Dyestuff–fibre interactions

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INTRODUCTION

Dye–fibre interactions are varied and their strengths or combined strengths determine both the outcome and permanence of a particular dyeing. A deeper understanding of these interactions may lead the colour chemist towards the development of dye–fibre systems that are more environmentally friendly. This approach is especially necessary when dyeing cellulosic fibres with anionic dyes, since in many cases high concentrations of salt are necessary to achieve adequate dye uptake; in medium to full depths of shade, dye uptake is inadequate leading to problems of colour in water courses.

It is important to discuss the various types of molecular interactions that may occur in dye–fibre systems. For non-covalent interactions, the different forces between two molecules, like or unlike, are usually divided into the following categories [1]:

(a) *Van der Waals (VDW) interactions*. These define the size and shape specificity of the interactions and are the sum of dispersion and repulsive energies. The thermodynamic strength of the VDW interaction is less than 8 kJ mol^{-1} [1].

(b) *Electrostatic interactions between static molecular charge distributions*. In dyeing processes these include, for example, obvious attractions between protonated amino groups in polyamide fibres and sulphonated anionic dyes. However, according to classical definitions, they also include hydrogen bonding interactions [2]. A recent review points out that this may be an inadequate definition [3] but for the purposes of this paper it is suitable. The hydrogen bond strength varies considerably but for neutral molecules it is 10–65 kJ mol^{-1} and when one of the components is ionic it rises to 40–190 kJ mol^{-1}.

(c) *Induction forces*. These arise, to quote Hunter [1], from the interaction between molecular charge distribution of one molecule and proximity-induced change in the charge distribution of the other; such forces are very small and can be disregarded in terms of the dye–fibre interaction scenario.

(d) *Charge transfer stabilisation*. This arises from interaction of a ground state (AB) with an excited state (A^+B^-). Again such interactions are so weak that they may be omitted in this analysis.

(e) *Solvophobic or hydrophobic interactions*. Hydrophobic interactions play an important role in determining both dye uptake by fibres and subsequent wet fastness in the aqueous dyeing systems upon which this article concentrates.

Since dyes and fibres such as wool, silk and polyester contain aromatic residues it is worthwhile to consider current thinking regarding π–π interactions. Hunter [1] points out that charge transfer and electron donor–acceptor effects are commonly used to explain interactions between two or more aromatic molecules, but current evidence shows that these are negligible compared to electrostatics [4].

Many people hold the view that, since aromatic molecules are planar, maximum VDW interactions occur in a perfectly flat stacked arrangement; in water, hydrophobic interactions will also favour stacking since the flat π-electron surfaces of the molecule are non-polar [5]. Thus papers [6] on dye-aggregation in aqueous solution tend to draw the aggregates as perfectly stacked molecules with maximum free aromatic ring overlap. Hunter and Sanders [7] have studied the geometry and energy contour plots of two stacked porphyrins and noted that the aromatic residues were in an offset or staggered arrangement. To explain these observations the authors concluded that electrostatics provide a large repulsive force, which pushes the π-systems away from the usually accepted maximum overlap position; the best model involved a positively charged σ framework sandwiched between two idealised π-atoms. Continuing this analysis led Hunter [1] to the conclusion that certain face-to-face arrangements of aromatic systems lead to repulsion and other arrangements, such as face-to-edge and offset, lead to attraction; he was thus able to construct a very useful diagram (reproduced in Figure 1).

This new way of thinking about π–π interactions [1] allowed a ready explanation of the characteristic herring-bone packing of aromatic hydrocarbons in the crystalline state [8] and also explained the phenylalanine–phenylalanine geometries found in X-ray crystal structure analysis of certain proteins [9].

The maximum electrostatic interaction for two π-electron systems was subsequently calculated as 6 kJ mol^{-1}, which is relatively weak. However, dyes are polyaromatic systems and in fibres such as wool, silk and hair the aromatic sidechain residues in phenylalanine, tyrosine and tryptophan often occur in the same region. Thus the

* Paper presented at the Society of Cosmetic Scientists Symposium, 'Keratechnics – Affairs of the Hair', Eastbourne, 24/25 April 1995.

