

Evaluation and Testing of Dyes Before Use in Textile Dyeing

J Park* and J Shore†

*Dymatecs Ltd
Unit 25
Long Furrow Industrial Estate
East Goscote
Leicester

†ICI plc
Organics Division
Hexagon House
Blackley
Manchester M9 3DA

Progress in methods of test for dyes and dyed textiles is reviewed. This is a broad topic which touches on many aspects of coloration technology and inevitably the treatment of some areas of the subject has to be brief and incomplete. Many recent trends in dye application technology affect both the nature of tests to be applied and the criteria considered when interpreting the results of the tests. This subject is reviewed from the viewpoints of both the dye manufacturer and the dye user, in order to bring out the essential similarities in approach. Typical parameters of dye selection are tabulated and classified according to the nature and purpose of the tests involved.

INTRODUCTION

Although most laboratories in the dyeing industry allocate substantial resources to dye evaluation, and although this aspect of product assessment is most important for efficient materials purchasing and for cost-effective operation of the dyehouse, little has been published on the subject that is easily accessible. The methods employed in product development and standardizing control by the dye manufacturer and in screening and quality checks carried out by the user have much in common. Research samples are screened until promising products emerge to justify commercial development. After exhaustive testing they are added to the manufacturing range and subsequent batches are tested for quality against an initial standard. In a broadly similar way, the dye user carries out extensive screening tests on commercial dyes to select those suitable for his process, machinery and in-service properties on the substrate to be dyed. Having selected a small range of dyes to achieve these targets, the user maintains routine checks on deliveries and compares similar products which may be available from several suppliers.

The techniques applied by the manufacturer and user in these dye screening and quality control programmes do not differ in principle or in their interpretation. The main variations in approach arise from the differences in objectives of the work. The manufacturer is screening speculative products at an incomplete stage of development, whereas the user is testing finished products from a variety of sources. In establishing and maintaining a quality standard, the manufacturer must attempt to meet the needs of users operating in widely different sectors of the textile industry, his product having to perform

satisfactorily within a wide range of exposure conditions. An individual dye user may need to satisfy a much narrower range of machine-substrate-process criteria, enabling closer definition of the preferred selection of dyes for his requirements. A laboratory representing a group of dyeing factories, perhaps situated in different countries, may have to make compromises based on local circumstances in evaluating the dyes available and selecting those most suitable for recommended use within the group.

Although the subject of dye screening is often mentioned [1-9], particularly when discussing in general terms the work carried out by various types of dyeing laboratory in the industry, information on individual aspects is widely scattered and few authors have attempted to deal with the topic comprehensively. Numerous parameters have to be considered by both manufacturer and user of the product before it is eventually applied to an appropriate substrate for a specific end-use. In Table 1 many of these factors are presented. Properties of particular significance during safety testing, manufacture, standardizing, transport and ultimate dispersing or dissolving ready for use can be regarded broadly as the response of the dye itself, uncomplicated by the presence of the textile material, to its environmental conditions. Health and safety standards are increasingly significant and are particularly relevant to handling of the concentrated product during manufacture and application.

Many more tests must be considered when the decision is taken to use the product in a dyeing process and these are all evaluations of the characteristics of the dye-fibre system, rather than of the dye alone. Cost-effectiveness is obviously essential for the user to retain any interest in the manufacturer's product and the user's customer invariably lays down certain requirements to which the dyed textile must conform. There often has to be a trade-off in properties; a cheap dye may achieve only borderline fastness with difficulty, or it may only be possible to meet severe fastness requirements at the expense of level-dyeing properties.

STANDARDIZATION AND STORAGE STABILITY

Commercial dyes are marketed at a strength convenient for consistent standardization and contain diluents, such as electrolytes, solubilizing agents or dispersing agents. The presence of manufacturing impurities, by-products, isomers and shading dyes may give rise to slight differences in colour between dyes of the same *Colour Index* number. The nature and amount of such additives and impurities may have an influence on the dyeing behaviour, so that equivalence of colour content does not necessarily imply similarity of behaviour during application. Chromatographic techniques [10-15] are usually used to separate the colour components of dye samples and to confirm the continuing presence of approved shading components in deliveries. The characteristic absorption spectrum of a dye is a convincing reason for employing spectrophotometry in quantitative analysis, but other techniques, such as potentiometric titration of cationic dyes [16], are sometimes useful. Established methods for estimation of the active dye content of

TABLE 1

Parameters for Dye Selection

Response of Dyes to Environment	Behaviour in Dye-Fibre Systems
<i>Standardization and sampling</i>	<i>Cost-effectiveness</i>
Homogeneity	Shade area
Absorption in solution	Colour value
Analysis and identification	Build-up
<i>Storage stability</i>	Reproducibility
Variation in moisture content	<i>Dye application properties</i>
Storage conditions	Levelling and migration
<i>Solubility and physical form</i>	Substantivity and diffusion
Aqueous solubility	Reactivity and fixation
Crystal modification	Sensitivity to temperature
Particle size	pH and redox behaviour
Commercial form	Compatibility
<i>Health and safety</i>	Cross-staining
Dustiness	Transfer and vapour pressure
Trace metals	Efficiency of wash-off
Eye and skin irritation	<i>In-service requirements</i>
Acute toxicity	Coverage
Long-term hazard	Penetration
Biodegradation	Fastness
Sludge adsorption	Tendering of substrate
Fish toxicity	Influence on finishes

commercial samples of reactive dyes have been compared recently with a technique based on hydrolysis using excess of alkali, followed by estimation of the alkali consumption [17]. A detailed discussion of developments in the analysis and identification of dyes is outside the scope of the review and this topic is adequately covered elsewhere [15,18-22].

