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Environmentally responsible dye application

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4.1 Introduction

Dyes have been applied to textile and other substrates for thousands of years, and dyers and their suppliers have continually sought to develop new processes and products that lead to better results or lower costs, in turn translating into commercial gain. Over the last few decades, the environmental impact of those products and processes has become an increasingly large part of the dyer's task. Given the growing emphasis on the environment, it is common to have almost any technical advance in the application of dyes, be it dye, auxiliary, or machine, claimed as environmentally beneficial, however spurious such a claim might be. Distinguishing real environmental advantage from apparent is not easy.

In seeking to achieve environmental responsibility in dye application there is no single solution since there is no single definition of what is green, or environmentally responsible. Even in a rare case where a dyeing operation is planned from first principles with environmental responsibility as a main goal, the best approach might be widely debated. More realistically, existing operations can be made 'greener' in many ways, with the different approaches each tending to answer a particular perceived impact. Local circumstances will often dictate which path is the preferred one. A recurring theme in the efforts to become more environmentally responsible is one of swings and roundabouts; a change made in one aspect of a dye application process for environmental reasons can often (negatively) impact another part of the process.

Environmentally responsible dye application involves the principles of pollution prevention that were developed and promulgated in the early 1990s with the hierarchy of 'reduce, reuse, recycle'.[1] This replaced the earlier 'end-of-pipe' response to growing environmental legislation.

A common mantra of the environmentally concerned is 'think globally, act locally', and this readily applies to dyeing and associated operations. A dyehouse may have limited impact on the immediate locality if its air emissions and wastewater are uncontaminated (or minimally so). For the former, volatile organic compounds (VOCs) and odour are the usual concerns. The main problems centre on water, where biological and chemical oxygen demand (BOD, COD), pH, total dissolved solids (TDS), temperature, oil/grease, heavy metals and colour are typically regulated. Since local government and nearby neighbours are the immediate constituencies to which a dyer has to answer, modifying processes to meet the legal limits for these pollutants is the starting point, and essential to staying in business. Unfortunately for the bigger picture, most limits are expressed as concentrations in waste water rather than as total mass or mass per unit of production, which encourages wasteful use of water and 'dilution as the solution to pollution.' Simple local environmental responsibility may come, therefore, at the cost of inefficiencies of water or energy, machinery, or the use of dyes and chemicals whose use is benign but whose synthesis creates pollution elsewhere. Thus, simply meeting regulations ('being as bad as the law allows') cannot be considered as environmentally responsible, and dyers must be creative and ingenious in modifying processes to go beyond what the law requires, and to minimise the effect of their work on a much larger scale.

To be effective and justifiable, broad and general changes, such as in the reduction of water and energy consumption or the reduction in mass of chemicals used or discharged, should be based on solid data, and ongoing environmental audits should be a routine. They will provide a baseline against which to measure progress, and may reveal financial as well as environmental advantages.[2]

The global impact of a locally 'clean' operation may be considerable, and it is ultimately worth considering to whom or what group environmental responsibility is answering. It may simply be a case of conscience, of 'doing the right thing.' It may also be in response to the demands of the customer who wishes to proclaim a product 'green'.

Environmental acceptability in textile products generally falls into one of two categories. The first and simplest to demonstrate is that the product will not harm the user, or harm the environment in use. A primary example is the Oeko-tex 100 scheme that certifies items being sold as environmentally sound, based on what is present or might be released from them.[3,4] The second category of greenness is based on the environmental impact of the production of the item: from cotton field or fibre factory to end use, and beyond to ultimate disposal. For some products, such a 'life-cycle analysis' is feasible, and produces clear results. The textile chain is long and complex, and weighing the balance of all the alternatives makes life cycle analysis for textiles difficult if not impossible. Which is worse: an antimony catalyst used in the production of polyester, or the herbicide applied to cotton? Obviously, the application of dyes is a key component in any such analysis, considering the effect of the application itself, and the fate of the dye when the item is composted or recycled. Efforts to judge textile materials' environmental impact in the architectural field have led the way and have begun to spill over into the apparel market.[5]

4.2 Background and scope

The general theory and practice of the application of dyes to fibres has been extensively covered in many standard sources.[6–8] These cover the different types of dye available, the various fibres to which they can be applied, and the types of machine used for the application at various stages of fabrication from fibre through to garment. The following discussion largely assumes the reader's familiarity with this background.

