POTENTIAL FOR COLOURANTS FROM PLANT SOURCES IN ENGLAND & WALES

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ARABLE CROPS &
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SUMMARY

1. Dyes and pigments found in plants have been used for centuries for colouring materials. The dye molecules may function in the plant as colourants and/or in other roles, eg, in photosynthesis.

2. The use of natural dyes in the UK and the rest of the Western economies has been replaced commercially by synthetic dyes, based mainly on aniline and using petroleum or coal tar as the raw stock. The range of synthetic dyes available is large and the dyestuff business is worth approximately £2.5 billion per year world wide.

3. Natural dyes represent an apparently more sustainable source of colourants than their synthetic counterparts, which are derived from non-renewable resources.

4. The yield of natural dyes from a plant source is usually low compared with the yields expected of modern synthesis processes. Their tinctorial strength tends to be less than that of synthetic dyes which means that a greater weight of plant material would be needed directly for use or for extraction of the natural dye than of the synthetic dye in order to obtain the same depth of colour. Thus any large-scale use would require many hectares to be cultivated with the plant species and the disposal of relatively large volumes of crop and processed residue.

5. Most plant species contain colorants, the better sources having been used and sometimes cultivated in the past. Some useful dye plants already exist as cultivatable crops but the majority of species would need selection from wild types to eventually produce acceptable crop plants. Husbandry techniques would also need development, eg, pest, disease and weed control, planting density, and harvest and post-harvest techniques.

6. There was some reluctance to reveal current research because of potential commercial exploitation.

Specific sectors

Textiles

7. In the textile industry the modern dyeing processes and machinery are designed for use with synthetic dyes. Natural dyes, used in the traditional ways, are generally more inconsistent in performance, and several require the use of additional chemicals that are potentially hazardous to the environment and need control procedures. Synthetic dyes have been designed to give good results on the textile concerned, including artificial fibres as well as natural ones. Many natural dyes do not perform well with artificial fibres.

8. A craft market for natural textile dyes exists and is likely to continue, perhaps with some expansion.

9. Any commercial market for natural textile dyes in the UK is likely to be a small, high value, low volume niche market. However, depending on the dye concerned, UK producers would be

competing with those in other countries, such as India, where a natural dye industry still exists and the product is likely to be cheaper. The drivers for the development of markets for natural dyes are likely to be fashion and public opinion, and, probably most significantly, legislation.

10. Manufacturers have invested in the production and use of synthetic dyes and are unlikely to make large changes without a major factor such as legislation or market pressures.

Food and drink

11. Natural colourants are already used widely in this industry. Use will probably increase with the need to have colourants that produce the required colour but with the minimum risk to the consumer. Some synthetic food colourants have been withdrawn as potential adverse effects on human health from their use have been identified. There is a particular need for a good red dye that is stable at higher pH levels. The public perception of natural colours is that they are safer and better than man-made dyes.

12. There may be opportunities for import substitution of natural colourants. Tumeric, curcumin, etc UK growers to produce plant stock for natural colours currently imported into the UK.

Inks and surface coatings

13. Although natural products provided the pigments for the first inks and other surface coatings, they are not used now, with the exception of carbon black and titanium oxide (both of non-plant origin). The requirements for modern inks are highly specific to the end use and printing process. The largest single use is for black newsprint-type inks.

14. There may be niche areas for inks containing pigments derived from plants. These would depend very much on the compatibility of the plant colourant with the formulation of the ink required by the printing process and end use. The plant-derived pigment would also probably need to have a unique property, such as edibility, not found in similar synthetic inks/coatings. The printing of labels and packaging in direct contact with food would be a possible specialised use.

Other uses

15. Natural plant dyes have been used for many centuries as hair and face colourants. An increased interest in them has led to the development of modern preparations including natural extracts or products. There is a market for such products although it is hard to quantify its value, longevity and extent.

16. It is possible that dyes could be used as a source of raw materials for the synthesis or extraction of other valuable, non-colourant products, in other words, not used as or grown for colourants. In addition, several plants containing colourants also contain other substances with pharmaceutical and other properties and it may be possible to develop the concept of multiuse crops where several different products are harvested from the same plants, for example, berries,

leaves and bark, each of which yield a separate product. This type of approach may be necessary if there is no single overriding use of sufficient value to justify growing the plant as a crop.

RECOMMENDATIONS

1. Any proposal concerned with natural dyes and pigments should be closely linked, ideally including funding, to the end use. The risk involved in developing a niche market could be considerable and there should be evidence of the likely returns before substantial public investment is committed.