Absorption spectrophotometry is widely used for determining the colour value of dyes in solution. But to assess cost-effectiveness reflectance spectrophotometry of standard dyeings on a standard subsystem is essential. The dye sample is tested against a standard control in both instances. The procedure for comparing competitive products is essentially the same as for testing a delivery against its standard. Reference books on spectrophotometry are available [23] and useful comments have been made on instrument requirements, application techniques and solvent systems [24,25].

A general procedure has been described for the spectrophotometric estimation of dyes in solution [26]. Dye solutions are prepared in selected solvents, together with additives to give stability, and then diluted for measurement. The dye under test and the standard are examined, using identical methods. Precision and accuracy of the method are discussed, as well as variables attributable to the solution and the instrument used. Sampling, standard control, choice of buffer and solvent, solution preparation, measurement, calculation, equipment and its care, are discussed in detail. Measurement of the same samples by a number of laboratories indicated significant areas of disagreement [27].

The factors which can affect the accuracy and precision of such measurements have been outlined [28]. The variables include the effects of temperature, pH, concentration, additives, solubilizing agents, solvents, dye interaction, dye hydrolysis, interfering ions, ionic strength, redox potential, light fading, fluorescence, irradiation and plating on the cell surface. The effects of aggregation on the Beer's law behaviour of dyes in solution [29] and the spectrophotometric analysis of

multicomponent mixtures of dyes which deviate in this way [30] have been investigated.

From the user's standpoint it has been suggested that control of dye strength within $\pm 5\%$ is satisfactory [31], but most manufacturers of dyes standardize within a tolerance of $\pm 2.5\%$ for strength and it has even been claimed that a range of only $\pm 1\%$ is necessary for automated dyehouses [32]. The manufacturer's approach to standardization [33] and the analogous procedures of delivery control in the laboratory of a dye user [31,34,35] have been described. Standardization includes the control of physical, chemical and tinctorial properties, and depends on establishing a quality standard, assessing the characteristics of individual batches against the standard control and then converting each batch to an acceptable quality in the final standardizing process.

It is essential that any sample is representative of the bulk of the material under test. Large drums should be core sampled and, in general, the top layer of solid product in an unsealed package should be avoided because of possible atmospheric contamination. Much useful information on sampling is given in relevant textbooks [36] and the limits given in Table 2 have been proposed for the proportion of material to be sampled in relation to the number of packages in a consignment under test. Differences between batches were found to be large compared to differences within batches when using a core testing method and sampling at five places within the container [37]. Liquid dye brands must be thoroughly homogenized before sampling.

Various methods of storing control standards are available [9] and the need for a suitable method of indexing has been stressed [34]. It is equally important that the results of dye screening and delivery testing should be recorded, either by the use of standard forms for each dye or in some tabulated scheme [37]. Quality control charts are convenient for monitoring dyes in regular use and test results must be communicated immediately to the dyehouse so that any variation can be

TABLE 2

Sampling of Solid Material

Number of Packages in Batch	Proportion of Consignment to be Sampled (%)	Minimum Number of Samples
2-20	≥20	2
21-60	≥10	4
61-200	≥7	6
201-500	≥5	15
501-1 000	≥4	25
>1 000	≥3	40

counteracted by appropriate alteration of current recipes. The provision of recipe storage and retrieval programmes in a colour physics computer package for the dyehouse will automatically ensure that this recipe updating is carried out.

With any hygroscopic material, moisture content is an important commercial factor, since variations in ambient conditions can affect the price-strength relationship for the product. This is especially important for dyes since no user wishes to buy water at dyestuff prices. Wide variations in moisture content of disperse dye powders have been recorded against time, depending on the prevailing conditions of storage [38]. If the moisture content of the dyes is changing during storage, poor reproducibility in batches dyed to the same recipe but at different times may result. Methods of determining moisture content depend on drying a weighed sample to constant weight in an oven, under conditions which will not cause charring or volatilization of the dye. Alternatively, the well-known Dean and Stark method (BS 756) may be used. Moisture contents of 2-3% at delivery are acceptable.