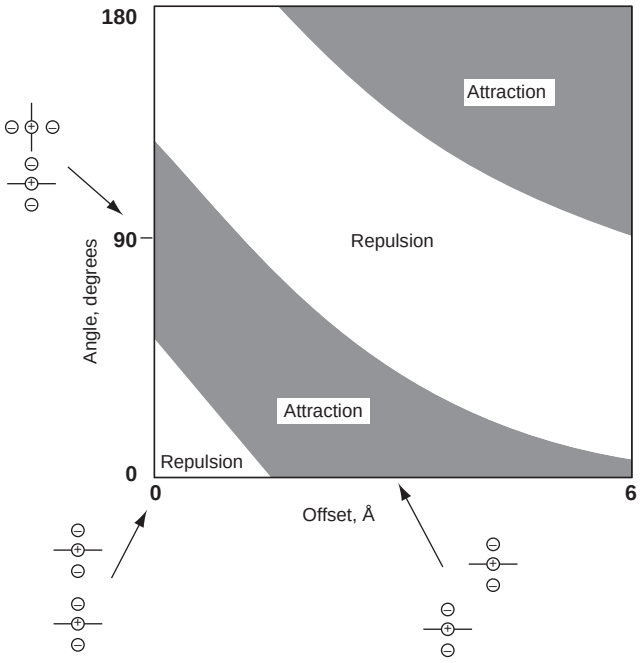


Figure 1 Electrostatic interaction between two idealised π-atoms as a function of orientation; two attractive geometries and the repulsive face-to-face geometry are illustrated [7]

overall small contributions when summed become significant.

In order to demonstrate the above principles and to introduce new concepts, this article is divided into the following sections:

(a) The uptake of anionic dyes by polyamide fibres
(b) The uptake of planar anionic 'direct' dyes on cellulosic substrates
(c) The special case of dyes that form covalent bonds with the substrate ('reactive' dyeing)
(d) Dyeing nonionic disperse dyes on hydrophobic and hydrophilic fibres.

THE UPTAKE OF ANIONIC DYES BY POLYAMIDE FIBRES

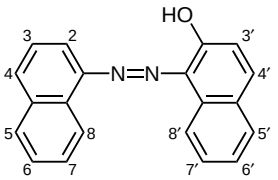
It is widely presumed that, under acidic conditions, the dyeing of polyamide fibres with anionic mono or polysulphonated dyes ('acid dyes') is described by an electrostatic attraction between the anionic dye and the protonated, hence cationic, fibre. This assumption forms the basis of the classical Gilbert-Rideal analysis. Dyeing of wool or nylon for example is normally achieved by applying these dyes from weakly acid solution at the boil; however, colour chemists quickly realised that anionic dye molecules were not absorbed solely by ionic interactions, but that solvophobic or hydrophobic interactions were also important. Working on wool, Meggy [10], Zollinger [11] and Meybeck and Galafassi [12] demonstrated the importance of hydrophobic interactions, both between dye and hydrophobic sidechains in the fibre, and between dye molecules themselves.

Hydrophobic interactions were employed to describe the phenomenon of nylon 'overdyeing' [13,14]. In particular White [14] employed model dyes with differing degrees of sulphonation (Figure 2) and, using radio tracer analysis, followed their uptake on nylon 6.6 film. It was clear from this analysis that the order of overdyeing was monosulphonate, followed by disulphonate and then trisulphonate. The tetrasulphonate dye, CI Acid Red 41, showed no tendency to overdye.