2. It is likely that there is greater potential development for natural dyes for food and drink than for textile dyes and other uses. The development of natural colourants for food and drink is likely to be a priority area for funding it is wished to encourage industrial co-funding, although such work is likely to be near-market.

3. Improving the quality and yield of natural dye substances is likely to be key in any development in this area. The following research areas are the most important:

   - to understand the physiological and agronomic factors affecting the quality and yield of colourants from the plant
   - to improve the quality and yield by selection, conventional breeding, and by genetic manipulation and transformation
   - to develop efficient systems of dye plant production (eg, nutrition, pest, weed and disease control, husbandry, suitable rotations and soil types).

4. The following areas are also of interest but probably of lower priority:

   - to increase the efficiency of extraction of the dye from the plant
   - to investigate the agricultural use of plant wastes from natural dyeing processes
   - to investigate the role of dye substances in plants.
   - to determine the environmental impact of cultivating dye plant species

5. A further area for work is the development of alternative uses for dyestuffs, eg, as chemical sources for other products or non-dye uses for glucosinolates such as pest control. It is suggested that such work should be done in collaboration of some sort with a potential user.

6. Use as colourants or for colourant production is unlikely to be priority area for the development of alternative crops in the UK.

1. DEFINITIONS & TYPES OF DYES

1.1 Dyes have been defined as intensely coloured substances used for colouration. They are retained in substances by physical adsorption, mechanical retention, the formation of covalent chemical bonds or of complexes with salts or metals, or by solution.

Pigments retain their crystalline or particulate structure throughout their application. Dyes lose their crystal structures during application by dissolution or vapourisation. These are the strict definitions: in the literature and common usage, the terms dye and pigment tend to be used rather loosely and interchanged but dye is often used for textile and food colourants, and pigment for inks, paints and cosmetics.

A water soluble dye can be converted to a pigment by making it into a lake, which combines the colour with a basic radical such as aluminium or calcium to make a salt on a substrate of alumina. The substrate is insoluble and thus provides an insoluble form of the dye, ie, a pigment.

1.2 Natural dyes can be defined as those colorants (dyes and pigments) obtained from animal or vegetable matter without processing. When used as textile dyes, they are mainly mordant dyes although some belong to other groups (vat, solvent, pigment, direct and acid). Most of the historically important colourants are members of the anthraquinone, naphthoquinone, indigoid and carotenoid groups. There are no natural dyes of the sulphur, disperse, azoic or ingrain types.

1.3 Dyes are classified in two ways; by chemical composition, principally used by manufacturers, and by application class or end-use, principally used by dyers. Each dye is described under the internationally accepted Colour Index classification system by a CI Number, relating to its chemical class, and by a CI Name, relating to use (Anon, 1971).

1.4 The classes of dyes defined by the application or end-use, and hence the terms most applicable to textile dyeing, are:

acid - water-soluble anionic dyes

basic - water-soluble cationic dyes

direct - water-soluble anionic dyes which are substantive to cellulosic fibres when dyed from aqueous solution

disperse dyes - water insoluble, nonionic dyes used for dyeing hydrophobic fibres from aqueous dispersion

fluorescent brighteners - not dyes as such, applied from solution, dispersion or suspension in a mass reactive dyes - form a covalent bond with the fibre (usually cotton, wool or nylon)

sulphur dyes - applied to cotton from an alkaline reducing bath

vat dyes - water insoluble dyes applied mainly to cellulosic fibres as soluble leuco (ie, colourless) salts after reduction in an alkaline bath

pigments - printed on to surface with resin binder or dispersion in a mass

solvent dyes - dissolved into the substrate (eg, varnish, waxes, inks, oils)

Colourant types

Synthetic dyes

1.5 The first recorded synthetic dye was picric acid which produced in the 1770's from the interaction of indigo and nitric acid. The synthetic dye industry is considered to have started when Perkins synthesised mauveine (mauve) in 1856 in the UK. The industry quickly developed, mainly in Germany, Switzerland and the UK. Since then the significant dyes discovered were: alizarine red, 1868, by Grabe and Lieberman; indigo in 1870 by von Bayaer; the azo dyes in 1880; anthraquinone vat dyes in 1901 by Bohn; disperse dyes for cellulose in 1922; fibre reactive dyes by ICI in 1956.