Since it is often the task of the dyer to prepare materials before dye application to ensure satisfactory results, and decisions about preparation can be taken in conjunction with dye application to minimise environmental impact, preparation is included in this discussion. Similarly, although textile printing is distinct from dyeing, as it involves the application of colour to textiles and shares the same preparation processes, it is given brief consideration here.

4.3 The influence of environment on the dyer's task

The aims of a dyer are to achieve the correct shade and fastness properties on a substrate in a level manner as efficiently and profitably as possible. Process changes to improve environmental responsibility can affect each of these aspects.

4.3.1 The correct shade

A dyer is usually trying to match the colour of some 'standard'. This may be electronic, in the form of reflectance data, or a real physical sample of coloured material. As the textile supply chain has become global, the move to numerically based standards has accelerated. In either case, the dyer should know under which light source the match is to be judged. It is helpful if the standard is as colour-constant as possible under different lighting conditions.[9]

Achieving a specific colour typically involves a mixture of three dyes. The usual dyeing primaries comprise a 'trichromie' of yellow, red and blue. A dyer will often have a preferred set of 'workhorse' primaries that have good dyeing behaviour and from which the widest range of shades can be economically obtained, along with additional dyes for specific requirements of shade, fastness or metamerism. Metamerism can be reduced by the choice of dyes used to create the colour, but not completely eliminated if different colorants are used to make the match than are present in the original standard. The mixture used should be formed of dyes that have compatible dyeing behaviour so that level dyeings are easier to obtain. If environmental factors limit the choice of dyes to be used, it can become more difficult to produce a non-metameric match and a compatible trichomie can also be more elusive.

The choice of dyes and the amount of each to be used (the 'recipe') can be based on trial and error laboratory scale dyeings, and/or an instrumental (spectrophotometer + computer) match prediction system (IMP). Recently, systems of standard colour swatches with associated recipes have been introduced. In addition to the quantities of dye required, a commercial dyeing recipe includes all the other variables that are under the dyer's control. These include the additives to the dyeing (auxiliary chemicals such as electrolyte, pH adjustment, levelling agents etc.), the time/temperature profile and the liquor ratio. Some of these may be dictated by the machinery available, for example, the liquor ratio and the degree of agitation. These in turn might control the rate at which the temperature can be increased. It is sometimes thought surprising that dyeings are rarely completely reproducible, but a well-known 'fishbone' diagram of the variables that can contribute to shade variation and that should be controlled makes it clear that dyeing consistent shades is not easy.[10] Dyers routinely add less dye than is required by the recipe, and make an 'add' to correct the shade. 'No-add' dyeings are sought after: a loftier ideal to which well-controlled dyehouses aspire is 'blind dyeing' where the goods are removed without being checked for shade. No-add and blind dyeing represent a level of environmental responsibility by minimising energy consumption.[11–13]

Given that dyeings are rarely completely reproducible, the question arises 'how close is close enough?' Instrumental colour measurement is now capable of making this judgement objectively, and more reliably, than the human eye, although getting to this point has taken much effort.[14] The CMC (2:1) colour difference equation developed in the 1980s has become the most widely used in the textile world. Objective passing of shades requires that the customer accept the method, and that dyer and customer agree on the pass–fail tolerance. As the textile supply chain has become global, the use of objective shade acceptance has necessarily increased, but instances remain when a subjective customer intervenes and tolerances shift with the demand for product. Dyers making repeated adds to get perfect matches waste valuable resources and risk damaging the substrate. Customers who accept objective shade passing, or who do not insist on unrealistically tight colour tolerances contribute to environmental responsibility by providing the dyer with known and achievable end points, thus limiting the time (and energy consumption) of the process.

