It must be green: meeting society’s environmental concerns

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Consumers today are increasingly demanding goods which not only conform to the public’s image of being ‘eco-friendly’ and ‘organic’ but of having been produced ‘ethically’. Meeting such high ideals has a down side, both in higher costs and often in that of having to accept more distant suppliers. Present trends in the coloration of foods with natural dyes rather than synthetic ones, increasing consumption of organic products (including fibres) and energy-saving trends in dye application methods, fuels and lighting, as well as the means of capturing solar energy, are discussed. The discovery of some interesting and historic green colours, the wider use of green (in both senses of the word) products and green chemistry’s future role in producing them are also reviewed.

Introduction

In a seller’s market, Henry Ford famously said of his Model T car: ‘You can have any colour as long as it’s black’, but present-day customers are increasingly saying to retailers: ‘What we buy must also be green’. Green in this sense means that the article should have been produced and transported under the best environmental conditions, with minimal energy consumption and, if possible, be made from naturally available materials, preferably from local sources. Unfortunately, green issues have become inextricably confused with ‘organic’ sourcing and production, particularly where food, drink, personal care products, and even to a degree, medicinal preparations involving herbal or homeopathic treatments, are concerned. To many members of the general public ‘chemicals’, ‘synthetics’ or ‘E-numbers’ are bad for us, the corollary being that anything ‘natural’ or ‘organic’ must be beneficial. Indeed, many people seem to be unaware that some of the most toxic chemicals known (e.g. ricin and botulin) are not manufactured but are natural proteins. With the plethora of ecological and ethical phrases now in common use, caution is needed as to the precise meanings accorded to them [1]. In fact, because our preoccupation with environmental matters is relatively recent, many eco-phrases have only come into common use since the millennium [2].

To satisfy an extreme demand, one could now (with difficulty) obtain organically grown cotton dyed with natural dyes, spun, woven and made into a garment by hand. To achieve this end, the cotton crop would firstly have to be grown without the use of pesticides (at present this is by far their greatest agricultural single usage), although possibly some manual operations would involve child labour. Whilst the fabric produced might have been dyed using a natural dye (with a somewhat toxic mordant?), it would have been processed at minimal labour cost and have had to be transported many thousands of miles! Transport is indeed a problem with organic food in the UK for, at present, some 75% is imported giving it a bad ‘carbon footprint’ [3]. This is also true in the textile field owing to mass importation of ready-made garments, mainly from the Indian subcontinent and China, but there is an increasing trend towards eco-awareness in European, American and Australian textile production and fashion design [4]. The awareness of the textile production industry has differed from that of fashion designers, who can focus on the end product itself, whilst dye- and printworks have had to pay much more attention to environmental legislation regarding the safe use of dyes, auxiliary products and chemicals, and particularly the disposal of works effluent.

No supplier can now ignore the apparent needs of a relatively new, but rapidly expanding, market segment of ‘natural and ethical consumers’ (forecast to double in Western markets in the next 5 years) [5], but the word juxtaposition in the title of one of the relatively newer journals, Green Chemistry (published by the Royal Society of Chemistry), might still leave a prejudiced member of the general public a bit puzzled. Many large retailers are indeed beginning to publicise their corporate social responsibility (CSR) policies. Examples are the supermarket chains demonstrating their increased sensitivity to ecological pressures by offering customer rewards for using their own or reused plastic shopping bags (by Tesco) and the use of biodegradable bags and packaging (by the Co-operative Group and Sainsbury’s) [6]. Some investors are scrutinising CSR procedures, whilst socially responsible investment groups take things a stage further by not investing where they doubt a firm’s ethical credentials. For their part, many retailers, especially in food and clothing, are members of the Ethical Trading Initiative which requires them to impose a code of conduct on their suppliers backed by independent site visits.

In European folklore, green has been variously associated with natural forces involving growth, fertility and regeneration and was personified in mythological characters such as the Green Man, although there were also more sinister associations with death, sickness and even devils [7,8]. Psychologically, in more recent times the hue green has been regarded as denoting something which is natural and safe which is why Health and Safety Regulations specify this colour for First Aid and emergency escape route signage [9] and gas cylinders with green-painted shoulders hold only inert gases. Green is also regarded as being cool, calm, restful and natural...
the development of cobalt green (CoO\(_2\)ZnO), a pigment and availability of the mineral smalt had led to hair. In the late eighteenth century, the production of arsenic, as did several keepsake samples of Bonaparte's visitor. When analysed, this was shown to contain (2 years after Napoleon's death) containing a sample of ex-emperor's wallpaper. Amazingly, someone not only anyone had a reliable reference to the colour of the programme in 1980, the public were asked whether subsequently known as Gosio's disease. Following a radio trimethylarsine gases, which give rise to a complaint produce a mixture of toxic arsine and di- and cancer) because Scheele's Green had been used to print the wallpaper in his apartment. Under damp conditions whilst investigating arsenic, the Swedish chemist Carl Wilhelm Scheele produced a new pigment, copper hydrogen arsenate, which he recognised was very toxic. At that time, artists needed a tinctorially stronger green pigment and this product was manufactured as Scheele's Green. Although a similar but somewhat faster pigment, Emerald or Schweinfurt Green (copper aceto-arsenite) was eventually introduced in 1814, the former pigment remained popular for many years. It is quite probable that the somewhat mysterious death of Napoleon whilst in exile on Elba may have been accelerated (he had stomach cancer) because Scheele's Green had been used to print the wallpaper in his apartment. Under damp conditions mould could grow on the animal glues then used as adhesives, and this can decompose the pigment to produce a mixture of toxic arsenic and di- and trimethylarsine gases, which give rise to a complaint subsequently known as Gosio's disease. Following a radio programme in 1980, the public were asked whether anyone had a reliable reference to the colour of the ex-emperor's wallpaper. Amazingly, someone not only knew it was green but produced a nineteenth century scrapbook they had inherited, with an entry dated 1823 (2 years after Napoleon's death) containing a sample of the actual paper cut from the wall of his room by a visitor. When analysed, this was shown to contain arsenic, as did several keepsake samples of Bonaparte's hair. In the late eighteenth century, the production of zinc oxide and availability of the mineral smith had led to the development of cobalt green (CoO\(_2\)ZnO), a pigment with superior stability to the former greens, but, although relatively bright, its tinctorial strength was poor and the cheaper copper/arsenic pigments continued in use.