In none of the above analyses was attention drawn to the anomaly that in aqueous systems hydrophobic interactions break down above about 60 °C and all of the above dyeings were produced at the boil; it is therefore proposed that aromatic or π–π interactions are largely responsible for these effects and have often been omitted from previous analyses. In the cases of nylon 6 and nylon 6.6, it has to be noted that there are no aryl groups present in the fibre and thus, at first sight, π–π interactions of the dye with the fibre are not possible; however 'dyed fibre' is a different substrate, as sorbed dye possesses aryl groups capable of undergoing π–π interactions with newly sorbed dye molecules.

Such is the importance of the above that Joy [15] has been able to dye human hair at pH 10 at 40 °C with the dyes shown in Figure 3. Polysulphonated versions of the dyes, however, showed little coloration of the hair under these conditions; clearly sulphonic acid groups on the benzene ring weaken π–π interactions. Hunter [1] has discussed the important effect of heteroatoms on polarisation and π–π interactions but the influence of sulphonic groups has yet to be fully clarified.

Clearly under these conditions both hydrophobic and aromatic π–π interactions are playing the major role as the



CI Acid Red 88	4-sulphonate
CI Acid Red 13	4,6′-disulphonate
CI Acid Red 18	4,6′,8-trisulphonate
CI Acid Red 41	4,3′,6,8′-tetrasulphonate

Figure 2 Structures of dyes employed by White [14]

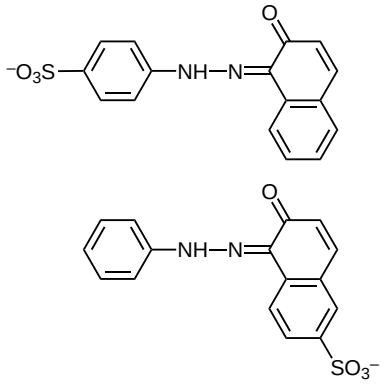


Figure 3 Hydrophobic acid dyes for dyeing keratin [15]

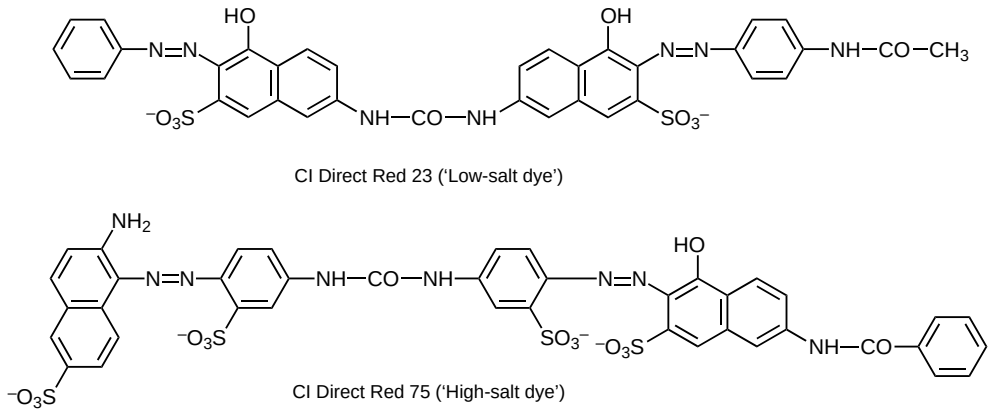


Figure 4 Direct dye structures and salt dependence

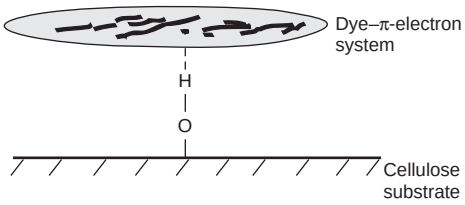


Figure 5 Schematic representation of Yoshida forces

driving force in the dyeing process; it is inconceivable that the protein will be protonated at this pH and will thus carry a large negative charge. These results are in accord with those of McIntyre [16]. The dyeing of polyamide fibres thus represents a continuum of interactions; for example under acidic conditions simple acid dyes will dye by electrostatic forces but as the pH moves upwards hydrophobic and π–π interactions will increasingly tend to predominate [17]; the magnitude of these effects depends greatly on the degree of sulphonation of the dye and, more especially, on the presence of an unsulphonated benzene ring.