4.3.2 Level dyeing

A level dyeing refers to one in which dye is distributed evenly throughout the substrate. Strictly speaking, each fibre should be fully and evenly penetrated, but this is rarely achieved in practice. Fibres in the middle of a yarn are often dyed lighter than those on the outside, and yarns within a fabric may have pale areas where they cross each other. As long as the overall appearance is level, such micro-unlevelness is acceptable. Unlevelness on a larger scale, unless it is a deliberate decorative effect, is not acceptable. Dyeings may have streaks, spots, crease-marks, as well as more gradual and subtle variations from side-to-side, side-to-middle, back-to-front, or end-to-end of a fabric. Unlevelness may render a material unsaleable, or require reworking which once again consumes additional energy, water and chemicals. Unlevelness can often be traced to poor fabric preparation ('well prepared is half dyed'). In manufactured fibre fabrics, unsuspected dyeability variations, from 'mixed merges', may be present. Beyond that, levelness relies on the use of the correct procedure based on the substrate, and the agitation provided by machinery being used. The use of compatible dye mixtures is desirable, especially in pale shades. Any limitation of dye choice for environmental reasons can make this more difficult.

Levelness derives from level initial padding of dye for a continuous dyeing, or an even initial 'strike' in batch (exhaust) dyeing. Conditions (temperature rise, pH, auxiliaries) can be adjusted in batch dyeing to achieve this. Levelness can also come from migration ('levelling') of low affinity dyes during batch processes extending the time of dyeing to 'even out' an initial rapid (unlevel) application.

Attempts to improve environmental responsibility and make processes more efficient by using higher rates of heating and cooling, by using low liquor ratios, or by adjusting conditions to achieve maximum exhaustion, all increase the risk of unlevelness. Unlevel dyeings may need to be stripped and redyed, wasting resources and risking damage to the substrate.

4.3.3 Fastness

Fastness is the resistance of a dye to removal or destruction. In both industrial processing (finishing, for example) and in ultimate use, a textile might meet a range of challenges. Standard laboratory tests put forth by, e.g. ISO or AATCC correspond to these agencies and predict their effects.

Fastness is achieved mainly by the selection of dyes. As with the issues of shade and levelness, restriction of dye choice for environmental reasons can limit the fastness achievable. Fastness also depends on the removal of hydrolysed reactive dye or any dye that remains loosely bound to the fibre surface at the end of the dyeing process. The use of rinsing processes that are efficient in water and energy use can reduce the impact of these rinses. Subsequent finishing processes should also be carefully controlled, since under the conditions of finishing, dye desorption can take place, and recontaminate the fibre surface. Customers can contribute to a reduced environmental impact by not requiring excessive or unnecessary levels of fastness.

4.3.4 Efficiency and environmental responsibility

Dyeing is a commercial process, and a notably competitive one, and success depends on achieving all the above factors (shade, levelness, fastness, no damage) while being as efficient as possible. Efficiency can involve machine time, energy, labour, water, dyes and chemicals, but must also consider environmental impacts of the process. Finding the best process that allows the most efficient and reliable dyeing is another reason why commercial dyeing is a skilled process.

Issues of environmental responsibility are thus encountered in trying to achieve each of the basic requirements of shade, fastness, levelness and efficiency. Holding fewer dyes in stock may be more efficient, and selecting dyes that are considered more environmentally benign might be environmentally responsible, but reduced dye choice may make a level, fast or non-metameric match harder to achieve. If dyes are not standardised accurately, or do not form a compatible combination, they may involve the dyer in additional machine time to make adds and/or reprocess the material. The efficient use of water, dye, energy and chemicals is promoted by using low liquor ratios, but as these decrease the likelihood of unlevel dyeing increases. Chemical auxiliaries might reduce dyeing time, promote levelness or increase exhaustion, but ultimately represent a burden in the waste stream.

Nor does the dyer exist in isolation. The customer's requirements may force a dyer to carry out a process that is not environmentally responsible by insisting on tighter than necessary colour tolerances or fastness.

4.4 General comments

4.4.1 Machinery

While dyers may specialise in the substrates they dye, or the volume at which they work, some level of flexibility is built into the way they do business. A dyeing operation may be equipped with different styles of machine, of different sizes, from different manufacturers.[15] At a certain scale, continuous processing becomes more efficient. Continuous working is quite common in fabric preparation, since fabrics are prepared on a larger scale than they are dyed, and is normal in textile printing, but it is relatively unusual in dyeing, where limited runs of single shades are the norm. Continuous processing also involves the application of relatively concentrated solutions to fabrics, and an opportunity to recycle leftover pad baths. Low-volume pads mean less to recycle, and reduce 'ending'.[16] In any continuous process, multiple low volume rinses and counter-current working should be the norm.