1.6 There are very many synthetic dyes available now. Their tinctorial strength, concentration, colour range and colour fastness, particularly to light and detergents, make them superior to natural dyes for nearly all uses. They are relatively cheap and have other advantages, eg, mordants may not be necessary, they can colour synthetic fibres. Manufacturers and processors using dyes have to deal with potential health, effluent disposal and other environmental requirements, usually to statutory limits.

Natural dyes

1.7 The plant dye groups considered to be most important are indicated below (with examples of pigments and sources). A plant species will often contain several dyes and a particular dye may well be present in other plant species than those used as the traditional source. This naturally occurring combination of dyes may be used or a particular dye may be extracted for use alone.

1.8 Anthracenes

The two major groups of the anthracenes contain several well-known dyes. Anthraquinones, eg, alizarin, mungistin, purpurin from Madder family; emodin from Persian berries, plus cochineal, kermes and lac (all derived from insects). Napthoquinones,eg, juglone (walnut) and alkanin; hypericin (St. John's wort). See also Tables 1 & 2.

1.9 Carotenoids

These are a family of yellow and orange pigments found in most photosynthetising organisms. Over 200 naturally occurring carotenoids have been identified but only a few are commercially available, including β-carotene, β-apo-8'-carotenal and canthaxanthin. The carotenoid pigments are terpenoids based on a structure of 40 carbon atoms, and are lipid soluble, not water soluble. One or both ends of the carbon chain has a carbon ring attached. As terpenoids, carotenoids are related to other important plant compounds such as latex and essential oils. They are found in the chloroplast membranes or in chromoplasts (specialised plastids). The concentration of the carotenoid in the chromoplasts can reach very high levels and crystals may be formed. The two major groups in the family are the carotenes (orange or red-orange) and the xanthophylls (yellow). β-carotene is the major carotenoid in algae and higher plants. Although the carotenoids can absorb light of particular wavelengths and are involved in some way with photosynthesis, their exact role in plants is uncertain. They appear to be able to act as accessory pigments by absorbing light energy and transferring it to chlorophyll.

They are active anti-oxidants and may have value in addition to their colourant properties in preventing or restricting the development of cancers and other disorders in mammals. In a plant carotenes seem to protect the chlorophyll by combining reversibly with free oxygen radicles to form xanthophylls. This situation can occur when chorophyll becomes excited by light, cannot transfer its energy to another pigment molecule and reacts with oxygen to produce a free radicle or superoxide. The enzyme superoxide dismutase is produced by plants to inactivate superoxide but carotenoids can dissipate excess energy without producing radicles. Carotenoids absorb blue light very strongly and in absorbing excess blue light may prevent the photooxidation of chlorophyll.

1.9.1 Carotenes

Carotene was first isolated as red crystals from carrots in 1831. It is closely related to vitamin A and generally occurs as a mixture of α-, β- and γ-carotene in the ratio 15:85:0.1.

Lycopene is the main colourant of tomatoes.

1.9.2 Xanthophylls

These are oxygenated carotenes. Examples are - lutein (nettles, French marigolds), cis-bixin (annatto), crocin (saffron).

Annatto is used mainly for colouring dairy products and is derived from *Bixa orellana*.

Saffron (*Crocus sativus*), whose main dye constituent is crocin, was a major colouring agent used since the Greeks and Romans. In the Middle Ages it was used particularly for producing an imitation gold on paper mordanted with iron. It is still grown as a dye crop, mainly for food, in parts of Spain but the labour costs are very high, the dye is restricted to the stigmas which means that many flowers are needed to produce a small amount of the dye, and there is likely to be little future for the crop.

1.10 Flavonoids

Flavonoids are derivatives of phenylalanine and the acetate coenzyme A esters, and are based on a C6-C3-C6 structure. The C3 link forms a heterocyclic pyrone ring. The oxidation state of this ring and the hydroxylation or methoxylation of A ring (first C6 group) distinguish the various groups of flavonoids. The three major groups are the flavones, flavonols and anthocyanidins; others include the anthocyanins, isoflavonoids, chalcones and aurones. Flavonoids tend to absorb UV-B light very strongly and it is thought that they may play a role in preventing damage to leaf tissues by ultraviolet radiation. They also attract insects such as pollinators sensitive to UV light by causing UV-reflecting patterns on flowers, etc.