THE UPTAKE OF PLANER ANIONIC 'DIRECT' DYES BY CELLULOSIC SUBSTRATES

Much has been written on the apparently strange substantivity of planar conjugated systems for dyeing cellulosic fibres [18,19] and the discussion will not be repeated in this article. The substantivity of planar anionic polysulphonated dyes for the negatively charged substrate was established empirically and a precise explanation of the phenomenon has yet to be given.

In the light of the new ideas on π–π interactions in solution it may be possible to further clarify why some direct dyes are substantive to the fibre in the presence of only a little electrolyte (0–10 g/l NaCl) whereas others require a relatively large salt addition (80–100 g/l NaCl) to achieve reasonable dye uptake. Typical structures that exemplify this are shown in Figure 4. Clearly the disulphonated 'low-salt dye' is more hydrophobic in character than the tetrasulphonated 'high-salt dye'; in the case of the former dye there also exists increased possibility for π–π interactions both in solution and in the fibre.

So-called Yoshida forces have been invoked to explain direct dye–cellulosic fibre substantivity [20]; Yoshida proposes a direct hydrogen bonding of the substrate with the extended π-electron system of the direct dye molecule; schematically this may be shown as in Figure 5.

Strong support for Yoshida's mechanism comes from Hunter's review [1]. If π–π interactions are considered in the wider context of electrostatic interactions then the existence of π-facial hydrogen bonds in direct dyed cotton appears very likely. Hydrogen bonds form part of a hierarchy of electrostatic bonds [21] varying from strong to weak; intermediate strength is shown by hydrogen bonds such as C–H- - -O and π-facial bonds which, for the direct dye–cellulose system, may be represented as shown in Figure 6 [22].

Figure 6 indicates that, given the choice, aromatic residues in the dye are more likely to hydrogen bond with the substrate –OH groups than hydrogen bond with themselves; this does not, of course, preclude π–π interactions as a strong association force.

'REACTIVE' DYEING SYSTEMS

Reactive dyeing differs from all other applications of water soluble dyes insofar as the final goal is to achieve a dye–

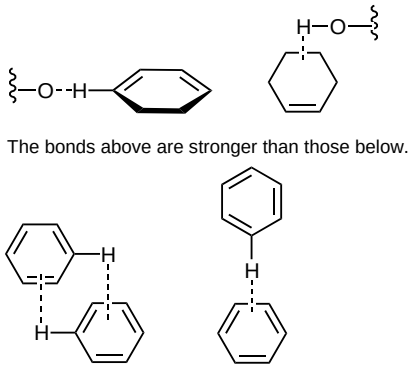


Figure 6 Hierarchy of hydrogen bonds

fibre covalent bond. The covalent bonds produced are usually of the following type:

where X represents the fibre nucleophile involved in the nucleophilic addition or substitution reaction. The energy required to break these bonds is of the order of 70–200 kJ mol^{-1}, which explains their excellent wash fastness properties.

Reactive dyeing of polyamides

In the case of wool dyeing with reactive dyes, mildly acidic conditions are used and the fibre nucleophiles involved are amino and thiol residues. Since these applications are carried out under mildly acidic conditions there is no problem of hydrolysis due to the competing OH nucleophile, and thus wool dyeing with reactive dyes is capable of giving extremely high levels of covalent bonding efficiency (>90%) [23].

In the case of vinyl sulphone dyes, a competing reaction with hydrogen sulphide, produced by the hydrolytic breakdown of cystine disulphide, leading to small amounts of inactive thioether dye, has been identified by Lewis and Smith [24]. It is expected that other types of reactive dye would also be rapidly inactivated by hydrogen sulphide; thus halo-*s*-triazines, α-bromoacrylamides and vinyl sulphones would give either a thiol triazine, a thiirane or a thioether dye respectively. The ability of wool reactive dyes to scavenge hydrogen sulphide explains their fibre protective effect when dyeing wool in medium to full depths; damage is related to the extent of the thiol–disulphide interchange or 'setting' reaction, which is promoted by the hydrogen sulphide produced due to cystine degradation in hot aqueous media.

