation of the well-established process of discharge printing was developed by Green Print International under the name DisTron, which is effectively a dry process not requiring steaming or washing off. Like conventional discharge printing, it involves the incorporation



into a pigment printing ink of a reducing agent which, during the drying and curing process, substantially destroys the dyes in the ground shade. Reducing agents for discharge printing are related to sodium dithionite, as used in the dyeing of vat dyes, but processing high stability until the temperature is raised to 100–125°C, when they become active. The most generally used product is the zinc salt of formaldehyde sulphonylic acid. This is prepared by dissolving SO<sub>2</sub> gas in aqueous formaldehyde. The resulting acid solution can then be reduced using zinc and acetic acid to form the zinc salt:



This compound can be activated by dry heat to give a discharge print not requiring post-washing on cotton fabrics dyed with selected reactive dyes, usually but not exclusively of the vinyl sulphonyl type. Another agent that works very well, providing that steam heating is used to develop the discharge, is thiourea dioxide (C.I. Reducing Agent 11):



Both of these agents are also used in printing with vat dyes, since their stability at room temperature makes it possible to prepare a print paste stable to the atmosphere. The second method for printing dyed fabrics is the widespread but rather less satisfactory use of plastisol inks. These are dispersions of pigments in a base containing finely dispersed vinyl chloride copolymers in nonvolatile plasticisers such as di-octyl phthalate, tricresyl phosphate, etc. The inks contain as much as 60–70% of the plasticiser. The highly viscous inks lie on the fabric surface hiding the underlying fabric. They do not dry but on heating to 140–160°C they coagulate to give a dry print.

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