Whether batch or continuous, machinery can become contaminated with colour and at times, machines have to be taken off-line to be cleaned. The need for such cleaning can be minimised by sequencing the colours or patterns being produced from light to dark. Incidentally, that also tends to be the case as dyers have, given a range of shades to dye in a given lot, traditionally made black the final shade as an opportunity to overdye any uncorrectable shade/levelness problems from prior colours.

In batch processing, machines that agitate well, while not damaging delicate substrates, and that work at low liquor ratios (especially when run at less than full capacity) are inherently more environmentally responsible.

4.4.2 Utilities, plant organisation

The majority of preparation and dyeing processes require heat, and water is by far the most common medium from which dyeing is carried out. Water has a high specific heat that makes heating and boiling it energy intensive, and the recovery of heat from waste streams a realistic and sensible thing to do. Heat exchangers can be installed on individual machines, or in a common collection point for hot waste streams. It is now surprising to think that in the late 1970s the use of organic solvents (with low specific heats) was widely researched for both dyeing and preparation as a means of reducing energy consumption.[17,18] The search for alternatives continues and the use of supercritical carbon dioxide as a medium for dyeing has been the subject of considerable research and semi-commercial application.[19] The technique has been suggested for virtually all dye–fibre combinations. While it is environmentally attractive, and eliminates drying, the method requires highly specialised equipment and dyeing auxiliaries and seems a long way from wide-scale implementation.

Most dyehouses have a constant stream of incoming water to be used in all processes. In some, the water has to be pre-treated to bring it to a level of quality that will not cause problems in processing. However, many processes do not require clean water, and it is feasible to collect grey water (e.g. from final rinses) to be used as is, especially when it is hot.

It is generally most efficient to maximise the amounts of material that undergo common processing. Thus, for example, in most cotton dyehouses, there will be a common preparation sequence (usually desize/scour/bleach) for all fabric. However, while an evenly absorbent fabric is essential, a perfect white is necessary only for pastel shades, and to bleach goods when they are to be dyed dark, dull shades is wasteful and unnecessary.

4.4.3 Dyes and auxiliaries

Surfactants are used in preparation of fabrics before dyeing. Depending on the dye–fibre system, a range of chemical auxiliaries may be present in the dyebath. They fall into various categories: electrolyte, pH, oxidising/reducing and surfactants. Some are chemically consumed in the process, but most survive unchanged and are present in the final bath. Inorganic materials are usually bought and used as generic products, but organic surfactant-type auxiliaries are often supplied as proprietary materials. These can be detergents, or added to slow strike, promote levelling, allow for the use of a preferred pH, improve fibre lubrication and reduce crack marks, improve penetration, and so on. Their use is well established, but many are based on alkylphenol ethoxylates, which are suspected endocrine disruptors, and substitution may be appropriate.[20,21] More generally, a dyebath additive is often the first answer in solving a problem. However, the more that is added, the more complex the system becomes, interactions increase, and new problems can occur. Simpler is better, and for environmental responsibility, 'less is more' and beyond choosing environmentally appropriate products, dyers should work to minimise the use of auxiliaries: it reduces cost, and reduces the environmental load.

In many dyeing processes, a proportion of the dye remains in the bath at the end of the process, along with the non-exhausting auxiliary chemicals. It is environmentally responsible to reuse the dyebath, and not waste either resource. The use of 'standing baths' is an old idea, but in a modern dyehouse, bath reuse requires careful monitoring to achieve correct shades, and avoid the build-up of non-dyeing impurities. It also requires that some system of holding tanks be installed to hold the bath while rinsing etc. is carried out. Dyebath reuse has been conducted on at least a semi-commercial scale for several dye–fibre systems, and suitable analytical hardware has been developed.[22–24] In the case of reactive dyes, where the dye present at the end of the process is hydrolysed and not available for recycling (except, perhaps, as an acid dye[25,26]) the bath typically contains large amounts of electrolyte that is worth recycling. Considerable work has examined the oxidative decoloration of such baths to allow the reuse of the electrolyte.[27–30]