Flavonoids are used by the plant as defence compounds and as signalling compounds in reproduction, pathogenesis and symbiosis. They are produced in relatively large quantites in the plant and have significant effects on the rhizosphere and soil composition when released form the plant. They may also be involved in allelopathy (plant-plant interactions). There is no definite evidence of other physiological roles of flavonoids although some studies suggested that some of the family may be involved in regulating plant growth. The isoflavonoids are known to act as the major group of phytoalexins in legumes and their production can be triggered by infection of the plant with a fungal disease such as *Phytophthora*. The chemistry of flavonoids is relatively well known.

1.10.1 Anthocyanidins and anthocyanins (scalets, reds, violets and blues)

These are the most highly coloured of the flavonoids. Twelve anthocyanidins are known. The degree of colour they show is determined by the degree of hydroxylation or methoxylation of the B ring (the second C6 group). Hydroxylation tends to increase blueness, methoxylation increases redness.

Anthocyanins are the glycosides of anthocyanidins, produced by the substitution of sugars for a hydroxyl group. Light, nutrient stress and low temperature stimulates the production of anthocyanins. Anthocyanins are found in plants much more commonly than the parent anthocyanidins. Colourant performance can be modified by the presence of metals, by pH and by interaction with colourless flavonoids. Glycosides of cyanidin are found in more than 80 % of pigmented leaves and 50 % of flowers. The most frequently occuring glycosides are those of cyanidin, delphinidin and pelargonidin. The most common anthocyanidins are cyanidin (red-purple), delphinidin (blue-purple), malvidin (deep purple), peonidin (red), petunidin (purple) and pelargonidin (orange-red).

The anthocyanins are water-soluble and are easily extracted into weakly acidic solution. This ease of extraction accounts for their wide early use as dyes and colourants. However, anthocyanidins and anthocyanins are both sensitive to pH and this can restrict their use as colourants in certain situations, eg, in foods.

Examples are - malvidin (mallows), cyanidin (several plant families). Also carajurin (*Bigonia chica*), awobanin (*Commelina communis*), dracorhodin & dracorubin also known as Dragon’s Blood (Natural Red 31) (*Doemonorops propingus*). The last has been used in the printing trade for preparing halftone plates for multicolour printing. The food dyes peonidin from cranberries and enocionia from grapeskins are anthocyanidins.

1.10.2 Flavonols and flavones (yellows).

Flavonols tend to fade in strong light, flavones tend to be more permanent but paler in colour. - quercetin, kaempferol and myricetin (many families); fisetin (fustic, nettles, etc), morin (fustic, Osage-orange, etc), apigenin (daisy family), luteolin (daisy, pea and weld), flavone (primrose).

Most natural yellows occur in the plant as glycosides or esters of tannic acid.

Luteolin was an important yellow dye and weld was cultivated for this use in much of northern Europe. A major use was the dyeing of gold braid. With the appropriate mordant (alum) on silk it is the most light fast natural yellow. It is reputedly still used in parts of Europe for dyeing leather.

Morin can be used on leather, silk, and wool and nylon when mordanted with chrome.

The major exploited source of quercitron is the inner bark of the quercitron tree (*Quercus tinctoria*) but it is present also in horse chestnuts, onion skins, tea and sumac, and several other plants.

See also Table 3.

1.10.3 Minor flavonoids

Chalones - coreopsidoside and mareoside (daisy family).
Aurones - sulphuroside (fustic, daisy family).
Isoflavones Tend to produce strong, permanent colours - genistein (pea family), osajin and pomiferin (Osage-orange (*Maclura pomifera*)).

See also Table 3.

1.11 Betacyanins (betalains)

These red dyes and the related group the betaxanthins (yellows) were thought to be flavonoids but differ in that they contain nitrogen and do not change colour reversibly in the same way as anthocyanins do to pH. They are glycosylated as are the anthocyanins. Apparently they are only present in a few families of the Chenopodiacae, such as the beet, portulacca and goosefoot families.

Betanin is an extract from the red beet (*Beta vulgaris*) that is used mainly as a food colouring. The extract contains red and yellow pigments. Betanin is the major component (95%) of the red pigments in the extract.

1.12 Flavins

Flavins are very common in living organisms, riboflavin and two of its derivatives being the three most common. Their precise physiological role in the plant is unknown but it is thought that they may be involved as receptors of blue light and UV-A. (The receptors for UV-B are unknown.) Riboflavin (an alloxan adduct) is a yellow dye closely related to vitamin B2 and used for colouring food. It can be synthesised.