Up to the middle of the nineteenth century, the dyeing of textiles was of course based on the use of natural products [14], greens being obtained from plants and lichens, but in 1856 the discovery of Perkin's Mauvein and several related products (including Perkin's Green) marked the birth of the synthetic dye industry [15]. This was to be followed in 1863 by Aldehyde Green from the firm of Meister, Lucius, Bruning (later to become Hoechst). The 1860s also saw the birth of triphenylmethane (TPM) basic dyes such as fuchsine (magenta), followed in the 1870s by Methyl Green, which was soon to be replaced by Malachite Green (Basic Green 4) that is still widely used as a bactericide in aquaria despite doubts about its toxicity. Peter Griess' discovery of the diazotisation of aromatic amines and coupling with naphthols subsequently produced an enormous range of mono- and dis-azo 'aniline dyes' although homogeneous greens were not very common. The first green direct dye in 1891 was Diamine Green B (Direct Green 1), a tris-azo colour based on benzidine and one of several dyes withdrawn in the 1970s because of their potential carcinogenicity. Similarly, there were only a few greens obtainable from the azoic combinations on Naphthol AS prepared cloth by coupling with the stabilised diazo Fast Colour Salts.

The dyestuff industry in the early twentieth century was dominated by German manufacturers but systematic research in Scotland by the firm of Morton Sundour alongside Scottish Dyes in 1920 produced a vat dye having outstanding fastness properties, namely Caledon Jade Green X (Vat Green 1) [16]. Scottish Dyes became part of the newly formed ICI in 1926 and it was at Grangemouth Works that the fast blue pigment, copper phthalocyanine (CuPc) was developed following investigation of a chance observation of dark insoluble deposits being formed in chipped, enamel-covered, iron trays which had contained molten phthalic anhydride. This led in the 1930s to the equally fast corresponding green pigments based on polychlorinated CuPc, the Monastral Greens. Innovation in ICI resumed after World War II, for in 1950 the soluble CuPc Alcian dyes were introduced and yielded very fast bright blue and green shades on cellulosic fibres. These were temporarily solubilised, 'ingrain' dyes which were converted to a pigment by after-treatment with alkali. These dyes became obsolete after the introduction of fibre-reactive dyes (again by ICI) in 1956 and of the first reactive monochlorotriazine turquoise blue dye, Procion Brilliant Blue H7G, which enabled the production of emerald green shades using mixtures with bright pyrazolone yellows. Today, there are a score of homogeneous reactive greens of several chemical types which have been introduced.

Over the last 150 years, chemists and dye technologists have contributed enormously to our colourful world and many of them were themselves colourful people. To take but three of the above examples, much depended upon scientists with enquiring minds turning an apparent failure into a success. William Perkin, trying to synthesise quinine at a time when structural organic chemistry was in its infancy, produced a black tar. Many would have discarded this and tried something else but, seeing the beautiful colour of an alcoholic extract and finding this dyed silk and cotton he, supported by his family, eventually became a very successful dye manufacturer [17]. Again, when problems occurred at the Grangemouth works in the production of phthalimide (used in the manufacture of indigo and produced by the action of ammonia on molten phthalic anhydride) it was observed that black occlusions were produced only in chipped enamel trays. The simple solution was to throw any...
damaged trays away but again the plant chemist, A. G. Dandridge, decided to investigate further and, although early experiments produced only dull colours, eventually a new bright blue pigment, copper phthalocyanine, was born whose chemical structure was eventually confirmed using X-ray diffraction images [18]. Then, 100 years after Perkin's discovery, reactive dyes for cellulose fibres were first marketed. The original work on reactive dyes at ICI's technical service laboratories in Blackley were for dyeing wool; amongst the more promising experimental dyes tested were the dichlorotriazines but these still did not fix very well. To attain better fixation, a strong alkali appeared to be required, which was of course impractical because it would have severely degraded the fibre. Not deterred, the dye technologist involved, Ian (later Professor) Rattee, in present day parlance ‘thought outside the box’ and decided that such conditions would, however, be quite acceptable for dyeing cotton and, in cooperation with Dr W. E. Stevens, the first three Procion dyes were born [19]. Initially, the ‘Saltfix’ application method involved padding the dyes and then passing the fabric through saturated brine containing caustic soda. In time it was found possible to apply these dyes under much milder conditions and, as they say, the rest is history.

Trends in food coloration

In most countries of the world, the use of added colour to foodstuffs has been highly regulated for a considerable time but ‘permitted’ colours vary from one country to another and these lists are being constantly updated. Two important classification systems are those in Europe, covered by the European Directive of 1994/1995 (94/36/EC, 95/45/EC), together with their subsequent amendments of 1999, 2001 and 2006 which clarified definitions and limitations of use, and those in the USA represented by the Food and Drug Administration (FDA) Federal regulations [20]. In Europe, food additives and colorants are classified by ‘E-numbers’ with their Colour Index (CI number) reference. This list includes both synthetic dyes and natural colorants, for example, lycopene and β-carotene, mostly obtained from natural sources, but chemically identical products may sometimes be made synthetically or biosynthetically, which may allow slight structural modifications [21]. In both the European and the American regulatory systems, the use of some colours is restricted to certain specific outlets such as animal feeds. In the USA, the 30 natural colours listed are, however, classed as exempt from certification. Synthetic colours are usually referred to as ‘artificial’ (or as ‘E-numbers’) by the general public in the UK and recent years have seen much publicity about certain products, such as tartrazine (E102, CI Food Yellow 4) used in confectionary and orange-flavoured drinks and thought to lead to hyperactivity in some children. USA Federal regulations on food labelling require that colour products from natural sources, although exempt from certification, must be described as ‘artificial’ or ‘added’ colours as the authority maintains that ‘natural’ colour can only be that originally present in the particular foodstuff. Details of all well-established sources and properties of natural food colours can be found in Hendry and Houghton’s ‘Natural food colorants’ [22]. The EFSA (European Food Safety Authority) is at present reviewing data on the presently permitted dyes and will eventually review the legislation, but this process is only at a very early stage.