Apart from these critical implications for reliable estimation of cost-effectiveness and attainment of satisfactory reproducibility in recipe formulation, storage of dye powders in a moist atmosphere can lead to caking, followed by delays or inaccuracies in weighing and difficulties at the dissolving or dispersing stage. Steel drums are tightly closed for transporting and polythene liners are often used for dyes to avoid ingress of moisture during storage; fibreboard drums contain a moisture vapour barrier composed of bitumen-lined or polythene-laminated kraft paper buried within the sidewall of the drum [39]. Contamination problems are minimized by storage inside lidded containers in a relatively cool, dry atmosphere; at least one firm in the USA has installed a constant-temperature and constant-humidity control system in the colour kitchen [40].

SOLUBILITY AND PHYSICAL FORM

The solubility of ionic dyes in water is a property that is becoming increasingly important as equipment becomes more automated, dyeing cycles are rationalized or streamlined, batch processes are operated at shorter liquor ratios and economic trends favour semi-continuous and smaller-scale continuous methods [41]. Traditionally it was sufficient to quote a solubility figure for the dye in near-boiling water, as assessed approximately by filtration through a closely-woven cloth. But now more precise figures are often required over a range of temperatures, to take into account the cold-dyeing or warm-dyeing methods advocated in the interests of energy conservation. Solubility is affected by electrolytes

contained in the commercial dye, in the water supply, or added to the dyebath.

Quantitative methods of determining the solubility of ionic dyes [42-45] rely on the preparation of a series of dye solutions ranging in concentration around the solubility limit at the temperature of filtration. The solutions are passed through a suitable filter, for which the dye has no affinity, supported by a temperature-control device such as a water-jacketed funnel. The solubility is determined by measurement of at least one, but preferably several, of the following: (a) dye residue on the filter by gravimetry or solvent extraction and spectrophotometric estimation, (b) dye concentration in the filtrate by spectrophotometry and (c) filtration time and viscosity of the filtered solution.

Measurement of the aqueous solubility of non-ionic dyes is less straightforward, but knowledge of this parameter, together with information on crystal form, particle size and response to dispersing agents [46] can be of considerable value in interpreting the dyeing behaviour of disperse dyes or vat pigment dispersions. Much valuable research has been devoted to methods of measuring the aqueous solubility of disperse dyes, initially in order to study the mechanism of dyeing cellulose acetate at 80°C and more recently [47-53] under the experimentally less convenient conditions of polyester dyeing at 130°C, but this field is outside the scope of this review.

Apart from aqueous solubility, other related properties such as wetting characteristics of the dye powder, and the specific gravity, viscosity and surface tension of the dye solution or dispersion, are of practical significance, particularly when automated dye-dispensing facilities are being considered. Individual dyes require their own calibrated pumps and meters, because the volume to be dispensed depends on the specific gravity of the liquid and this varies with the dye selected. With dye dispersions that tend to settle out arrangements must be made for automatic flushing of the system after each recipe has been used, or alternatively a metering system with recirculation is used [39]. The metering of thickened pastes for textile printing presents special problems. Air entrained in print pastes during power mixing cannot be removed and leads to errors in the volume displaced because of pressure changes on the suction and discharge sides of the pump. Dispersions of disperse dyes or vat pigments are abrasive, particularly when concentrated and at low viscosities, and this can lead to progressive wear of the pump components [54].

The selection of disperse dyes is closely dependent on application properties determined by (a) the particle size distribution in the initial dispersion and the stability of the dispersion to subsequent temperature changes, (b) concentrations of dispersing agents and electrolytes present, (c) liquor flow and (d) the form of substrate to be dyed [55]. Four types of instability of a dye dispersion can be distinguished: agglomeration of particles, crystal growth, change of crystal modification and recrystallization from solution during cooling [56,57]. Improvements in application techniques, such as the trends towards lower liquor ratios and rapid jet [58] and package [59] dyeing of texturized polyester, have been an incentive to the manufacturer to improve the physical form of dyes supplied to the user [60]. The dependence of sorption by cellulose on the quality of the vat dye dispersion when dyeing cotton by the vat acid method has been investigated recently. Increasing the pH to 6.5-7 and adding a miscible organic solvent (2-5 g/l) improves the dyeability [61].

Test methods have been described [62,63] for the

selection and quality control of disperse dyes covering dusting properties of powder brands, viscosity and thixotropy of liquid brands, foaming of concentrated dispersions, sedimentation and filtration tests to assess the degree of dispersion. The particle size distribution is of great importance in dyeing processes where a filtration effect can occur, such as the package dyeing of yarn, beam dyeing of fabric, or in fact any technique in which dye-liquor is circulated through a densely packed substrate. A major breakthrough in particle size measurement was achieved by the development of the disc centrifuge [64] and this resulted in a marked improvement in application properties of commercial forms of vat and disperse dyes. A practical method for assessing differences in particle size distribution relies on the use of a cotton fabric wrapped around the spindle inside the package of texturized polyester yarn; dye samples with unsuitable characteristics are filtered out on the cotton fabric where it covers the perforations of the spindle [65].