1.13 Dihyropyrans

These are closely related to flavones. The most important dyes are haematin and haemotoxylin, which are the principal colourants found in logwood (*Haematoxylon campechianum*), used traditionally in Mexico and Central America to dye textiles blue. Logwood is used in the leather industry for tanning and dyeing. Historically logwood was the major source of dark colours on a wide range of natural fibres.

The other dyes of significance in this group are brazilin and brazilein, from the genus *Caesaplina*, which produce a vivid but fugitive red.

1.14 Tannins

Tannins are present in most plant tissues but are especially associated with damaged tissues and with bark. They are produced from the flavonoids, especially the anthocyanins, when tissues break down.
Hydrolysed tannins (yellowish colours) - gallotannins (fustic and oak), ellagitannins (eg, sumac, water-lilies).
Condensed tannins (reddish colours) - eg, in oak, willow bark, cutch and water-lilies.

1.15 Indigoid dyes

The two most important dyes in this group are Tyrian purple, derived from the molluscs *Murex trunculus*, *M. brandaris* and *Purpura lapillus*, and indigo.

The main dye chemical in Tyrian purple is 6,6'-dibromoindigo; the natural source is not used now because of the large number of shellfish needed to produce even a small amount of the dye and because of the relative scarcity of the shellfish.

Indigo is known to be present in a small number of plants; indigo (*Indigofera* spp), woad (*Isatis tinctoria* and other species), a Japanese knotweed (*Polygonum tinctorium)* and common knotweed (*P. aviculare*), *Nerium tinctorium*, Marsdenia and *Lonchocarpus cyanescens*. These plants contain the glucoside indican or isatan B, which is soluble in water and hydrolysed to indoxyl in the dyeing process. Oxidation, usually by exposure to air, turns the indoxyl to indigotin (or indigo blue), which is insoluble in water, ether and alcohol. Other dyes such as indirubin and kaempferol may also be present.

In 1976 the estimated world demand for indigo was 13,000 t (Chemistry Week, 3 March 1976). Most industry analysts consider that there will always be a comparatively high demand for indigo. It is the most important dye, in terms of volume. There are at least 30 different pathways known for the synthesis of indigo. The major synthetic route used yields about 94% of indigo. The yield of indigo from the best natural source available (*Indigofera*) is about 60% (Clark *et al*., 1993).

The synthetic product is known as CI Vat Blue, CI Number 73000; the natural product as CI Natural Blue 1, CI Number 75780. The colour produced by the two products differs slightly because natural indigo also usually contains other dye chemicals (such as indirubin, indigo brown, indigo gluten and indigo yellow).

1.16 Chlorophyll

Chlorophyll is the major pigment used by plants for capturing light energy. A chlorophyll molecule consists of a porphyrin head (four pyrrole rings containing nitrogen arranged in a ring around a magnesium ion) and a long hydrocarbon tail. The hydrocarbon tail is lipid-soluble. There are four types of chlorophyll; chlorophyll a is found in all higer plants, algae and cyanobacteria, chlorophyll b in higher plants and green algae, chlorophyll c in diatoms, dinoflagellates and brown algae, and chloropyll d in red algae only.

The dye is extracted from natural sources (usually stinging nettle, spinach, alfalfa or corn) and used extensively in colouring inks, resins, soaps and waxes, edible fats, cosmetics, liniments, lotions, perfume, mouthwashes and leather. The dyestuff is known as CI Natural Green 3, CI Number 75810.

It is very difficult to prepare chemically pure chlorophyll and the commercial product contains a mixture of the two chlorophyll a and b (in the ratio of 3:1) and several carotenoids. The commercial process for extracting chlorophyll from plant material involves many steps using solvents such as petroleum ether and acetone.

1.17 Phycobilins

These are accessory pigments using in capturing light energy by red algae and cyanobacteria. Three of the four known phycobilins are involved in photosynthesis - phycoerythrin (phycoerythrobilin), phycocyanin (phycocyanobilin) and allophycocyanin (allophycocyanobilin). In structure they are similar to the chlorophylls but are linked to a protein. Phycobiliproteins appear as red or blue pigments and are being investigated as possible colourants for foods and cosmetics. The fourth phycobiliprotein is phytochrome, which also is very important in higher plants as a light receptor, especially in plant development.

1.18 Other dyes include the diaroylmethane curcumin (from tumeric), the pterocarpans (from sanderswood), the neoflavonoid berberine (from barberry and mahonia).