Reacting to pressure from consumer groups and general public demand, much has been achieved in the display of data on packaged processed food with regards to its components and nutritional value, as well as there being an indication of the presence of any additives such as preservatives and colours, all identified by E-numbers. E-number products total over 300, only 42 of which are colours. Packaged foods now also display labels with a ‘traffic light’ system to indicate the levels of salt, sugar and fats based on a ‘guideline daily amount’ for adults. The recent display on some packaged snack foods of the ‘carbon footprint’ of its contents in grams of carbon dioxide is, however, somewhat meaningless to the purchaser. In Europe, the market for organic foods is estimated at €15 bn and growing at around 10% per annum [23], whilst in 2006/2007 the UK showed an even higher rate of increase of about 30% [24]. To be certified as organic, products must be grown or manufactured in a manner that adheres to standards set by authorities in individual countries and in the UK these are the Organic Farmers and Growers [25] and the Soil Association [26]. Although scientific evidence for the direct benefits to the consumer of organic food are still in dispute [27,28] there are benefits in reduced ecological damage and the overall consumption of energy, if one neglects subsequent transport costs [29]. Many other aspects of the production, nutrition role and safety of organic foods have been recently reviewed [30]. It does seem likely that more food will have to be grown without the use of pesticides because new European Union (EU) legislation looks likely to ban perhaps 90% of them [31]. This in turn may increase the need to accept pest-resistant genetically modified (GM) foods.

Heightened customer awareness to environmental issues has led to strong public resistance to the introduction of GM crops or the sterilisation of food using ionising radiation. There is a particular expectation that if it is required to add any colour to organic food it should be a natural product. Those derived from fruit and vegetables such as the betalains (from beetroot) and lycopene (from tomatoes) may thus seem particularly attractive, but only if the customer recognises their origin. There are few problems using natural colours where yellow or orange shades are required but most approved reds and blues are synthetic. The recent rapid expansion of the organic food market has therefore led to a renewed interest in natural colours, developed in modified forms if necessary (Table 1). Some analysts predict a 10–15% per annum growth for natural colours, which is 10 times that for synthetics. Some natural food colours such as the carotenes are surprisingly stable to extremes of pH and temperature, but others are inferior to synthetics in such respects, a specific example being that concerning the colouring of tinned peas. Without the use of added colour, the thermal processing of tinned marrowfat and

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Table 1 UK permitted natural colours

| Generic name                      | Source          | Shade                | Identification (EU) | Colour index (CI) |
|----------------------------------|-----------------|----------------------|---------------------|-------------------|
| Curcumin                         | Turmeric plant  | Green–yellow         | E100                | CI Natural Yellow 3 |
| Riboflavin (and phosphate)       | Yeasts          | Yellow               | E101                | CI Food Yellow 15  |
| Cochineal                        | Scale insects   | Red                  | E120                | CI Natural Red 4   |
| Chlorophyll/chlorophyllin (Cu complex) | Spinach, alalfa, etc. | Green | E140                | CI Natural Green 3/5 |
| Caramel                          | Corn syrup      | Brown                | E150                | CI Natural Brown 10 |
| Vegetable carbon                 | Vegetable charcoal | Black              | E153                | CI Natural Black 3 |
| Carotenoids                      |                 |                      |                     |                   |
| β-Carotene                       | Carrots, etc.   | Orange–yellow        | E160(a)             | CI Natural Yellow 26 |
| Annatto (bixin/norbixin)         | Bixa seeds      | Yellow–orange        | E160(b)             | CI Natural Orange 4 |
| Paprika (capsanthin)             | Capsicum seeds  | Orange–red           | E160(c)             | CI Natural Red 34  |
| Lycopene                         | Tomatoes/rose hips | Orange–yellow      | E160(d)             | CI Natural Yellow 27 |
| Lutein                           | Mangolds        | Yellow               | E160(f)             |                   |
| Beetroot red (betaxanthin/betacyanin) | Beetroots     | Red                   | E162                | CI Natural Red 33  |
| Anthocyanins                     | Algae/mulberry fruit | Red–blue–violet  | E163                |                   |

mushy peas would leave the contents with an unappetising olive brown colour and the desirable bright green shade has traditionally been attained using a mixture of Green S (E142) and tartrazine (E102). The change of shade during heat treatment of green vegetables is because of the instability to acid of their own natural chlorophyll, which tends to lose its coordinated magnesium and form pheophytin. In fact, it is because of the potential instability of natural chlorophyll (E140) that it is also sold as its copper complex (E141). Similarly garden peas and spinach can be treated so as to preserve more of their fresh chlorophyll green colour during the canning process by the introduction of zinc or copper ions [32], but in a recent exercise by the Co-operative Group supermarkets to replace all synthetic food colours with natural ones, it was found impossible to find a sufficiently stable natural colour to replace Green S. This retailer has in fact decided to withdraw some 27 product lines which cannot be reformulated satisfactorily using natural colours [33]. Most of the major UK food retailers have since followed this lead and reformulated the colours used in their ‘own brand’ ranges of food products, some retailers even claiming that their foods will be ‘free of E-numbers by 2008’, a statement which further fosters the public misconception that only synthetic dyes carry this designation.

Other uses for food grade colours

Natural food colours are manufactured in various forms but principally as water- or oil-soluble (or dispersible) preparations, depending on the required application. A third type of formulation which is required for the specialised printing of food wrappings is pigment dispersions. Here, it is clearly a requirement that these do not transfer to the food product itself. Few EU-approved pigments are listed but include three iron oxides (all listed under E172), calcium carbonate (Pigment White 18), titanium dioxide (Pigment White 6) and Lithol Rubine BK (Pigment Red 57.1); the last named can, however, only be used for colouring cheese rind. It has been argued that if the print on packaging is never in contact with the food and the wrapping is itself impermeable then no contact colour transfer can occur [34]. The situation in this field is at present unclear because printing inks are not specifically covered by EU legislation other than the general food safety Framework Regulation (EC Regulation No. 1935/2004) and three Directives (80/590/EEC, 89/109/EEC, 89/109/EC). Other draft Directives have long been under discussion but there is still no imminent legislation. General guidance on the selection of pigments for printing packaging can be found in ‘Colourants for food contact plastics’ published jointly by Eurocolour, ETAD (Ecological and Toxicological Association of Dyers and Organic Pigments) and the VdMi (Verband der Mineralarbenindustrie) [35].