Many of these environmentally responsible process modifications require a level of planning and organisation that is not the norm in a working dyehouse. They are difficult to retrofit to an existing operation. As discussed earlier, changes should be quantified and referenced to a pre-change audit of the operation. The benefits, however, are often substantial. Ultimately (depending on the processes carried out and the level of waste treatment available to the facility), a plant may be able to operate as a closed loop system for water, representing an ideal of environmental responsibility.

4.5 Preparation

The goal of fabric preparation is a substrate that is free of impurities and colour that might interfere with subsequent dyeing processes. Preparation is typically carried out in the same plant as dyeing. The subject is generally covered well in texts related to the dyeing of the various fibres.[31–33]

Cotton comes to the dyehouse in the least pure state. It originates in agriculture, it requires sizing to be woven successfully, and it usually has had no prior wet treatments. It therefore requires the most extensive preparation treatments. The global nature of textile processing means that the knitter or weaver and dyer are often far apart, and the precise nature of the impurities, especially the knitting oils or size used, may be unknown. Since much of this ends up in the dyer's waste stream, the effluent problems of a dyehouse can often be traced to this source. In an ideal world, a dyer would receive fabric from an environmentally responsible weaver who used a recyclable size and removed it before shipping the fabric. In practice, some of the worst problems of dyehouse effluent often involve the high BOD/COD from the size, made worse with any preservatives or insecticides present. Knitting oils are generally present in lower amounts, but may be water-insoluble.

The basic steps in woven cotton fabric preparation of desize/scour/bleach may be accomplished in a variety of ways and with a range of different chemicals. The choice is often based on the scale of the operation with fully continuous processes the most efficient on the large scale, and pad-batch, or batch processes (the latter often in dyeing machines) preferred on the small scale. While hypochlorite bleach has been essentially replaced by peroxide and other oxygen-based bleaches (making spurious any environmental claim of 'no chlorine bleach used'), the use of alkali is an essential part of the traditional process, and waste streams are overwhelmingly alkaline, requiring neutralisation. Carbon dioxide from boiler exhaust can be used: an interesting example of combining two waste streams to generate a benign effluent. The concentrations of alkali are generally too low to be successfully recycled; in contrast, the higher concentrations of caustic soda from mercerising are routinely recycled.

These basic preparation steps can be made more environmentally responsible by all the usual efficiencies: reducing water, chemical and energy use, etc. Combining the basic steps, all of which can be accomplished by alkali and oxidising agents, is an additional opportunity for efficiency, and oxidative desizing has been re-examined.[34] More interesting is the trend to develop enzyme-based processes that operate at lower temperatures and near-neutral pHs. While amylase has been used for many years to desize starch-sized fabrics, the broader use of enzymes in fabric preparation has been widely researched, and offers many potential environmental advantages. Much work has been reported on the use of pectinases and other enzymes to scour cotton.[35–38] The product is absorbent, but not white, and still contains seed fragments. This may be sufficient for dyeing dark colours, but the broader goals of totally enzyme-based preparation are yet to be realised. 'Bio-polishing' with cellulases has become well established and is, incidentally, part of the preparation of lyocell fabrics in a defibrillation step.[39,40]

Catalase enzymes are suggested for use in destroying excess peroxide in bleaching that might otherwise damage dye in later dyeing. In contrast, with the use of peroxide-resistant dyes, combined dyeing and bleaching becomes possible and represents an opportunity to reduce processing by one step.[41,42]

The other common natural fibre is wool. The environmental impact of raw wool scouring, which occurs before yarn spinning, is beyond the scope of this chapter. Wool processing is generally on a smaller scale and mostly batch-wise processes are employed. Grey fabrics that come to the dyehouse will undergo many possible processes and combinations thereof and wool dyers are adept at making these efficient. Scouring and milling are commonly combined. Sulphuric acid is used to carbonise wool: the acid left in the fabric may be used as an auxiliary in acid milling, and/or acid dyeing.