Work on physical form has been spurred on by environmental requirements, which favour the greater use of grains or liquids owing to their non-dusting properties. Liquids are easy to handle and do not require special methods of dispensing, which can offer advantages in automated colour kitchens. Metering pumps are already widely used for liquid dispensing in the paper industry and in the American carpet industry. Liquid forms of disperse or vat dyes [66] are dispersions, not solutions, so that homogenization of the liquid before use is essential to overcome stratification and settling during storage. In warm conditions, agglomeration of the dye particles can occur, or freezing may occur in cold conditions. The requirements for obtaining stable highly concentrated solutions of basic dyes have been discussed [67]. Such products must be readily miscible with water, and withstand prolonged storage at varying temperatures without crystallization or decomposition of the dye. They should also contain non-toxic, preferably non-flammable, and non-volatile solvents to avoid crusting occurring in the drum or in the withdrawal equipment. Particular attention has been devoted to the design of plastic containers for products which may suffer from sedimentation or superficial drying out. These usually have a much wider opening than usual, so that the contents can readily be stirred.

HEALTH AND SAFETY TESTING

Tremendous efforts are now being undertaken worldwide to identify, measure, evaluate and eliminate the undesirable effects of chemicals, including dyes, on man and the environment. Every supplier must now supply ecotoxicological data on his range of products, including information on methods for safe handling and on any hazard that might be encountered in use. The safety and toxicological aspects of handling chemicals in the colour-using industries [68] and potential environmental problems associated with the manufacture and use of dyes [69] have been reviewed. The need to meet health and safety requirements has had a significant effect on the cost of dyes. The impact of new product legislation will make it increasingly expensive to launch new chemicals on to the market in future. Hence new dyes are unlikely to be developed unless they make a significant advance on existing products [70].

Heavy-metal ions, such as copper, chromium and cobalt from the manufacture of metal-complex dyes, or mercury from catalysts, become a problem in clarification plants because of their toxic effect on micro-organisms and their tendency to accumulate in the food chain.

Trace metals are present in commercial dyes in such low concentrations nowadays that they should cause no insuperable pollution problems for the effluent-treatment plant in future. Exceptions to this are the direct and mordant dyes which are aftertreated with copper or chromium salts to develop the full fastness properties; if use of these products is unavoidable, the effluent should be processed separately. An afterchroming method giving effluent almost free from chromium through controlled addition of the metal salt has been described [71].

In the textile dyeing industry, the main potential hazard is the effect of dye dust on lungs, skin and mucous membranes while the dyes are being weighed and handled. Much work has been done to eliminate this problem by developing improved physical forms such as non-dusting free-flowing granules, liquid brands and pourable pastes. A minimum test programme has been drawn up to assess safety in handling, and in many firms all dyes undergo the full programme. The tests involved are those to determine acute oral toxicity in rats (LD_{50}), skin irritation in rabbits (skin compatibility) and eye irritation in rabbits (compatibility with mucous membranes). A major survey of systematic testing according to this programme, by member firms of the Ecological and Toxicological Association of Dye Manufacturing Industry, did not uncover any recognizable structure—toxicity relationship, which confirmed other evidence of the generally low acute toxicity of dyes [69].

Possible chronic toxicity effects of chemicals which have attracted most attention are carcinogenicity and, to a lesser extent, sensitization. Unless epidemiological data are available, only long-term bioassay results on animals give a sufficiently reliable assessment of carcinogenic risk. At present, none of the short-term alternatives can be used to establish whether a compound will be carcinogenic in humans. Positive results indicate the need to carry out long-term animal tests, but negative results in short-term testing do not absolutely confirm the safety of the agent. Employee organizations have been assessing the long-term hazards to personnel working in textile dyeing and finishing. A study of mortality statistics for operatives who had worked in the UK textile wet-processing industry gave no indication of an increased occupational risk or of increased susceptibility to cancer and lung diseases [69]. Epidemiological studies for dye-manufacturing plants have shown similar results [68,72,73].

Dyes undergo partial biological elimination (40–80%) by sludge adsorption in sewage treatment plants [74], but practically no biodegradation of the dye takes place under anaerobic conditions of treatment. At first sight this resistance to biodegradation may seem a drawback, but on closer examination it must be considered an advantage. Owing to their strong affinity for organic polymers and other adsorbents, intact dye molecules are much more readily eliminable from effluents in biological and chemical treatments than are simpler chemicals. Only very dilute solutions enter open water courses after such treatments and dye accumulation in river sediments has diminished as a result of continuing improvements in control of effluent disposal. Very few dyes are toxic to sewage sludge or digested sludge [75]. Studies of fish so far indicate that dyes show little or no tendency to accumulate [76] and have low toxicity. [69].

COST-EFFECTIVENESS OF DYES

Increasing economic pressures have compelled dye users to select dyes with greater care in order to use the minimum number of dyes to obtain the maximum colour

gamut, to reduce stocks and to gain from bulk purchasing price concessions. More stringent technical requirements have meant that for certain end-uses only a few dyes will meet the required specification. The adoption of automation and the need for cost-effective processes both favour the use of rationalized small ranges of dyes. Several papers have described the factors, including dye application parameters, which must be controlled within well-defined limits for success to be achieved in automated plants [32,77–82]. However, satisfactory results will still be unattainable if application parameters alone are controlled and those in other areas, such as weighing, are ignored. Many of these investigations culminated in the delineation of limits of accuracy for the various factors.

