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Whither textile colour application research?

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Dedicated to Dr. A.T. Peters in recognition of nearly half a century of outstanding research, teaching, writing and editing in the area of colour chemistry

Abstract

Colour and colour application science and technology are widely practised throughout the world today. However, there are questions which are still unresolved, and sometimes this is due to the experimental difficulties involved in pursuit of the answers. In the USA and Western Europe, recent years have seen the added commercial problems of excess global dye and chemical capacity, international sourcing, and pricing pressures. The result has been a complete reorganization of those multinational chemical companies with textile colour related divisions, followed by divestments, mergers, acquisitions, downsizing of services and a broad loss of colour and coloration expertise. Technical and commercial problems both have an impact on the future of textile colour application research, and this paper addresses some of these problems. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Colour appearance; Colour distribution; Fluorescence; Laser scanning confocal microscopy (LSCM); Shade sorting

1. Introduction

It is now about 50 years since the appearance of Vickerstaff's landmark text *The Physical Chemistry of Dyeing* [1]. This work has been the basic reference source for much of the subsequent broadening of our scientific understanding of the processes involved in dyeing, and its importance cannot be over estimated. In retrospect, Vickerstaff pulled away the shroud of mystery which surrounded the dyer's art, and replaced it with awareness that dyeing was based on the same principles as all other physical and chemical processes.

However, the development and growth in importance of the man-made fibres and of disperse and fibre reactive dyes have left this text incomplete. Many of the gaps have been plugged [2], but there are still some basic areas where our appreciation of the underlying causes of practical problems needs to be heightened. It is also of some concern to the author that, to paraphrase McGregor [3], some dyeing systems are so complex that when they are studied with scientific rigour there is a real danger that very few will be able to appreciate the details.

For an industry producing billions of pounds of satisfactorily dyed goods each year, there would

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seem, at first glance, to be little further need for scientific exotica. What is needed is a reservoir of well trained and experienced colour technologists with a general appreciation of the underlying principles which govern all physical sciences and, perhaps even more important, with an appreciation of the impact of economic pressures on coloration practices. It is only in the light of this knowledge of process economics that potentially exciting scientific and technological innovations can be seen for the academic curiosities they too frequently are.

Today, in the USA and Western Europe, the textile companies engaged in dyeing and finishing are being pressured on all sides. There have been more than 116 US plant closings since January 1999, as well as a dozen major mergers and acquisitions. In the greige areas the flood of imports from the emerging countries is a constant threat. In wet-processing, many have relied heavily on technical services provided by leading 'first tier' dyestuff manufacturers. These manufacturers are themselves in a state of reorganization and, while their products are generally of the highest quality with respect to lot to lot consistency in standardization and in-plant performance, the prices are often high relative to those imported by 'second tier' dye suppliers. For some years it has been possible for mills to overlook these high prices, because the technical service support has been of the highest calibre. However, the financial problems of these major dye manufacturers have resulted in contractions in staff and services with consequent loss of valuable expertise [4]. Most textile mills do not have back-up expertise of their own, and even if they could afford to employ suitable staff, where will it be found?

The major textile universities in the USA and the UK all have some level of problems with the enrolment of a sufficient number of suitably qualified native undergraduates to satisfy the technical needs of the existing textile industry. At the graduate level in the USA there is a preponderance of Indian and Chinese students whose work can be hard to fund because, rightly or wrongly, the textile industry sees in them the embodiment of the economic threat to the national industry. If there is to be advanced textile colour and colour application research in the USA and Western Europe in the 21st century, where will it originate? The answer seems to be: from those universities and colleges where suitable sources of research funding may be found, and which are prepared to conduct private research in exchange for that funding. In the USA, the National Textile Center [5] plays a pivotal role in ensuring that textile research work is not only undertaken, but that such work is generally available to interested parties. But how far into this century will adequate NTC funding be available, and are the academic projects undertaken of much help to the beleaguered industry?

Bearing all this in mind, the Millennium issue of '*Review of Progress in Coloration*' addresses, in a number of excellent articles, several authors' predictions for the future of colour and coloration research. The articles by Freeman [6] and Lewis [7] are of particular interest, and, because they are so complete, they leave the author free to address several outstanding problem areas of colour and coloration with which he is personally involved, where one stumbling block or another stood, or still stands, between the known phenomena and their ready quantification.

2. Problem areas

2.1. Colour appearance vs colour concentration

Qualitatively, it is well understood that the apparent depth of a colour on a textile substrate depends on the actual location of the colour. For example, if an *individual fibre* is ring dyed, i.e. more heavily dyed at its outer surfaces, it is understood that the fibre will appear lighter than if the same amount of dye were uniformly distributed throughout the fibre cross-section. It is equally well understood that if the *outer fibres in a yarn bundle*, or the top and bottom *surface fibres of a textile substrate*, are preferentially dyed darker, then the goods will look darker than expected. A good example of the latter would be found in polyester seat belts, which had been dyed continuously by thermofixation. A relatively small percentage of dye is needed to dye such belts a heavy black. But, cut through the belt and the centre is nearly white.