Dyeing nylon with reactive dyes leads to lower fixation levels in medium to deep shades than similar dyeings produced on wool; this problem stems from a paucity of nucleophilic end-of-chain amino groups. The average amino group content of nylon 6.6 is 0.036 moles per kilogram of fibre; it can readily be demonstrated that dyes that contain an activated double bond and that react by a nucleophilic addition mechanism are capable of double addition at the end-of-chain amino group. For example, Figure 7 shows the reaction of nylon with a vinyl sulphone reactive dye. Double addition means that the maximum depth of shade achievable with a mono-functional vinyl sulphone dye of molecular mass 500 is 3.6% pure dye o.w.f.; in practice, lower values will be recorded due to the build up of negative charge from the sulphonate groups on the fixed dye molecules, giving rise to strong electrostatic repulsion effects. Development of disperse vinyl sulphone reactive dyes [25] and cationic vinyl sulphone dyes [26] would thus be worthwhile objectives.

Interestingly, species II in Figure 7 may not be very stable to acid boiling conditions since it may β-eliminate to reform the reactive vinyl sulphone dye; this reaction is

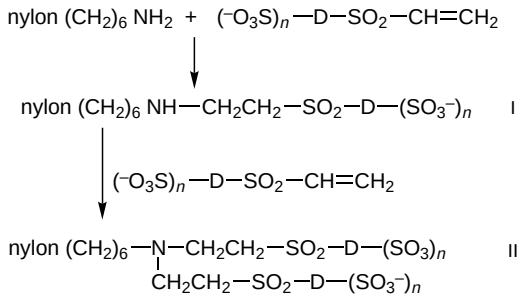


Figure 7 The reaction of nylon with vinyl sulphonyl dyes, where D represents a chromophoric residue

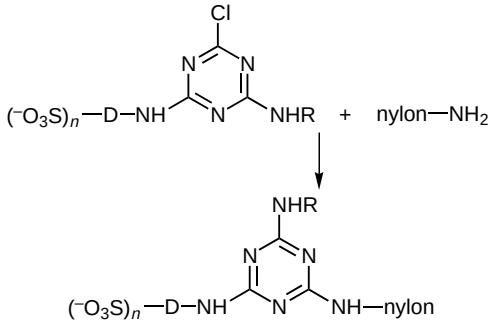


Figure 8 The reaction of nylon with monochloro-*s*-triazine dyes

well documented in the case of *N*-methyl-taurine-ethyl sulphone dyes, sold by Hoechst as Hostalan E reactive dyes. These secondary amine blocked vinyl sulphones were designed to β-eliminate to the reactive vinyl sulphone dye on boiling at pH 5–6 [27].

Other common reactive dye systems based on halogenated nitrogen heterocycles (e.g. monochloro-*s*-triazines (MCT)) will not give even moderate build up since they are capable of only single reaction with a primary amine group. Thus a monochloro-*s*-triazine dye of molecular mass 500 will maximally give a fixed dyeing of 1.8% pure dye o.w.f.; the same problem described above, involving fixed sulphonate anion build up as reaction proceeds, will make this limit even less attainable in practice. The MCT dye will fix to nylon 6.6 as shown in Figure 8.

Reactive dyeing of cellulosic fibres

Most reactive dyes are covalently fixed to cellulosic fibres under alkaline conditions, since it is necessary to dissociate the hydroxyl groups to form the required amount of sufficiently nucleophilic cellulosate anions. There is, however, a major disadvantage in working under alkaline conditions in that the competing hydrolysis reaction with the hydroxide nucleophile results in the production of inactive hydrolysed dye. Molecular engineering to incorporate two or more reactive groups in the dye molecule [28] increases the likelihood of dye–fibre reaction; even so, in deep shades significant dye wastage occurs. The latter phenomenon is not only due to hydrolysis but is related to a build up of negative charge on the cellulosic fibre due to covalent fixation of

polysulphonated dye. Figure 9 demonstrates this situation for an MCT dye.