The choice of dyes, the determination of the recipe for a particular colour and the definition of the application procedure and final treatment are the important steps in control of the dyeing process [83]. Continuity of quality is essential and dyes are often chosen according to whether technical performance or price is paramount. There are two commonly used empirical methods of selecting dyes to produce a given colour [31,35,84]. One approach is to base the majority of colours on a tertiary combination of bright primary dyes and to supplement this by a small range of dyes compatible with the main combination, giving a wide gamut of attainable colours, particularly in depth and brightness. Approximately twelve dyes are required for this approach, which is adopted when homogeneous dyes are not available throughout the entire colour gamut, for example with acid, basic, disperse and reactive dye classes.

In the second method, a dye is chosen close to the colour required and small amounts of shading dyes are added to reach the desired target. This method gives a high degree of reproducibility and the best chance of level results, particularly if the concepts of internal primaries and colour mapping are employed. This approach is possible with dye classes containing homogeneous dull members of the range, such as 1:2 metal-complex, direct and vat dyes. In an elegant application of the concept of internal primaries [8], reflectance data were used to construct colour maps, so that dyes in any given area of the gamut form a triangle of internal primaries. The technique is supported by a suite of computer programs to aid dye selection and recipe formulation. This work has recently been extended and a summary of the steps in the selection process given [85].

A general procedure has been specified for determining the dye strength of a sample relative to a standard by measuring the reflectance of dyeings and calculating the result using the Kubelka–Munk function [86]. Problems associated with preparation of the dyeings, sample preparation and measurement are discussed in detail. Precision and accuracy of both dyeing and measurement are considered. A computer-based technique for the value analysis of dyes has been developed [87], whereby the minimum-cost method can be chosen. A surface in ANLAB colour space representing equal depth at all points (Control Depth) is defined by a constant value of Integ, an integration of a weighted function of the measured reflectance values of a dyeing throughout the range of visible wavelengths. The amount of dye that must be applied to a substrate by a specific dyeing method to give this Integ value may be determined by experiment and is called the Control Strength of the dye. The relative colour values of dyes on this substrate can be estimated and compared, irrespective of minor differences in hue, by multiplying together the Control

Strength and the selling price in each case. The dyer's variables of shade and strength have been interpreted in the context of ANLAB colour space so that measured colour differences can be expressed in more familiar terms [88]. Instrumental colour measurement has been used to optimize the preparation of printing pastes based on reactive dyes [89].

Many dye properties can only be assessed by actual dyeing tests and hence it is essential to develop test methods which correlate with one another, and preferably give a high degree of reproducibility between laboratory and bulk scales [82]. Systematic mathematical and statistical analysis of the effects of deliberate variation of critical parameters forms a valuable basis for such correlations: recent investigations of this kind have been concerned mainly with the application of reactive dyes to cotton and of disperse dyes to polyester and polyester/cellulosic blends [32,79,90]. The influence of subjective errors in the communication of recipe details and other instructions should not be neglected as a source of colour variation in routine bulk-scale production [91].

A standard laboratory-scale dyeing procedure of high precision has been developed for cellulose acetate, acrylic, nylon and polyester fibres using the low-temperature version of the Launder-Ometer [92]. Many types of sophisticated laboratory dyeing machine are available and these have been critically assessed for productivity, reproducibility and versatility of application [93–96]. A laboratory-scale machine suitable for continuous spectrophotometric monitoring of the rate of dye uptake was developed to study relationships between dyeing rate and control parameters [95]. The examination of dyeings obtained in these tests is now greatly assisted by the use of reflectance spectrophotometers and tristimulus colorimeters giving numerical results rather than subjective visual assessments, which are open to differences of interpretation.

DYE APPLICATION PROPERTIES

The degree of levelness is a direct measure of the technical success of the dyeing operation and it is thus not surprising that great attention is paid to the properties of dyes which govern this factor. The Society of Dyers and Colourists has been foremost in developing tests to classify dyes according to their dyeing properties [97,98,100,105–109]. This programme began many years ago with tests for the migration properties and salt sensitivity of direct dyes in cotton dyeing [97]. Migration and strike-levelling tests were also published for vat dyes [98]; more recently, substantivity curves have been used to classify vat dyes and their exhaustion properties have been compared with other dyeing systems [99]. Five tests were developed to determine the optimum conditions for obtaining an economic degree of exhaustion of acid dyes on wool. A migration test was also developed, in which equal weights of dyed and undyed material are treated in a blank dyebath under standard conditions with dye transfer being assessed on a grey scale [100].