To a lesser extent this is also true for the polyester fibres in continuously dyed polyester/cotton goods. The consequence is that non-uniform colour distribution in textile goods could result in the goods being either darker or lighter than anticipated [8].

However, it is no mean feat to make cross-sections of fibres, yarns and fabrics and take microdensitometric measurements on numbers of individual fibres, in order to obtain a profile of what concentration of dye is in what location and within what fibres. Microdensitometry is a feasible, but difficult, technique with films. But, it becomes rapidly unmanageable with fibres, particularly those which do not have circular cross-sections. It is valuable with films. But who dyes films? Enter laser scanning confocal microscopy (LSCM).

In an outstanding piece of recent work, carried out under the funding of the National Textile Center, Srinivasaro and co-workers have shown the power of this relatively novel technique to overcome many of the experimental problems of dye distribution measurement encountered by previous researchers [9].

2.2. *The effect of different colour distribution on appearance*

In recent work conducted at Clemson, a simple model system was used to replicate the kinds of coloristic effects which might be observed if two differently coloured fibres were blended under different conditions, i.e. with different fibre distributions within the yarn, or (since the fibres were differently coloured) different colour distributions within the yarn.

The system chosen was to blend equal weights of mass pigmented black and white, 100% polyester staple fibres of the same staple length, denier per filament and other physical characteristics. These were either intimately blended or draw-frame blended in a variety of configurations of the draw frame slivers, and then either open-end or ring spun from roving.

The study showed that the differences in apparent depth possible due to variations in ideality of blending, are about 15.1±3.3%. This is almost an order of magnitude greater than the sensitivity of the human eye to detect "just-perceptible" colour differences, which is about ±2% [10]. There is no doubt that in colour matching blends of pre-coloured fibres, it will be critical for all those involved to be aware of the possible effect of variations in fibre distributions on the colour of the resulting product.

Now, in practice, whenever two or more different fibres are blended, and the product is dyed with dyes appropriate for each fibre, it should be readily apparent that unless the component fibres are dyed to a perfect union (identical reflectance curves), the resulting colour appearance of goods will be dependent on the distribution of the different fibres within the yarn. Such situations are the bane of the commission dyeing business. They often lead to the warning "not for cross-dyeing" being stamped onto greige goods contracts, notably for polyester/cellulose blended fibre fabrics.

Clearly, this study only analysed the simplest and most visually obvious situation for differential colour distribution in fibre blends. In order to broaden the information obtained here, more complicated (but more realistic) situations with other coloured fibre blends should be examined in a similar manner, and extended first to cross-dyed then to union-dyed fibre blends. As in Section 2.1, the key to all future work would be a rapid, accurate and economical way to describe quantitatively the distribution of individual fibres or colours within not just the single fibres of LCSM, but also within yarns and fabrics.

2.3. *Diffusion data obtained from textile dyeing processes*

This author would advise against taking too seriously the apparent 'poetic erudition and seeming technological sophistication' [11] of much of the research work on dyeing kinetics, approached by means of studies of diffusion and diffusion equations. Such work is problematical.

For example, the approximations which require fibres to be round are only valid in special cases. Dyers might even be excused for agreeing with Adkins: "Basic research (of this type) is like shooting an arrow into the air, and where it lands, painting a target" [12].

On the other hand Nobbs and his co-workers understood that the parameters needed to describe dye diffusion across boundary layers could not be calculated, a priori, to anticipate the behaviour of real dyeing systems, but must be constantly adjusted throughout the dyeing cycle. Such complexity seems reasonable, and the work could lead to advances in process control [13,14].

2.4. Fluorescence measurement

A variety of fluorescent compounds are used in the general textile art, from man-made fibre pigmentation through dyeing, finishing and subsequent domestic laundering processes. They are generally sub-divided into fluorescent brightening agents and fluorescent colours.

Fluorescent brightening agents (FBAs), although they are practically without colour, are aromatic and heteroaromatic organic molecules which can have anionic, cationic or non-ionic character, which have a range of solubilities in water and substantivities for different fibres which parallel the range of colorants, from readily water soluble dyes (direct, acid, basic, reactive), through sparingly water soluble dyes (disperse dyes), all the way to pigments. They are applied by methods entirely analogous to dyeing or pigmenting processes. Even the chemical nature of the primary parts of their molecules has equivalents in the chemistry of colorants [15,16]. Like colorants, they influence the appearance of treated textile materials by influencing the energy distribution and intensity of light reflected from textile materials in the visible region (380–720 nm). However, they do so only if they have been exposed to and absorbed radiation in the ultra-violet region (340–380 nm). In this case they will re-emit absorbed energy from the invisible UV light in the visible region, with peak emissions in the 425–450 nm range. They are sometimes referred to as fluorescent whiteners, optical bleaches or optical whiteners, but the Chemical Abstracts designation is adopted here, since they neither bleach nor whiten.