Silk is usually degummed, and this process has been the subject of research to make it more environmentally responsible.[43]

Synthetic fibre fabrics are generally cleaner and require less preparation. In many cases, the surfactant-based dyeing auxiliaries (levelling agents, for example) are sufficiently detergent to allow scouring to be combined with dyeing.

4.6 Dyeing, fibre by fibre

4.6.1 Cellulose

Cotton is by far the largest volume of the cellulosics, but most of what applies to cotton applies to other natural and regenerated cellulose fibres. The dye types for cellulose reflect a range of strategies depending on fastness and shade requirements. In general, dye exhaustion is lower on cellulose fibres and, thus, waste streams are more highly coloured. The greater exhaustion of dye on protein fibres was noted centuries ago and, in the nineteenth century, processes for 'animalising' cotton were researched. The most recent incarnation of such efforts has been the treatment of cotton to incorporate cationic moieties to which anionic direct and reactive (and acid) dyes are attracted with high exhaustion and minimal use of electrolyte.[44–47] Despite the extensive work, the added complication and perhaps the later 'scavenging' of colour in laundering has hindered commercial development.

Reactive dyes

In recent years, the 'default' choice has come to be reactive dyes for their generally good fastness to wet treatments, and good range/brightness of shades. The dyes range in substantivity and reactivity, rendering them more or less suitable for long liquor exhaust applications, blends with polyester, continuous application etc. Some are metal complexes, most often with copper. In exhaust application, electrolyte is required, often in amounts large enough to be considered a pollutant and, as discussed earlier, a candidate for recycling. Unique to this class of dye is the distinct separation at the end of the process between fixed and unfixed dye. The latter must be removed in thorough rinsing to achieve optimum fastness properties. Rinsing processes have been most studied for reactive dyes[48] and enzymatic processes for decolorising the rinse water have been developed.[49] The rinsing process is most efficient when the dye has a high fixation and low substantivity. These two seemingly antagonistic requirements (and hence environmental responsibility) are best achieved in cold pad-batch application.[50] Little or no electrolyte is required, energy is minimal, and fixation is high. Unfortunately, this method of application does not allow 'adds' to adjust the shade, and dyers have been reluctant widely to adopt this method of dyeing.

In other application methods, 'low salt' dyes have been developed,[51,52] as have dyes with high fixation, often via the use of two or more reactive groups of the same (homo-) or different (heterobifunctional) types.

Vat dyes

Vat dyes offer the best levels of fastness on cellulose. Their manufacture tends to be polluting, so their use raises some environmental questions on the global scale. The reducing agent used in their application, most commonly sodium dithionite (hydrosulphite), is an environmental burden. Alternatives continue to be sought:[53] most recently electrochemical means of reduction have been explored and offered on a commercial scale.[54,55] Oxidising agents to bring the dye to its final oxidised form can, with care, be replaced by exposure to air.

Direct dyes

Direct dyes still have their place in the market. Environmental responsibility means ensuring that none of those based on potentially carcinogenic amines should be used.[56,57] The use of copper-based after-treatments to boost the limited fastness is now largely outmoded. Direct dye baths can be recycled.[58,59]

Sulphur dyes

Sulphur dyes have long been used for economical dark shades of fairly good fastness. Sulphides, the reducing agent used in their production (and thus inevitably present in the dye as sold) and their use are polluting, and as dyemakers have minimised the free sulphide present in the dye, dyers have sought non-sulphide reducing agents with which to apply them. Glucose-based materials seem to be satisfactory and have been widely adopted.[60,61] As with vat dyes, the use of electrochemical reduction has been explored.[62] In contrast to vat dyes, the oxidation of sulphur dyes is a less straightforward process, with the shade and fastness of the resulting dyeing depending markedly on the oxidising agent used. Chromates were ideal, but are environmentally unacceptable: the current favourite seems to be sodium bromate with sodium metavanadate present as a catalyst.[63]

4.6.2 Dyeing wool

Dye application on wool is generally more straightforward than on cellulose fibres: exhaustion is higher, auxiliary levels are lower and pH values nearer neutral are often preferred. Waste dyebaths are thus more readily disposed of, and less stringent rinsing is required. Since exhaustion is readily accomplished, it is customary to use larger volumes of water to ensure levelness, however. Where specialised auxiliaries are used (for example, to allow the use of pHs that minimise wool damage) dyebath reuse can be advantageous.