Today, consumers are possibly oversensitive to the ‘sell-by’ and ‘use-by’ dates printed on packaged food, for the rate at which the product deteriorates is largely determined by the storage conditions, particularly the temperature. A novel type of label which changes colour according to a time/temperature function has been proposed [36]. This consists of a colourless layer containing Crystal Violet lactone (see Scheme 1) and a second layer containing an acid donor which is attached only when the food is first packaged. The acid, which is slowly released thereafter, at a temperature-dependent rate, causes an increasing degree of violet colour change until it becomes noticeable.

Those who feel that present-day regulations may be too stringent, particularly those concerning the very low levels of metal contaminants specified in colorants, might be reminded that despite tight import controls it is still possible for major lapses to occur, as exemplified by the massive recall by Mattel of painted children’s toys which were manufactured in China [37]. The problem is that toys which might be handled by very young children may also be sucked, leading to ingestion of potentially toxic metals and hence the very low permitted levels [38,39]. This had to be borne in mind in the rather unusual case of producing for the
diet supplements are approved natural colorants which are also sold as human food colorants. Whether this leads to improved night vision [44]. Other human trials are now being carried out in the USA to see if a similar increase in the response of retinal sensors to red light and night vision can be replicated.

In animal experiments, a diet containing the supplement drug is extracted (e.g. lycopene from tomatoes) seems more effective than the purified component and more scientific study is needed [45]. This finding does, however, emphasise the recommendation that for a healthy diet it is probably simpler to try to eat five portions of fruit and vegetables each day as most of these contain natural anti-oxidants. Chlorophyllin tablets were once popular as breath fresheners but may also help protect against carcinogenic aflatoxins and mycotoxins [46].

Many drugs in pill or capsule form are surface coloured using food grade products for their identification, which can be recognised by reference to the MIMS (Monthly Index Medical Speciality) Colour Index [47], a commercial CD-ROM database displaying thousands of colour pictures of drugs, or its online version from TICTAC [48]. There is no set meaning for the specific colours, although different colours do appear to affect people’s attitudes, green pills being associated with inducing relaxation and sleep and in general being considered as good for you. Bright colours are usually avoided as they can attract children to think the pills are confectionery.

Trends in textile colouration

The past decade has seen major increases in the cost of energy, with crude oil now trading at over $100 a barrel, a higher level (in real terms) even than that which resulted from the oil crisis of the 1970s, and this is being felt by the general public as well as by industry. Any possibility of decreasing our overall energy consumption, whether it be by using more fuel-efficient vehicles, increasing the efficiency of heating systems or minimising water consumption, not only decreases direct costs but contributes to cutting our contribution to global warming [49]. In fact, many of the machinery and process developments on show at the International Textile Machinery Manufacturers’ Association (ITMA) exhibition in 2007 followed a general theme of energy and water consumption savings. This has been a theme for the past decade in textile processing, with continual improvements in the efficiency of dyeing processes aimed at minimising their environmental impact [50]. Recent examples include:

- attaining approaching 90% dye fixation on cellulosic fibres by batchwise dyeing using poly-functional reactive dyes [51,52];
- considerably shortening the total dyeing time and energy consumption when batchwise dyeing disperse and reactive dyes to produce blacks on polyester/cotton blends [53];
- more than halving the energy, water and chemical consumption in the continuous dyeing of polyester/cotton blends [54] and
- a reawakened interest in cold pad–batch dyeing processes using reactive dyes [55,56].

Scheme 1

First, truly coloured bubbles using dyes which neither stained the skin nor clothing but which were also acceptable environmentally. To achieve this it is not only necessary to select a colorant that associates with the micelles of the chosen surface active agent on the bubble’s surface but can also be prevented from staining by including suitable dye blocking agents in the formulation. Finally, when the bubbles burst they were to become colourless. This aim was finally achieved by using TPM dyes having a labile leuco form; for example, Crystal Violet lactone (normally used in carbonless copying papers), which only becomes coloured when the lactone ring opens to yield the carboxy form (Scheme 1) [40]. For creating the world’s first truly coloured bubbles, the inventor, Ram Sabnis, was presented with a Grand Innovation Award in 2005 [41]. Certain natural colorants are promoted as diet supplements although positive evidence for their efficacy is limited, other than the fact they contain anti-oxidants which are ‘good for the heart’. One of the leading causes of blindness in people over 65 is age-related macular disease (AMD). Some types of AMD can be treated by photodynamic therapy, using targeted treatment of the retina by a laser beam of shortwave ultraviolet (UVA) radiation. Prior to this the patient is injected with a photosensitising drug such as fluorescein or Indocyanin Green, which accumulates in this location [42]. Lutein and its stereoisomer zeaxanthin are always present in the foveal region of the human eye and are thought to serve as UV filters and as anti-oxidants [43]. Both are recommended as dietary supplements, ostensibly to prevent or delay the onset of AMD. Both carotene and lutein are used as food supplements in poultry feed as a means of controlling the colour of both egg yolks and the flesh.

In animal experiments, a diet containing the chlorophyll derivative, chlorin e 6, has been shown to double the response of retinal sensors to red light and human trials are now being carried out in the USA to see whether this leads to improved night vision [44]. Other approved natural colorants which are also sold as human diet supplements are β-carotene and lycopene (both anti-oxidants) and turmeric, an anti-inflammatory. In some cases, it has been shown that the original food from which a supplement drug is extracted (e.g. lycopene from tomatoes) seems more effective than the purified component and more scientific study is needed [45]. This finding does, however, emphasise the recommendation that for a healthy diet it is probably simpler to try to eat five portions of fruit and vegetables each day as most of these contain natural anti-oxidants. Chlorophyllin tablets
Manufacturers have also helped by continual refinement of textile machine design and its control equipment, which together with dye selection and reliable recipe prediction systems in the laboratory have contributed to a high proportion of ‘right first time’ dyeing [57].