A chromatographic method was developed for classifying wool dyes, based on degree of penetration into a column of felt discs through which dye-liquor is passed under well-controlled flow and temperature conditions [101]. The tests used to classify dyes for application to wool and cotton have been reviewed and a more quantitative approach described using rate-of-exhaustion and degree-of-migration curves [102]. The SDC migration test for acid dyes [100] is unsuitable for assessing 1:2 metal-complex dyes and an alternative combined strike-migration test has been introduced [103]. Rela-

tively little has been published on the levelling properties of reactive dyes, probably owing to their generally poor migration behaviour. A recent investigation was concerned with the influence of temperature, applied depth and degree of mercerization on the migration properties of reactive dyes for cotton [104].

In recent years, much of the work on dyeing tests for levelling and migration has been focussed on dyes for synthetic fibres. This has included a long SDC programme concerned with disperse dyes on cellulose acetate [105], triacetate [106], nylon [107] and polyester [108], as well as basic dyes on acrylic fibres [109]. The tests were designed to correspond to practical dyeing conditions and results are assessed using grey scales. Recent work on the levelling behaviour of disperse dyes for polyester has evaluated rates of exhaustion and levelling coefficients [110], the influence of levelling agents under package-dyeing conditions [111] and the so-called Fringe Test, developed to estimate the degree of levelness of a dyed fabric in relation to penetration into the substrate, even under the conditions prevailing in a jet machine [112].

Interest in rapid-dyeing methods and automatic control systems has encouraged study of more sophisticated methods of regulating the initial rate of sorption, to shorten the process by eliminating the need for any subsequent migration. In a system developed recently [113,114] for ionic dye systems, such as acid dyes on nylon, the relevant data are fed into a computer program which yields the following output: critical temperature zone, critical rate of heating, pH for $\leq 90\%$ exhaustion, starting temperature and flow rate in circulations per minute. The Colorex system provides on-line spectrophotometric control of the critical heating rate and has been developed particularly for basic dyes on acrylic fibres [115]. The problems in continuous monitoring of exhaustion rates of trichromatic dye combinations, where the component exhausting at the most rapid rate determines the critical rate of dyeing, have also been investigated [116,117]. It has been shown that the maximum permissible exhaustion rate must fall progressively in proportion to dyebath concentration as dyeing proceeds [118], rather than following a linear profile, as many earlier workers had assumed.

Interest in saving energy and cutting dyeing time has led to numerous processes which may result in ring dyeing. Both the rate and the degree of diffusion of dyes into synthetic fibres greatly influence the productivity, reproducibility and quality (appearance, and sometimes fastness) of the dyed substrate [119]. In the so-called Kombi Test the relative penetration rates of disperse dyes into a roll of polyester film are taken as an approximate measure of diffusion properties [120]. More recently a microphotometric method has been used to investigate the effects of dyebath variables on the rate of diffusion into polyester [121]. The dependence of affinity and diffusion properties on dye structure has been discussed for basic dyes on acrylic fibres [122].

Tests of the relative dyeability of different substrates, including measures of partition coefficients and saturation uptake, are of considerable practical importance for the design of rational dyeing processes. The work of the SDC Basic Dyes Committee included a test to define the saturation characteristics of commercial basic dyes on acrylic fibres under practical dyeing conditions [109]. Methods of estimating the content of anionic groups in acrylic fibres have been compared [123] and the dyeability of various acrylic types has been assessed in relation to polymer molecular weight and extrusion conditions [124]. In an interesting survey of disperse

dyes for polyester, relationships were established between chemical structure and several fundamental application parameters, such as partition coefficient, solubility parameter, sublimation temperature, migration and coverage properties [125].

Tests to estimate the reactivity of the dye and substrate, and extraction techniques to determine the degree of fixation, are obviously of great importance when attempting to optimize application methods for reactive dyes. The efficiency of cotton preparation can be a vital factor: recent investigation has shown that reactivity of the dye towards certain impurities is decisive in limiting the colour yield obtainable on an imperfectly prepared fabric [126]. Other workers studied the influence of the aggregation state of reactive monochlorotriazine dyes on their sorption isotherms, affinity and fixation behaviour on viscose rayon [127]. The relative advantages of high-reactivity and low-reactivity dyes in exhaust and pad—batch dyeing of cotton were reviewed recently [128].

Considerable attention in recent years has been devoted to improved methods of extracting unfixed reactive dyes from wool [129–132]. The hydrolysed form of the dye often has considerable affinity and may be difficult to extract totally without damaging the wool or hydrolysing the covalent dye–fibre bonds linking the reacted dye to the fibre, because not all the dye–fibre linkages have the same stability to hydrolysis. For a different reason, estimating the fixation of disperse dyes on polyester is also difficult. Severe conditions of solvent extraction are necessary and some dyes show inadequate stability to such treatments. Extensive studies of the relative effectiveness of different extraction solvents have been described [133,134]. An earlier scheme for the extraction and classification of various dyes from acrylic fibres [22] has recently been revised to avoid classifying some basic dyes incorrectly [135].