The major environmental challenges are based on the choice of dye. Metal (usually chromium) complex dyes, either as 'premetallised' complexes, or those formed *in situ* by the separate application to the fibre of dye and dichromate are widely used to provide dark, fast shades. Where dye and chrome are applied separately, some chrome is inevitably discharged. Modifications to the dyeing method to minimise the amount of chrome used and discharged were widely studied, along with means to ensure that any discharge was as Cr(III) and not as Cr(VI).[64–66] Premetallised dyes (produced in a way that minimises free chromium) are less of an environmental challenge since the bound metal is less, or perhaps not, bioavailable. Nonetheless, alternatives are sought. Despite limited use in routine wool dyeing, where levelness may be challenging, reactive dyes for wool have been suggested and, in some cases, adopted as non-metal alternatives for fast, dark colours.[67] The use of the environmentally benign iron as an alternative to chrome in metal complex dyes continues to attract interest.[68,69]

4.6.3 Dyeing nylon

Like wool, nylon is most often dyed with acid dyes, and the issues involving the chrome content of premetallised dyes are the same. Nylon is subject to more challenges in use, and the fastness of dyeings is of concern. The use of post-dyeing treatments to improve fastness is common. Backtanning processes (involving antimony salts) have largely been replaced by 'syntans'. Modified after-treatments, and non-antimony tanning systems have been examined.[70,71] The use of alternatives to acid dyes, such as sulfur dyes, vat dyes and reactive dyes have been suggested as ways to improve fastness, although the environmental impact of these alternatives is not clear.[72,73]

4.6.4 Dyeing with disperse dyes: polyester and acetate

Disperse dyes were developed first for use on acetate: these dyes were later found to be useful when polyester was introduced. Newer disperse dyes specifically for polyester were eventually developed. Until the introduction of polyester in the 1950s, there had been little need for dyeing machines to be pressurised to achieve temperatures above 100 °C, but diffusion of dye into polyester is slow at the boiling point of water. The satisfactory dyeing of polyester initially involved the use of 'carriers', essentially fibre plasticisers. These materials, typically phenols or chlorinated aromatics, were used at quite high concentrations (2–5 $g.l^{-1}$) and ended up as pollutants in the waste stream. Over the past half-century, as polyester has become the most widely used fibre in the world and its dyeing has become commonplace, pressurised dyeing machines have largely obviated the need for these chemicals. The machines have also allowed faster dye cycles. For some dyes/shades/fibres carriers are still required and more benign 'migration assistants' with carrier-like function have been developed. In general, polyester dyebaths are well exhausted, and a good candidate for the reuse of the levelling and dispersing agents they contain.

When dyeing dark shades, the low aqueous solubility of disperse dyes leads to the presence of surface dye and low rubbing fastness. This is traditionally removed in a 'reduction clearing' process with dithionite and alkali, with the same environmental question marks as for their use in the application of vat dyes. Dyes clearable on alkali treatment have been developed.[74] In most polyester dyeing processes, a pH of 5–6 is maintained for dye stability. Recent interest has focused on the selection and use of dyes stable in alkaline baths. As well as their benefits in the dyeing of polyester cotton blends discussed below, on polyester their use reduces the need for post clearing, and reduces oligomer deposits.[75–77]

4.6.5 Dyeing acrylic fibres

The dyeing of acrylic fibres presents few specific environmental challenges beyond those discussed previously. Dyes exhaust well. Levelness can be challenging, which tends to increase the use of levelling agents. Both factors would make dyebath reuse an attractive proposition.

4.6.6 Dyeing blends

Fibres are blended for both technical and economic reasons, and myriad blends and blend levels are encountered. Dyers may be required to reserve one fibre, cross-dye, union dye, or produce a tone-on-tone effect. The subject has been extensively covered.[78] The same principles of environmental responsibility as for single fibre fabrics apply here, in somewhat more complicated form.