The upsurge of concern with all things ecological has in extreme circumstances certainly affected some consumers’ interest in organic textiles, principally cotton. To be classed as organic the cotton fibre used to produce the fabric must have been grown from genetically unmodified seed varieties, without the use of herbicides or pesticides and with ethical labour employment standards. Certain bioengineered cotton varieties have, however, been shown to have good natural pest resistance and in the USA and China have also produced improved yields [58,59] so it seems a pity that such varieties are excluded for what appear to be psychological reasons. One cannot, however, treat this trend as just a fad when major manufacturers such as the Levi jeans and Nike sportswear companies have been promoting the use of organic fibres in a number of their internationally established brands. Through the auspices of an international working group a ‘global standard specification’ for such goods has been drawn up (http://www.global-standard.org). Minimum colour-fastness standards seem rather low but much more critical analytical data are specified to meet low residues of bactericides, pesticides, formaldehyde and heavy metals. Some dye manufacturers are now publishing lists of dyes that have been approved by the Institut für Markto¨kologie (IMO) in Weinfelden, Switzerland.

A number of authorities have introduced certification and labelling schemes for eco-textiles but most still rely on the IMO as the certifying authority. In 1992, the Oeko-Tex Standard 100 was introduced by the International Oeko-Tex Association to provide a scientifically founded evaluation standard for the human ecological testing of textiles [60]. More recently the Oeko-Tex Standard 1000 has been introduced as a means of certifying an acceptable level of environmental and ethical control during the production process. Firms that can demonstrate controlled production right from the original fibre through to the final garment can be awarded an IVN (Internationaler Verband der Naturtextilwirtschaft) label. Where the natural fibre alone is to be covered by a label scheme, there are those of the Organic Trade Association in the USA, the textile standards of the Soil Association in the UK and the textile programme of Demeter International certification in Germany. There is also an EU Regulation, EEC 2092/91, covering organic textiles and criteria for the award of a community eco-label (EEC Council Regulation 2002/371/EC).

In order to meet the present-day high levels of dye fastness of textiles expected by consumers, it is certainly fortunate that, in all the abovementioned organic certification schemes, there is no mention of a need to use natural dyes, although there is a very small market niche for ‘one of a kind’ garments [61]. Some designers claim that it is an advantage (as providing originality) when using natural dyes because ‘no two dye baths are identical’ but for textile coloration it seems unlikely that the question ‘Is there a future for natural dyes?’ will ever be posed again [62]. In a few cases it may, however, prove possible to produce some dye intermediates from natural sources [63].

### Green dyes in biomedical applications

The extensive range of biological staining dyes, among them many ‘classical’ greens, that have found uses in histology has been recently reviewed [64]. Although the Alcian dyes were withdrawn from sale for textile dyeing in the 1960s, the use of Green 2GX (Ingrain Green 1) continues for the staining and identification of mucopolysaccharides [65]. It has also been used to visualise skeleton structures in the study of embryonic development of animals [66]. The phenazidium dye, Janus Green B is used as a diagnostic stain in the study of the endothelial cells of the cornea but is considered too toxic to be used in vivo. Green B is also used as a stain for identifying mitochondria [67]. The TPM dye, Fast Green FCF has been used for studies on human kidney function but its use is not permitted in the EU or the USA and it has been replaced by Green S (Food Green 4). This dye is also used as a third component of Gabe’s Trichrome, a mixed stain which simultaneously can differentiate between nuclei, cytoplasm, collagen and red blood cells [68]. Indocyanin Green is used as a stain but has been used in low concentrations as an aid to examinations or surgery on macular holes and the blood vessels of the retina, in conjunction with a scanning laser ophtalmoscope or infrared fundus camera [69]. In this case there is some evidence that the outcome of such treatments is little different without the use of the stain [70].

### Green fluorescing dyes

There are several examples where luminescent and fluorescent effects can be observed in nature and the colour of the emitted light is often greenish. Luminescent effects range from those caused when certain marine dinofflagellates (Pyrophrya) are mechanically disturbed [71] to the luciferin-based bioluminescence of fireflies and glow-worms [72]. Using a wide selection of dyes, such as substituted fluoresceins and rhodamines, which can selectively complex with specific end groups in protein-like molecules, various techniques for identifying drugs, hormones, antigens and DNA fragments, etc. have been devised. Much use has been made of genetically engineered forms of the naturally occurring fluorescent green protein [73], originally obtained from the jellyfish Aequorea victoria, to produce biosensors. When used in living systems, these are much less toxic than the standard fluorescent marker dyes, such as fluorescein isothiocyanate, whose application is confined to in vivo analysis methods such as automated DNA (deoxynucleic acid) sequencing, much used in human profiling for criminal forensics and the study of genetic disorders [74].

Fluorescence microscopy [75] is a relatively simple system in which a sample, tagged with a fluorophor, is examined visually when illuminated with light of a specific wavelength. The emitted light from the sample is
imaged electronically, having first passed through a dichroic mirror which excludes the illuminant beam. Oregon Green (difluorofluorescein) can, for example, be used to measure protein and nucleic acid interactions [76]. It has been suggested that this relatively simple technique could be used to detect pathogens such as Escherichia coli or the severe acute respiratory syndrome (SARS) virus using a novel, synthetic DNA molecule which is described as a ‘tree (Y) shaped nanobarcode’. The fluorophor’s three ‘legs’ fluoresce red, yellow and green, respectively, and complex to differing degrees with each pathogen, which thereby enables their identification [77].

A wide variety of fluorophors, mostly derived from the basic fluorescein structure, are used in the more powerful technique of flow cytometry. This is a system which can selectively separate and identify a range of biological cells from their shape, size and fluorescent responses. Modern flow cytometers are extremely versatile as they can operate with up to four laser beams (to excite fluorescence at different wavelengths) as the analyte is passed in a fine jet stream through the laser beam and can measure both reflection and transmission responses in up to 18 fluorescent wavebands [78]. Flow cytometry is thus a very powerful analytical technique which is applicable in an enormous range of sciences, including pathology, haematology, immunology and plant and marine biology.

There has been increasing use of ‘quantum-dot’ fluorophors, which are multi-shell nanoparticles consisting of a phosphor core (typically cadmium selenide/zinc sulphide or indium gallium phosphide) with a polymer coating and sometimes an outer biomolecular layer. Compared with conventional fluorescent dyes, these fluorophors, which are now used for fluorescence microscopy, spectroscopy and flow cytometry, have higher quantum yields, brighter fluorescence and greater photostability [79].