Reproducibility problems in dyeing systems can sometimes be attributed to fluctuations in dyebath conditions, because certain dyes show undue sensitivity to such factors as solution temperature, pH or reduction potential. Screening tests to assess dye sensitivity therefore are a further aid to dye selection, particularly when there is known to be a difficulty in controlling one or more of these variables. Modern developments in rapid-dyeing techniques have created a need for careful studies of the influence of temperature on dyeing rate for: disperse dyes on polyester [136], acid dyes on nylon and basic dyes on acrylic fibres [137]. Control of pH is important for achieving the optimum balance between dye hydrolysis and reaction with cellulose and this has been studied for batchwise [138] and continuous [139] application of reactive dyes to cotton.

Certain azo dispersive dyes are sensitive to reduction by cysteine groups in wool during the dyeing of polyester/wool blends, especially in enclosed equipment at 105°C. This problem can be minimized by keeping the pH close to 5 and by adding formaldehyde to inhibit decomposition of the wool [140,141]. Systematic regulation of pH and redox conditions are particularly important in vat dyeing of cotton; continuous titration with selected reagents [142], preferably using automatic titrating equipment [143], has been recommended. Instability arising from the decomposition of certain dye structures influences the choice of vat dyes for continuous pad—steam methods [144].

The mutual compatibility of dyes is important for cost-effective dyeing since it affects dyeing time, reproducibility and levelness. The practical significance, theory and methods of evaluation of compatibility in the dyeing of synthetic fibres have been discussed [103,145]. Test

methods to determine compatibility values for basic dyes on acrylic fibres are now well established (109,117, 146,147) and the compatibility of disperse dyes on polyester has been assessed by dip tests [148] and measurements of dyeing rate [149]. Interaction between dyes of different classes is another problem often encountered on the dyeing of blends; chromatography has been used to investigate reactions between disperse and monochlorotriazine reactive dyes in the one-bath dyeing of polyester/cotton [150].

Incompatibility between dyes and auxiliaries can be as serious a problem as mutual incompatibility of the dyes themselves; the screening of dyes for this property can be extremely time-consuming, owing to the large number of possible dye-agent combinations which may be relevant. Auxiliaries designed to modify the rate of dyeing, such as carriers for disperse dyeing [151-155], non-ionic agents used with vat [156] or with acid (157) dyes, and retarders used with basic dyes for acrylic fibres [158], must obviously be included in appropriate dye screening programmes if undesirable interactions are to be avoided. Recent interest in foam dyeing systems, intended to lower costs by conserving water and energy, has introduced a further set of solubility and compatibility criteria for dye selection [159,160].

The volatility of disperse dyes when heated to an appropriately high temperature is a characteristic exploited in several methods of coloration, such as Thermosol dyeing or transfer printing of polyester, and introduces further parameters into dye selection programmes. Knowledge of sublimation properties and ease of transfer from cellulose to polyester are essential for optimizing fixation treatment in the continuous dyeing of polyester/cotton blends [161]. Measurements of vapour pressure [162,163] and heats of sublimation of disperse dyes have been discussed in terms of molecular structure [164]. Special equipment and techniques have been developed [165] to study the behaviour of dyes in vacuum transfer printing, in order to relate the degree of vacuum to transfer efficiency and time of transfer.

Even when dye fixation is complete, further questions arise which have a bearing on dye selection. In textile printing, for example, important parameters influencing the washing-off behaviour of reactive prints on cotton, of acid prints on nylon, and of disperse prints on polyester include the amount of unfixed dye present, the rate of dye removal under the washing conditions imposed, and the tendency of the unfixed dye to stain back onto unprinted areas during washing [166]. Quantitative measurements of disperse dye removal rates from dyed nylon 6 have been published [167]. A computer program has been designed to predict from measured data the effect of washing parameters on the removal rates of unfixed reactive dyes from cotton yarn [168].

IN-SERVICE REQUIREMENTS

Many aspects of testing for cost-effectiveness and dye application properties are linked indirectly with the end use of the material to be dyed. It is essential that quality standards for dyed textiles be considered, before any dye screening programme is undertaken, to provide guidelines for operating ranges and pass/fail limits in such tests. There are certain in-service requirements, however, of direct relevance to specific dye screening tests: fastness properties are an obvious example, because here the results of generally recognized tests play an important part in determining the commercial acceptability of the dyed textile. Many fastness tests are well defined in the appropriate publications [169,170] and detailed

reviews of development in this field have appeared elsewhere [171].

The degree of dye penetration into the fibre is another property of the dyed material which has a direct bearing on user acceptability, since the appearance and sometimes the fastness properties can vary with differences in penetration. Photographic equidensitometry has been used to estimate the concentration gradient in the cross-section of a ring-dyed fibre or the peripheral staining of a polymer film [172], and a microscopic method of assessing dye penetration of fabrics in the vicinity of yarn intersections has been described [173]. An improved mathematical treatment of the relation between the colour of a dyed fibre and the concentration of dye present was derived [174] to explain why, for a given average dye concentration, the reflectance of a ring-dyed fibre is higher than that of a uniformly penetrated one.