1.19 Lichens and fungi

Lichens are composite organisms of fungi and algae, and have long been used for dyeing textiles. The colors obtained from the dye-bearing lichens range from oranges, yellows and browns to reds, pinks and purples. They tend to grow slowly and only in unpolluted conditions, so their use on a large-scale for colorants would not seem to be ecologically desirable or sustainable. However, their dyes are substantive, extremely fast to light, washing and salt water, and generally require a short, simple extraction process. Species of particular value include *Cladonia impexa, Evernia prunastri, Hypogymnia physodes, Lobaria pulmonaria, Ochrolechia parella, O. tartarea, Paramelia omphalodes, P. saxatilis, Rocella tinctoria, Umbilicaria pustulata,* and *Xanthoria parietina*.

Little seems to be known about the dyes present in or produced by lichens. *C. impexa* contains usnic acid. The dye from *R. tinctoria* was used as a substitute for royal purple when the dye industry based on the shellfish species collapsed. The colour range suggests similarity to the anthocyanins and other flavonoids but their fastness indicates otherwise. Likewise, little seems to be known about the colourants shown by fungi but, in most cases, the colour is restricted to the epidermis. It seems likely that the colourants produced by lichens derive wholly or mainly from the algal element of the organisms.

Lichens may be difficult to work with but the qualities of the dyes may repay study and development given suitable and economically viable uses for them. In recent work in the US, reported in the New Scientist, the genes responsible for pigment production in one type of lichen have been identified, opening the way to introducing them into other plant species more amenable to cultivation.

Monascus fungi have been used for a very long in parts of Asia to colour foods such as rice, wine and soybean products (Jacobson & Wasileski, 1994). The pigments can be extracted, modified to produce red pigments that can be used as food colourants. They can also be used directly by growing the mycelium on a food substrate which is then dried, ground and incorporated into the food to be coloured. The traditional cultivation method is to grow the fungus on trays of steamed rice. The pigments produced include carotenoids, iridoids, flavanoids and phycobiliproteins.

1.20 Dye source

All parts of a plant may yield a dye but the same plant species can give different colours and intensity depending on the part used and its age, the locality and conditions for growth, and the time of year. In craft dyeing generally about twice the weight of plant material to the weight of the fibre is used but the density of colour is affected by several variables, such as the heating time and and contact time. Generally less plant material by weight is needed when dyeing with lichens.

Relatively little seems to be known about the causes and management of variation in colour and intensity in dye plants. The production of the anthocyanins is known to be affected by several environmental factors and it is likely that some of the other classes of dyes are similarly affected.

Likewise, few, if any, of the dye plants grown in the UK have been selected and developed as varieties or as agronomically sound crops. The EC co-sponsored a project (Contract no. AIR.CT94.0981(SC)) which investigated the cultivation and extraction of natural dyes for industrial use in natural textiles production for four major and previously important dye plants, woad, weld, golden rod and madder (Mangan *et al.,*1995). The University of Bristol was the UK partner.

Indigo is a tryptophan-based pigment and as such could well be amenable to production from micororganisms by fermentation (Jacobson & Wasileski, 1994).

1.21 Dye Yields

A modern synthetic dye contains about 50% by weight of pure dye content (Severkow, 1988). The concentration of natural dyes in plants is usually quite low; typical values quoted are carotin 0.007%, carthamin 0.3%, curcumin 5% (dry weight), hypericin 0.15%, indigo 2%,of which 20% is pure dye content (from indigoferas, concentration in woad is lower), madder 1.9%, and crocin (from saffron) 1% (Severkow, 1988). At least four times the weight of woad leaves per unit weight of indigoferas or polygonums is needed to produce the same depth of colour. Clark *et al.* (1993) state that a good quality indigo contains about 60% pure indigo.

However, in looking at the efficiency of dyes the tinctorial strength (weight needed to produce a colour of a standard strength in the substrate) also needs to be considered. About 1.5 g of a modern synthetic dye is required to dye 100g of fibre (Severkow, 1988). About 120-240 g of dry plant dye would be needed to achieve the same result (Glover & Pierce, 1993) or the equivalent of 500-1000g of fresh plant material. They calculated that 1 g of synthetic dye is equivalent to 400 g of fresh dye plant. The amount of fresh plant material needed to replace synthetic dyes with natural dyes for the annual production of cotton was estimated to be 15 million t per year, and 176 million t for wool.

In Italy, Angelini *et al* (1996) found that the yields of alizarin extracted from the roots of one hectare of madder plants 30 months after planting was sufficient to dye 16 t of yarn. Enough luteolin to dye 5 t of yarn was obtained from one hectare of weld plants.