**Green photoemitters**

Considerable advances have been made during recent decades in reducing the power requirements for illumination and some types of colour display. Thus, major savings can be made using modern ultra-bright light-emitting diodes (LEDs) as replacements for tungsten filament bulbs in traffic lights, by replacing conventional fluorescent tubes in chain stores and warehouses with more economical types and, domestically, everyone is being urged to reduce their carbon footprint by fitting the newer, more compact, energy-saving light bulbs. A recent innovation is the replacement of the conventional xenon flash tube as the D65 illuminant in spectrophotometers by an LED array which is pulsed in synchronism with the measurements of the reflected beam, thus eliminating any effect from ambient light and allowing online colour measurements in continuous coloration processes [80].

Cathode ray tube (CRT) picture displays have largely been replaced by liquid crystal displays (LCDs), which are more compact and now freely available in large-size displays. LCDs now seem able to compete with plasma displays, which had previously dominated the larger-size, flat-screen market. In the UK, the British Broadcasting Corporation satellite and cable high-definition television (HDTV) transmissions, which are best viewed on a larger screen, started in December 2007 and the gradual changeover to terrestrial digital TV transmissions is causing a boost to the sale of ‘HDTV-ready’ sets. There seems no general agreement as to which main picture definition will be used, the individual programme makers being able to choose between the 720- and 1080-lines (interlaced or progressive scan) standards.

As far as small screen displays are concerned, the demand for multipurpose hand-held equipment, particularly mobile phone and miniature computer displays, continues to be met mainly by LCDs, but organic light-emitting diode (OLED) displays that are lighter, require no back light and have a wider angle of viewing also consume less power and look particularly attractive for such applications [81]. Sony is the first to market an extremely slim, OLED, 11-inch colour-screen TV receiver [82]. An astonishing array of inorganic phosphor compounds have been investigated which, when irradiated with varying types of electron beam, produce visible light. Table 2 illustrates the types and uses for such compounds, selected from those that produce light in the green waveband, which in TV displays is that carrying the main luminance signal.

| Phosphor | Designation | λ<sub>max</sub> | Application (properties) |
|----------|-------------|----------------|-------------------------|
| ZnS:Cu,Al,Au | P22G | 565 | CRT monitors, TV tubes (short/medium persistence) |
| Y₂SiO₅:Tb | P39 | 525 | Projection CRTs (very high luminance, short persistence) |
| ZnS:Cu,Ag | P31 | 550 | Oscilloscopes (high luminance, short persistence) |
| Y₂Al₂O₁₇:Ce | P46 | 530 | Beam index (single electron gun) CRT tubes |
| Y₂Al₂O₁₇:Tb | P53 | 545 | Field emission and electroluminescent displays |
| Cd₂O₂S:Tb | 545 | X-ray screens |
| Ca₂Al₂S₄:Eu | 520 | Electroluminescent devices [111] |
| MgAl₁₂O₁₉:Ce,Tb | | | Plasma displays [112] |
| YBO₃:Tb + MgAl₂O₄:Mn | | | Plasma displays |
| (La, Ce,Tb)PO₄ or (Ce,Tb)MgAl₁₂O₁₉ | | | Trichromatic fluorescent lampsa (high luminance, long persistence) |

a Energy-saving light sources using one-quarter of the electric power and having five times the life of tungsten filament bulbs; colour temperatures range from 2700 (warm white) to 6500 °K (daylight) [113]
matching cabinet are unsatisfactory and also determining identifying when the illuminants in a particular colour Colourists (SDC) is currently examining means of Measurement Committee of the Society of Dyers and sources are summarised in Table 3. The Colour illumination. The properties of these and some other light optical whites and fluorescent samples) ultraviolet European store lighting (TL84; Illuminant F11) and (for (Illuminant D65), ‘tungsten filament light’ (Illuminant F), normally have the ability to produce ‘artificial daylight’ particular account in colour-matching cabinets which are required for colour matching and this is taken into fluorescent tube types is critical where precise conditions smooth as those of the broadband types. The choice of desired industrial application, although the spectral power distribution curves with these tubes are not as smooth as those of the broadband types. The choice of fluorescent tube types is critical where precise conditions are required for colour matching and this is taken into particular account in colour-matching cabinets which normally have the ability to produce ‘artificial daylight’ (Illuminant D65), ‘tungsten filament light’ (Illuminant F), European store lighting (TL84; Illuminant F11) and (for optical whites and fluorescent samples) ultraviolet illumination. The properties of these and some other light sources are summarised in Table 3. The Colour Measurement Committee of the Society of Dyers and Colourists (SDC) is currently examining means of identifying when the illuminants in a particular colour-matching cabinet are unsatisfactory and also determining the suitability of colour-matching rooms.

**Fluorescent lighting**

The nature of the light output from a fluorescent tube (which is based on a mercury discharge lamp) is determined mainly by the choice of the phosphor coating on the inside of the tube. Tubes can be produced as standard, broadband or narrow tri-band types. Compared with a standard tube, the broadband tubes have better colour-rendering properties because they use multiple phosphors, whilst the tri-band types, as their name suggests, have three, narrow-band-emitting, rare earth phosphors which together produce a highly efficient white light. The output can be tuned to a range of colour temperatures; for example, to correspond to the Committee Internationale d’Eclairage (CIE) D50 or D65 standard sources of artificial daylight, depending on the desired industrial application, although the spectral power distribution curves with these tubes are not as smooth as those of the broadband types. The choice of fluorescent tube types is critical where precise conditions are required for colour matching and this is taken into particular account in colour-matching cabinets which normally have the ability to produce ‘artificial daylight’ (Illuminant D65), ‘tungsten filament light’ (Illuminant F), European store lighting (TL84; Illuminant F11) and (for optical whites and fluorescent samples) ultraviolet illumination. The properties of these and some other light sources are summarised in Table 3. The Colour Measurement Committee of the Society of Dyers and Colourists (SDC) is currently examining means of identifying when the illuminants in a particular colour-matching cabinet are unsatisfactory and also determining the suitability of colour-matching rooms.