Variations in the dyeability of different yarns within the same batch of material are outside the direct control of the dyer, but they can have a decisive influence on acceptance or rejection by the customer. It is essential to select dyes to give the best possible coverage of such irregularities, particularly for the batchwise dyeing of texturized nylon [175-178] or polyester [177,179-182], which are prone to show dyeability differences arising from variations in the conditions of false-twist texturizing. Ninhydrin and alkali solubility tests have been applied in a study of the causes of irregular dyeing in carbonized wool [183], and a test method has been designed to detect possible causes of streakiness in the dyeing of continuous-filament viscose yarns [184].

Dyes which promote (or protect against) a loss in strength of the textile substrate during dyeing, or during washing and wearing of the finished garment, pose a further problem, particularly if the finished material has marginally acceptable strength. The accelerating effect of certain vat [185] and sulphur [186] dyes on the photodegradation of cotton cellulose has long been known and preventive selection can be made. The mechanism of phototendering of dyed nylon and polyester has been studied [187]; inhibition of degradation has been noted for certain premetallized disperse, acid [188], direct and vat dyes [189], but conventional disperse and reactive dyes were much less effective [188]. Evidence from aminoacid analyses of dyed wool suggests that reactive dyes can partially protect this fibre against photo-oxidative damage [190].

Recent trends towards more stringent requirements for flame-proof fabrics have included investigations of the influence of dyes on the effectiveness of flame-resistant finishes. A comprehensive report tabulated the effect of direct, reactive, vat and sulphur dyes on the burning characteristics of cotton flannelette [191]. More recent studies were concerned with the influence of dyes on the flame resistance of nylon 6 [192] and aromatic polyamide fabrics [193].

CONCLUSION

Laboratory dye screening on a technical basis, followed by a commercial selection of the more promising candidates, with the necessary subsequent routine testing to ensure continuity of quality, whether carried out by dye manufacturers or dye users, is an extremely detailed subject involving numerous aspects of coloration technology. An attempt has been made to review the widely scattered literature that touches on the subject, but for reasons of space some topics have had to be mentioned only briefly. Dye evaluation and testing is an important

part, but only a part, of the work which must be undertaken to achieve high efficiency and cost-effectiveness in the colour-using industries.

In considering the tests mentioned in this review, it is interesting to note how many of them have had to be introduced or modified following changes now taking place in dyeing and printing. Health and safety testing is a good example, where a whole range of new or more stringent criteria has arisen as a result of new legislation. More critical requirements for flame-resistant fabrics have justified detailed studies of how dyes affect the flammability properties of various substrates.

Automation, as well as more severe economic pressures on the dye user, have favoured the rationalization of dye ranges to simplify methods and minimize stock-holding, and dyes derived from certain hazardous intermediates have been withdrawn by most manufacturers. Although fewer new dye structures are being produced, they are being marketed in a wider range of commercial forms to meet the requirements of different methods of application. Developments in pad-Thermosol dyeing and transfer printing have increased interest in the vapour pressure, transfer efficiency and rate of transfer of disperse dyes. Liquid brands of disperse dyes with improved properties for continuous dyeing and textile printing processes are continuing to make progress, and the growth of producer dyeing of acrylic fibres in the unstretched gel state has increased demand for liquid basic dyes.

Automated dye-dispensing equipment obviously puts greater emphasis on mobile liquid brands and increases the significance of specific gravity, viscosity and surface tension of dye solutions or dispersions. Current trends towards rapid dyeing, energy saving by operating at lower liquor ratios and temperatures, and the adoption of semi-continuous or compact continuous dyeing units put stricter demands on the cold solubility and solution stability of water-soluble dyes, and on the physical form and dispersion stability of disperse dyes. The introduction of partly-filled jets and overflow machines, as well as the recent developments in foam-dyeing techniques, have created a need for measurement of the foaming characteristics of commercial dyes and for study of possible incompatibility between dyes and foaming agents.

The shorter dyeing times and lower temperatures associated with rapid dyeing and energy conservation reinforce the need to ensure dye diffusion rates under these conditions are adequate for satisfactory penetration, so that colour stability and fastness are not adversely affected. Blind-dyeing techniques demand an exceptionally high standard of reproducibility and levelness, with freedom from sensitivity to small variations in dyeing temperature, pH or redox potential. Optimization of the initial rate of sorption of dyes requires a much more exact knowledge of critical temperature range, rate of heating and optimum flow rate in circulating-liquor processes.

Growing interest in on-line methods of spectrophotometric control of exhaust dyeing processes has provided the impetus for renewed investigation of the absorption characteristics of dyes in solution, particularly in trichromatic combinations for which the critical rate of sorption is defined by the most rapidly dyeing component. In spite of the practical difficulties involved in the development of versatile systems for the spectrophotometric control of dye sorption, these techniques may eventually approach the level of general applicability already reached by the methods of instrumental recipe formulation based on reflectance measurement of

dye substrates. It is clear that the story of dye testing and evaluation has not yet reached its conclusion.

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