Since cotton and polyester together make up around 70% of all fibre consumption, it is not surprising that their blend is where the majority of attention has been focused. The fibres have very different dyeing behaviour, and extensive published work has described considerable ingenuity in turning a two-bath, two-stage batch process into a more efficient one-bath, two-stage, or even a one-bath one-stage process.[79–82] The rewards in terms of reduced time, and energy and water consumption, are potentially large. The success of such efforts has been mixed. The feasibility is rarely applicable to all cases; a successful short procedure for pale shades of limited fastness may not be applicable to heavy depths where cross-staining may occur and good fastness to laundering or rubbing is required. In continuous dyeing similar efforts have been expended.[83] The opportunity to employ a single class of dye on both fibres has attracted attention, but is of little environmental value.

4.7 Textile printing

Textile printing is usually continuous. The most widely used printing process involves the application of thickened colour pastes through screens. The lack of reliable colour mixing prevents the use of primary 'process' colours and each colour in the design must be applied as pre-mixed 'spot' colour. Thus, a print may involve the application of up to 20 different print pastes. At the end of a print run, there will be 20 excess pastes to deal with and 20 screens to clean. Environmental responsibility requires waste minimisation meaning that just enough paste is prepared for the job in hand. This is best accomplished by initially preparing a limited amount of each paste, monitoring the use ($kg.m^{-1}$) in the pattern being printed, and then preparing whatever is needed to finish the job exactly. If there is excess paste, it should be reused, or worked off by incorporating it into another colour. Akin to the use of IMP in dyeing, software can predict how to work off excess paste in new colours.[84,85] Even the rinse water from screen washing can be used as make-up water in the production of dark-colour pastes. Most pastes are stable, the exception being those based on reactive dyes mixed with alkali, which have a limited 'pot-life', and any reuse must be relatively expedient.

Unlike the level application of colour in dyeing, where the use of pigments is largely confined to the continuous application of pale shades, the coloration of textile prints is evenly divided between dyes and pigments. Each type has environmental considerations.

In printing with pigments, the sequence is simply print-dry-cure and so the use of water and energy is low. The use of a low-solids thickener is required, since it remains with the fabric after printing. The former use of essentially zero-solids emulsion thickeners (mineral spirit and water) that generated large amounts of VOCs has largely ceased. The low solids acrylic thickeners that replaced them do contain some solvent, however, and air emissions are the usual environmental concern.[86]

When dyes are printed, a steaming step is usually employed to provide the energy and moisture that will allow the dye to penetrate the fibres. A thorough washing is required to remove unfixed dye, and all the auxiliaries in the print paste (thickeners, pH controllers etc.). These end up in the waste stream, and they should be chosen to minimise their impact. The same comments about washing efficiency that apply in continuous dyeing or preparation apply here.

The use of ink-jet printing is increasing. This technology does use process colours that mix on the substrate, so each pattern and colour is generated from the same inks, and waste is minimal. While the volume of ink-jet printed material remains low due to the limited print speed, it has found wide use in strike-off prints. Sample patterns can be printed, and screens are only manufactured for those that find orders. This represents a measure of environmental responsibility in avoiding the production of large numbers of nickel mesh screens that will not be used in production. The drawbacks of ink jet printing stem largely from the need to pre-prepare the substrates with all the auxiliaries required for fixation.[87]

4.8 Conclusions

A dyer (or printer) wishing to engage in environmentally responsible colour application has many avenues to explore beyond meeting local regulations. Reduced water and energy consumption can bring economic as well as environmental benefits, and can be achieved in many ways: more efficient machinery, heat recovery, elimination of redundant processes. Many options exist for the replacement or reduced use of chemicals, particularly those that are environmentally questionable. More advanced methods for reducing the environmental burden of dyeing such as dyebath reuse, enzymatic preparation or dyeing from supercritical carbon dioxide, have been tested on a commercial scale. Many others have been the subjects of detailed research.

It is understandably challenging to devote time and money to aspects of a competitive business that may not bring immediate reward. Ultimately, the dyer will respond to the needs of the market place. When environmental consciousness is important to the customers, many methods of demonstrated effectiveness may find implementation.

4.9 References

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