These relationships have important implications for the production of dye crops when considering the replacement of synthetic dyes with natural dyes.

1.22 Post-harvest processing and handling

Most plant-derived dyes are used directly from the fresh plant material or from plants dried and stored for later use, depending on the dye. These are the traditional ways of using natural plant dyes. The dried material may be used whole chopped or powdered. Roots and wood may be chipped before use or drying. Some plants were treated in a different way, the most well known example being woad. Leaves were picked and crushed by heavy, horse-drawn rollers. The resulting mass was balled and air-dried. The woad balls were stable chemically and could be stored and handled more easily than the fresh material. It overcame the problem inherent in most plant dyes of seasonality of supply. Later, the balls were powdered by rollers and fermented to a fine powder. The powder was then packed and dispatched to the dye houses for use. *Indigofera* and *Polygonum tinctoria* can be treated the same way. This treatment is unnecessary for indigo-containing plants if used fresh.

The problems arising from handling, storing , transporting, drying and other processing would need to be addressed if large-scale production of plant-derived dyes was developed. Primary processing at the point of production to produce a concentrate of some sort may be possible. To make production as cheap as possible it would be desirable to transport as little water as possible, to use as little heat and space for drying as possible and to store as little material as possible. al needs to be achieved with the minimum use of labour. Countries where labour, heat and transport are cheaper than in the UK would have the advantage.

Continuity of supply is another area that would need to be addressed. The production and collection of fresh material is usually seasonal, and the quality of the colourant variable through the season and with the age of the material. The simplest solution is the storage of material by the producer or the user; both have cost and, possibly, quality and environmental implications.

Table 1. Examples of natural anthraquinone dyes

Dye name	CI Number	CI Name	Natural source
alizarin	75330	Natural Red 6,8,9,10,11,12	madder, chayroot
purpuroxanthin or xanthopurpurin	75340	Natural Red 8, 16	madder, munjeet
rubuadin	75350	Natural Red 8,16	madder, *Gallium*
morindanigrin	75360	Natural Red 19	*Morinda umbellata*
munjistin or purpurin-xanthin-carboxylic acid	75370	Natural Red 16,8	madder, munjeet
morindadiol	75380	Natural Red 18	morinda root
sorajidiol	75390	Natural Red 18	morinda root
chrysophanic acid	75400	Natural Red 23	turkey rhubarb
purpurin	75410	Natural Red 16,8	munjeet, madder
pseudopurpurin	75420	Natural Red 14,9,8	*Gallium*, madder
morindon	75430	Natural Red 19, Yellow 13	oungkouda
emodin or frangula-emodin	75440	Natural Green 2, Yellow 14	Persian berries
laccaic acid	75450	Natural Red 25	*Coccus laccae*
kermesic acid	75460	Natural Red 3	*C. ilici*
caminic acid or cochineal	75470	Natural Red 4	*C. cacti*

Source: Kirk et al (1979).

Table 2. Examples of natural alpha-naphthoquinone dyes

Dye name	CI Number	CI Name	Natural source
lawsone	75480	Natural Orange 6	*Lawsonia inermis*
lapachol	75490	Natural Yellow 16	taigu or lapachol wood
juglone	75500	Natural Brown 7	walnut shells
deoxysantalin	75510	Natural Red 22,23	sanderswood, barwood
alkannan	75520	Natural Red 20	*Anchusa tinctoria*
alkaninor or anchusin	75530	Natural Red 20	*Anchusa tinctoria*
shikonin or Tokyo violet	75535	-	*Lithospermum erythrorhizon*

Table 3. Examples of natural flavonoid dyes

Dye name	CI Number	CI Name	Natural source
pratol	75570	Natural Yellow 10	red clover
apigenin	75590	Natural Yellow 1,2	Greek chamomiles, weld
luteolin	75590	Natural Yellow 2	dyers rocket, dyers wood
fulsugetin	75600		Garcinia spicata
genistein or prunetol	75610		dyers broom, greenweed
fisetin	75620	Natural Brown 1	Venetian sumac
datiscetin	75630	Natural Yellow 12	bastard hemp
kaempferol, trifolitin or indigo yellow	75640	Natural Yellow 13,10	natal indigo, dyers knotgrass
kaempferol 7-methyl ether	75650	Natural Green 2, Natural Yellow 13	sap green, Hungarian berries
morin	75660	Natural Yellow 8,11	dyers mulberry, osage orange
quercetin, meletin or sophoretin	75670	Natural Yellow 10, Natural Red 1	Persian berries, toon or Indian mahogany tree
isorhamnetin	75680	Natural Yellow 10	red clover
rhamnetin	75690	Natural Yellow 13	buckthorn
xanthorhamnin	75700	Natural Green 2, Natural Yellow 13	sap green, Hungarian berries
rhamnazin	75710	Natural Yellow 13	Persian berries, dyers buckthorn
quercimeritrin	75720	Natural Yellow 10	Indian cotton
quercitrin	75730	Natural Yellow 10	quercitron bark
rutin	75740	Natural Yellow 10	Chinese or Avignon berries
gossypetin	75750	Natural Brown 5, Natural Yellow 10	Indian cotton