**Miscellaneous energy-saving systems involving colour**

**Greener processes for the manufacture of dyes and related chemicals**

Having accepted that, at least as far as the coloration of textiles is concerned, we must continue to rely on manufactured dyes, there are many possibilities that they may in the future be synthesised using greener chemistry; for example, using less energy, eliminating or more efficiently recycling organic solvents or achieving higher yields with minimal by-product formation. Today, green chemistry is a subject in itself and particularly good progress is being made using novel, selective homogeneous, heterogeneous or bio-catalysts, which give high product yields under very mild reaction conditions [83,84]. General examples appropriate to dye manufacture are those involving sulphonation, nitration, halogenation or diazotisation, in which the formation of large amounts of inorganic salts is prevented by replacing the conventional stoichiometric quantities of mineral acids and alkalis. By using recyclable solid acids and bases, which are preferably present in only catalytic amounts, yields approaching 100% can be achieved. Biocatalysis is illustrated by the Mitsubishi process, using the nitrile hydratase enzyme, for the production of acrylamide from acrylonitrile, a process which proceeds at 5 °C without the need for a polymerisation inhibitor [85]. In the case of an improved biosynthetic, enzymic production method for indigo, technology seems to have gone full circle [86]. Another example concerns intermediates for fibre manufacture. The precursor for nylon 6 is ε-caprolactam, which is produced from cyclohexanone using a two-stage process involving aggressive chemicals and high-reaction temperatures, creating large amounts of ammonium sulphate as a by-product. It has been shown that this conversion can be achieved at low temperature in a single stage with a nanoporous, aluminophosphate catalyst using only air and ammonia [87]. Biosynthetic methods of production of some natural dyes used as food colours, such as β-carotene, riboflavin and phycocyanin, have also been devised.

Where water cannot be used in a conventional synthesis method, there has long been the aim of avoiding the chance of releasing volatile organic chemicals by replacing conventional organic solvents with supercritical carbon dioxide or ionic liquids [88], which, for example, have been examined as solvents for cotton linters, a process that would be much more environmentally acceptable than that at present used for the production of viscose fibres [89]. It is not, however, always essential to use solvents, for some reactions, particularly those involving the formation of metal complexes, can surprisingly be carried out efficiently in the solid state, simply byball milling the reactants together [90].

**Solar energy conversion**

With the ever-increasing cost of energy, it is natural to try to find improved methods of harvesting the radiation received on the earth’s surface (on average 340 W/m²) to supplement the diminishing natural resources of gas, coal
and oil, in which are stored the energy received from the sun some 400 million years ago. In hot, sunny climates it was possible to use this energy directly for some processes, such as sea-water evaporation in brine ponds to obtain valuable sea salt (another product which the eco-consumer somewhat illogically prefers to mined, recrystallised and purer salt, which is still just as natural). In recent times, there was some use made of a dye, Solavap Green [91], which absorbed, particularly in the infrared wavebands, to accelerate the solar evaporation process. Domestic solar pre-heating of water using rooftop heat exchangers is viewed as ecologically desirable, but the climate of the UK means that the payback period is rather long. This is even more the case with electrical solar cells, despite the advances that have been made in their design and efficiency. There remain, however, problems of storing and converting the power for normal domestic consumption. The main applications for arrays of such cells has therefore been to power traffic signs in remote locations (where they are often backed up by small wind-powered generators) or as trickle chargers for batteries feeding low-power electronic equipment.

The most efficient solar cells are still based on costly silicon technology, but there has been much research into a completely different system which is inherently simpler and cheaper to produce, namely the use of dye-sensitised, crystalline dispersions of titanium dioxide in so-called Grätzel cells, so named after their inventor [92,93]. These consist of very thin (10 µm), transparent, layers of titanium dioxide nanoparticles, in a liquid or gel-like medium sealed behind a transparent conductive electrode. In addition, the dispersed crystals of titania are coated with a photosensitiser dye. These dyes may be substituted fluoresceins [94], porphyrin compounds [95,96] coumarin dyes [97] or some novel ruthenium polyppyridyl dye complexes [98] which also absorb light in the infrared and avoid the need for a liquid medium. An alternative to microcrystalline titania, in the form of zinc oxide nanorods, has been proposed [99]. The efficiency of these cells ranges from ca. 8% to 12%, which is not as high as that of the very best attainable with silicon cells (ca. 15–20%), but they will be much cheaper to manufacture, particularly as it has proved possible to 'print' the titanium dioxide layer onto polyethylene terephthalate films. The first commercial application of these is as solar chargers for mobile phones, but UK production of much larger solar panels for domestic use is planned. In America the manufacture of thin film, printed, solar cells based on a CIGS (copper indium gallium diselenide) nano-particle material, with an energy conservation efficiency of about 15%, has started [100].

Alternative green fuels

There has been considerable recent publicity given to the development of new transport fuels to augment or replace existing oil-based products, the chief contenders being bioethanol and biodiesel. Bioethanol, produced by fermentation of the carbohydrates in soya beans, corn (USA) or sugar cane (South America) is now used as an additive (10–15% maximum) to petrol engine fuel, whilst biodiesel, derived from seed oils such as corn or rape or made from reprocessed cooking fats, has a small share of the market. Biodiesel has already been tested as a jet engine aviation fuel and, from a logistics point of view, the North Atlantic Treaty Organisation (NATO) would like to have a common fuel for its air and land transport system [101]. The problem with making fuels from agricultural crops is the loss of productive capacity for foodstuffs. Thus, in 2005, bioethanol production in the USA used 14% of the entire corn harvest, whilst in Brazil it consumed almost half of the sugar crop and shortages have already adversely affected the commodity prices of both corn and sugar [102]. The process for producing biodiesel from recovered vegetable oils is relatively simple but involves saponification of the glycerides it contains and methanol to esterify the fatty acids produced, whilst leaving the problem of disposing of the glycerol by-product.

Second generation biodiesel fuels will therefore almost certainly be based on conversion processes using biomass (waste wood, sawdust, straw or even leaves) that will be subjected to high-temperature pyrolysis and the released gases converted via a catalytic Fischer Tropsch process to biodiesel [103]. This process was much used in South Africa because of import sanctions imposed during the days of apartheid. The Fischer Tropsch process could also be applied directly to convert the abovementioned glycerol by-product into fuel [104].

All the above processes are roughly carbon neutral, in that only the same amount of carbon dioxide originally locked in the plant material will be released again into the atmosphere. Another more distant possibility is to trap the carbon dioxide emitted from power stations by using the exhaust gas to cultivate certain green algae which produce glycerides, from which a biofuel could then be extracted [105]. Exhaust carbon dioxide has also been used in greenhouse cultivation of crops such as tomatoes which can be grown hydroponically in 'polytunnels', the plastic sheeting for which may be coloured with a green pigment which transmits the two photosynthetically active wavebands around 450 and 650 nm [106].