Environmental considerations are prompting the colour chemist/textile chemist to produce modified dye–fibre systems which do not suffer from the above problems of relatively low fixation and poor dye uptake. Reactive dyes of higher substantivity may be one solution [29] for long liquor applications, perhaps coupled with a polyamine aftertreatment. The latter products, being cationic, increase wet fastness due to the formation of ionic bonds between the cations and the sulphonate groups in the dye.

Alternative approaches have included the modification of the cellulosic substrate to incorporate amino residues [28,30], thus producing a fibre that behaves in a manner similar to wool. Advantages of these suggestions include the possibility to dye and fix most reactive dyes under neutral conditions in the absence of salt; disadvantages include the cost of the pretreatment and, in some cases, the toxicity of the pretreatment agent.

A rather different approach has involved the use of 'reactive fibres' rather than reactive dyes but in this case it is necessary to prepare a suitably nucleophilic dye; such dyes may readily be prepared by the reaction of existing reactive dyes with ethylene diamine or by the reaction of vinyl sulphone dyes with ammonia [30].

Typically substrates have been modified with *N*-methylolacrylamide and 2,4-dichloro-6-(2-pyridinium-ethylamino)-*s*-triazine (DCPEAT) [30,31].

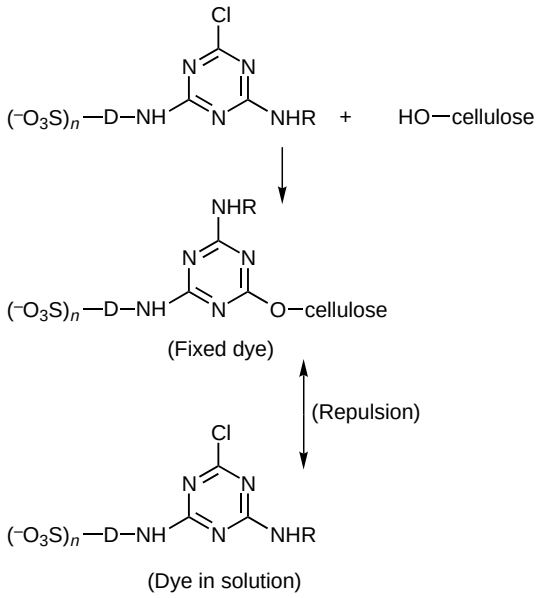


Figure 9 Build-up of fixed anions on cellulosic fibres leading to repulsion of dye in solution

DISPERSE DYEING OF NATURAL FIBRES

Nonionic disperse dyes have little substantivity for natural polyamide and cellulosic fibres. Modification of such fibres to increase the substantivity of nonionic disperse dyes is desirable for two major reasons. Firstly, disperse dyes are widely employed in the sublimation transfer printing process and so suitable modification of cellulosic fibres would provide an extended use of this process. Secondly, polyester/cotton blend fabrics are highly popular apparel fabrics and a method to dye such blends with a single class of dye would be valuable. At the present time, the polyester part of the blend is dyed using disperse dyes, whilst the cotton part is frequently dyed using water soluble reactive dyes. Such processes are expensive and time consuming, especially if using two-step methods involving first dyeing the polyester portion with the disperse dye at 130 °C, reduction clearing, dropping and resetting the bath, reactive dyeing the cotton portion and finally clearing unfixed dye.

A number of workers have shown that increasing the hydrophobic character of cotton cellulose and natural keratin fibres gives a fibre that is more readily dyeable with disperse dyes. The hydrophobic character of such fibres and their potential for π–π interaction with disperse dyes can be increased by reactions that incorporate bulky aryl residues in the fibres.