Fluorescent colorants are just as susceptible to being called dyes as are conventional colorants. But, many of them are, in fact, pigments [17]. However, they are closely related to both colorants and FBAs in their ranges of both solubility and substantivity. The primary difference is that they are coloured and may simultaneously both absorb and re-emit light within the visible spectrum, making them coloured whether or not they have been irradiated with UV light.

The big problem with all such fluorescent brighteners and fluorescent colours is that while they absorb radiant energy at shorter wavelengths, they re-emit radiant energy at longer wavelengths. Further, the intensity of the emitted radiation is dependent not only upon the concentration of the product on the substrate, but also on the intensity of the radiant energy to which they are exposed. Then there is the sparingly explored phenomenon of quenching!

In order to properly characterise the behaviour of the fluorescent materials a spectrometer is needed which will successively irradiate samples with discrete wavelengths starting in the UV and measure the complete reflectance spectrum of the goods at each different irradiation wavelength. Such an instrument requires two monochromators: one between the light source and the sample and one between the sample and the detector.

This technology has just recently received a significant boost by the general marketing of a reasonably priced bispectral fluorescence spectrometer. At last it will be possible to characterise accurately the reflectance and emission spectra of fluorescent textiles when illuminated by different lights, to study UV protective textiles, to develop colorimetric means of predicting formulae for matching fluorescent textiles and to predict the effect of laundering with FBA's on the colour of dyed and pigmented textiles. A short four-paper bibliography on measurement of fluorescence is appended [18–21]. Interestingly, in the USA, the ASTM sub-committee E12.05 (on fluorescence) is working on a major revision of ASTM E1249 on identifying fluorescence in object-colour specimens [22].

2.5. Domestic laundering and oxidation catalysts

In the past few years, consumers and retailers, particularly in the USA, have become increasingly concerned by the unexpectedly poor colour-fastness to laundering of some garments, particularly cotton goods dyed with reactive dyes. It is no surprise that this growing concern has emerged since the introduction of bleach activators in domestic laundry products based on perborates.

The principal objects of current scrutiny are the activators tetracetylethylenediamine (TAED) and the sodium salt of nonanoylbenzene-sulfonate (SNOBS), which under oxidising conditions become peracetic acid and pernonanoic acid respectively. The TAED is found primarily in Europe, while the SNOBS is found in North America. The latter is more aggressive. It is to be hoped that test methods will soon be developed and adopted which will closely replicate the actual performance of garments to multiple launderings with detergents containing such activators. It is already apparent that the molecular configuration of some dyes is less susceptible to destruction by multiple oxidative washing than others. For example, *o*,*o*′-disulfonatoazo groups are less susceptible than either *o*-sulfonatoazo or simple azo groups [23].

Recent papers by Phillip and eight co-workers from laundry detergent manufacturers characterise the efforts in this important and topical area [24–26].

2.6. Shade sorting

There are so many reasons why successive textile production dyeing lots should not be identical in colour, it is remarkable that any are sufficiently close to be acceptable for use together. Therefore, populations of production goods are routinely segregated by some form of colour sorting. Since the original paper on colour clustering techniques of shade sorting [27] there has been considerable interest in, but very restricted commercial adoption of, this technique by the textile industry. General awareness of the deficiencies of the current 'fixed-grid' or 555 shade-sorting systems is quite wide spread, but 'grid-free' shade sorting has only been adopted in a limited way.

There has been a recent review of shade-sorting [28] which re-emphasises the benefits of clustering, and a paper on the mathematical techniques available for clustering has been accepted for publication in the journal *Color Research and Application* [29].

However, this appears to be an area where the reluctance of industry to abandon the established colour sorting paradigms (which were simple but ineffective), could well be due to the inherent cost of venturing into new departures at a time when the textile and colour businesses are under financial stress.

Other means of organizing goods by means of numerical colorimetric values include 'shade tapering'. This is particularly effective for arranging of pieces of indigo denim goods in an order which depends on variations primarily of depth of shade [30], and ensures that rolls of goods which are nearest neighbours in the warehouse are very close matches.

3. Conclusion

There are still many questions about practical dyeing technology which need to be solved before dyeing becomes completely routine. But, in the author's opinion, the number of them which will be solved by new physico-chemical researches on the detailed nature of the dyeing process will be few and far between. Certainly, there is considerable room for progress in the more technological areas of machinery and instrumentation developments, in computer programs associated primarily with process and quality control and even in the chemistry of more efficient dye–fibre reactions. However, totally outside the reach of this present paper, there is enormous scope for improved management and accounting techniques to ensure the most cost efficient and environmentally friendly use of available resources.

The key to problem resolution on all fronts is extensive knowledge, and it is in the more general acquisition and dissemination of such knowledge that universities will continue to play a vital role.

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