For identification and tax enforcement purposes, fuels are often coloured; for example, in the UK and Spain agricultural diesel is red but green in Norway and Ireland. During, and for a time after World War II, when fuel was rationed, commercial vehicles used red petrol and this was coloured with Solvent Red 19 or 24, which were relatively easy to remove, but the fuel was further tagged with a colourless additive, dimethylamine. This could be detected even in the engine exhaust fumes using test papers impregnated with aniline acetate which gave a red colour reaction. Nowadays, red diesel, which has a considerably lower taxation level, is a slightly different distillation fraction containing more sulphur than fuel used in vehicles. In the UK it is illegal to use red diesel for other than agricultural vehicles and machinery, commercial maritime vessels and, until October 2008, privately owned pleasure craft. It is equally illegal to use heating oil as a diesel fuel. In the UK, colourless markers are therefore still in use; for example, quinizarin is added to red diesel and coumarin to heating oil at such a concentration as to be unnoticeable until a fuel sample is...
shaken with a small volume of aqueous alkali. An equally simple test, in this case shaking with an acid solution, produces a colour reaction when Crystal Violet lactone is used at low concentrations as a fuel marker. A further approach is to use compounds which can be detected spectrophotometrically by characteristic fluorescence or infrared absorption peaks, but this has the disadvantage of not being applicable for on-the-spot testing. At present in the UK, despite these controls to enforce collection of the appropriate tax, private individuals are surprisingly free to set up a small plant to produce biodiesel from waste vegetable oil which, as long as it is used personally, attracts no taxation from HM Customs and Excises.

For some purposes it is necessary to colour not the fuel but the exhaust gases when a fuel is burned. The fuel may be initially fluid or solid, depending on the application, but similar solvent soluble dyes are used in both cases. To heighten the effect of acrobatic or fly-past displays it has long been the practice to colour the exhaust gasses from jet engines. Aircraft smokes are produced by dissolving a suitable dye, such as Quinizarine Green SS (Solvent Green 3), in a mixture of perchlorethylene and diesel fuel and injecting this into the exhaust of the aircraft’s jet engine. Similar dyes are used to colour smoke flares and military smoke grenades, the use of which raise more safety issues than aircraft smokes. Safety distress flares for maritime emergency use are usually red and contain a solid pyrotechnic mixture with the addition of Solvent Red 1 or Disperse Red 9. Military smokes are produced in a variety of forms, but consist of a solid fuel which used to be based on sodium chlorate and sulphur, with sodium bicarbonate added to reduce the burning temperature. More recently these compositions have been modified by replacing sulphur with sugar and sodium bicarbonate with the more effective magnesium bicarbonate. The selection of the dyes (e.g. benzanthrone) used in smoke grenades has also been modified following toxicity testing on animals, although no serious side-effects of the smokes have been reported for human inhalation, the main concern being mainly the possibility of allergic dermatitis [107].

Where wind-tunnel testing of vehicles or model aircraft designs is to be carried out, it has been usual to generate laminar streams of white smoke by feeding an oily, smoke-producing compound onto a series of vertical or horizontal heated wires [108]. The airflow can then be visualised and, if different colour-producing smokes are produced at different locations, colour photographic records can be obtained for later study [109].

Finally, one rather frivolous application for the production of coloured smoke comes from the USA where, after much experimentation, it proved possible to incorporate a solvent dye into rubber tyre compositions to produce a colourful smoke effect when cars are skidded on the race track [110]. These tyres are now commercially available for enthusiasts but are not recommended for use on public roads!

Conclusions

There seems to be no doubt that the pressures on suppliers and retailers to source their goods ethically and with minimal adverse effects on the environment will continue to increase. These demands arise not only from consumers but from many national and international organisations whose aim is to raise public awareness of such issues, particularly where food is concerned, but they also consider more general factors such as climate change, the ecology, energy consumption, recycling, employment ethics etc. Every apparent improvement carries a downside. Ethical employment standards ban the use of child labour yet in some countries the alternative for the children themselves may be starvation. Buying a ‘Fair Trade’ item may make us feel good but, like organically produced food, is more expensive and it is clear that there is a section of the public that simply wishes to buy the cheapest food. Nevertheless although eggs produced from battery-reared hens are undoubtedly the cheapest (but the least ‘natural’ as far as the chickens are concerned) some UK supermarkets are now to sell only barn or free range eggs.

As far as food colours are concerned nearly all the major retail groups have already changed (or are actively involved with such changes) from synthetic to natural colours, with the supposed aim of ‘eliminating E numbers’, but the removal of many other food additives whilst maintaining a product’s expected shelf life may prove more problematic. Scientific evidence of serious adverse effects with any of the present permitted synthetic colours is very limited, so these changes merely meet a public perception, whilst a more cynical view might be that this is largely another means of promoting a company’s image and of course its sales.

In many regions of the western world the general level of obesity (with other issues of heart problems and diabetes) is said to be increasing so clear labelling of food with dietary information is of considerable value. Several organisations whose aim is to raise public awareness of such issues, particularly where food is concerned, but consumers but from many national and international organisations whose aim is to raise public awareness of such issues, particularly where food is concerned, but they also consider more general factors such as climate change, the ecology, energy consumption, recycling, employment ethics etc. Every apparent improvement carries a downside. Ethical employment standards ban the use of child labour yet in some countries the alternative for the children themselves may be starvation. Buying a ‘Fair Trade’ item may make us feel good but, like organically produced food, is more expensive and it is clear that there is a section of the public that simply wishes to buy the cheapest food. Nevertheless although eggs produced from battery-reared hens are undoubtedly the cheapest (but the least ‘natural’ as far as the chickens are concerned) some UK supermarkets are now to sell only barn or free range eggs.

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In many regions of the western world the general level of obesity (with other issues of heart problems and diabetes) is said to be increasing so clear labelling of food with dietary information is of considerable value. Several systems are in use and a truly simple, universal mode of display, such as the ‘traffic light’ one at present recommended by the Food Standards Authority and used by a number of stores, is still desirable.

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