Natural cellulosic fibres may be acylated by the Shikibo-Uni process [32,33] involving sequential treatment with 20% sodium hydroxide solution and benzoyl chloride. The use of benzoyl chloride as an acylating agent is unsatisfactory due to its hazardous, lachrymatory nature.

Thomas [34] demonstrated that activated phenolic or mercapto esters of carboxylic acids reacted with cotton cellulose at high temperatures (150–200 °C) to form the cellulose-carboxylic acid ester. The esters employed by Thomas were water soluble due to the presence of pendant carboxylate groups and so may be applied to cellulosic fabrics under mill processing conditions, the reaction with cellulose being promoted by a baking procedure in thermosol equipment. Examples of water soluble reactive esters prepared by Thomas included sodium benzoylthioglycolate (BTG) and sodium benzoylsalicylate.

The use of highly lachrymatory benzoyl chloride is not advisable for industrial processing; Broadbent and Lewis [35] therefore prepared the above-mentioned water soluble benzoylthioglycolate and studied its reactions with cotton. A pad–bake procedure was employed since this agent is non-substantive; the effect of baking time and temperature on the colour yield (*K/S*) of the subsequent disperse dyeing with CI Disperse Blue 183 is shown in Figure 10.

Clearly a viable level of reaction (BTG with cotton) is achievable at 200 °C for 60 s. A linear relation was subsequently found between *K/S* and the degree of substitution (DS) (based on Ar–CO– groups); using the BTG pad–thermosol technique it was difficult to exceed a DS of 0.09, which gave a *K/S* value of 9.25.

Einsele, Sadeli and Herlinger [36,37] showed that a degree of substitution between 0.15 and 0.25 for benzoylated cellulosic fabric gave optimum disperse dye substantivity. According to Thomas [34] such benzoylated cellulosic fabrics could also be dyed with selected acid and 2:1 premetallised dyes. For a degree of substitution of 0.12,

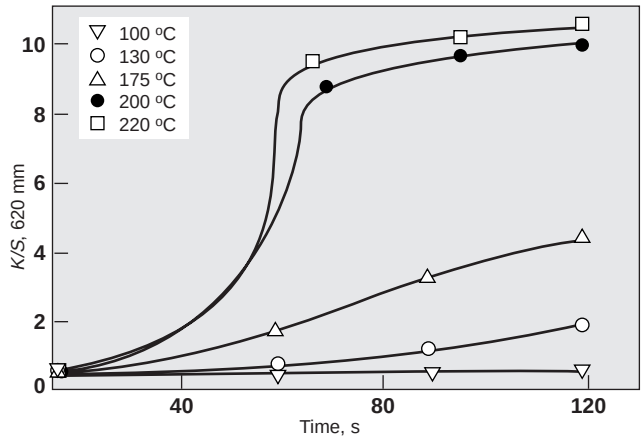


Figure 10 The effect of baking time and temperature on the colour yield of a disperse dye on BTG modified cotton (+ 2% Na_2CO_3)

approximately 3% of the cellulosic hydroxyl groups would be modified. A DS in the region of 0.12–0.15 is required to give a modified fabric that can be effectively transfer-printed with sublimable disperse dyes, but in order to achieve good wash fastness properties, a degree of substitution in the range of 0.3–0.4 is required [38].

In addition to showing improved disperse dye substantivity, cellulosic fabrics modified by incorporation of bulky hydrophobic residues possess improved thermal stability, improved crease and wrinkle resistance, and improved wash fastness of disperse dyeings, and also show a slight decrease in water retention properties.

CONCLUSIONS

This article has demonstrated that given a deeper understanding of dye–fibre interactions progress can be made towards designing, through chemical changes, both fibres and dyes to maximise desirable characteristics of dyeing systems. These systems may not be those in current use but one can imagine, for example, the dyeing of wool or cotton with disperse dyes, which has important technological implications.

Equally the cosmetic chemist may be able to modify human hair so as to increase the uptake and subsequent wet fastness performance of disperse dyes.

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