2. Legislation

2.1 Introduction

Legislation is increasingly becoming a major driver for change and development in industries in the UK, EU, and elsewhere such as the US, especially in the areas of environmental protection and occupational health. The industries in which dyes are used are particularly subject to legislation concerning pollution, disposal of wastes, and toxicity of chemicals. The potential for natural colourants has to be considered within the context of existing and possible future legislation.

The following is not an exhaustive list of pertinent legislation but indicates the range relating to actual or potential use of natural dyes, and some opportunities.

2.2 Pollution

Pollution has long been a problem associated with some dyes. Elizabeth I forbade any woad processing within five miles of any royal estate because of the pungent and evil-smelling odour produced during fermentation. Also, she would not travel near any town where woad was being prepared for dyeing.

2.2.1 Liquids

In the UK, under the Control of Pollution Act 1974 and the Water Act 1989, effluent discharges to water courses are controlled by the NRA (National Rivers Authority, now part of the Environment Agency) and to sewers by the water companies. Also, the Environmental Protection Act 1990 places a general duty of care on the discharger. The EC Directive on Control of Dangerous Substances (76/464/EEC noL129) includes several substances on the Black List or Grey List whose discharge to water is prohibited or severely limited.

The use of mordants for most dyes presents a potential pollution problem, as many mordnats contain metals such as tin, lead copper, iron and chrome, that cannot be discharged into water courses, rivers, etc, under the EC Directive. This is not a problem associated only with natural dyes as mordants are also used with some synthetic dyes but it is potentially a greater obstacle because the need for use is greater with natural dyes in order to produce the colours required and fastness to light and detergents. Heavy metals, mainly chromium, are used in about 70 % of wool dyeing (Watson, 1991). Dye assistants may present similar problems as many of those used in commercial dyeing are organic compounds included in the EU Directive. Commercial dyers have had to develop closed systems where all harmful substances are removed before discharge of wastes to rivers and water courses and recycled where possible.

The waste liquid from a dye bath is more or less coloured, depending on the dye used. Although coloured effluent does not necessarily present an environmental hazard, it is unsightly and thus controlled under consents. However, dye can react with carbohydrates present in domestic sewage and produce coloured, unreactive molecules that cannot be de-coloured biologically. The use of bleach on sewage is effective but not environmentally friendly. Effluent can be bleached by treating with ozone before discharge and this is a technique increasingly used at dyeing works. Many natural dyes remain in considerable quantity in exhausted dye baths and would require bleaching or other treatment before disposal. Dyes themselves may present environmental problems; Ciba-Geigy has reportedly withdrawn about 40 dyestuffs from the market for this reason (Watson, 1991).

Vat dyes, of which indigo is an important example, usually need the use of a reducing agent, often sodium hydrosulphite. The breakdown products of the agent have a severe effect on biological oxygen in watercourses if the effluent is discharged untreated. The use of naturally produced indigo from woad, for example, would almost certainly require similar effluent treatment.

Under the polluter pays principle, the discharger of liquid waste into sewers pays according to the treatment level required by the level of pollution. This is calculated according to the volume, toxicity and amounts of suspended solids, and in relation to the Trade Effluent Base Strength (based on the COD - Chemical Oxygen Deficit - loading). Dye effluent from the use of synthetic dyes is often less expensive to treat than that from processing fibres. Natural dyes effluent would need to equal or better the cost of treating synthetic dye effluent.

The production of natural dyes from plants where the plants are not used in the whole or unprocessed state could generate liquid wastes that could need treatment before disposal. Plants are predominantly water and all contain chlorophyll, as well as other substances such as sugars, starches, cellulose and lignin. Using fresh or dried plants directly could add extra pollutants to dye bath effluent also needing treatment before discharge.

2.2.2 Plant wastes

The Environmental Protection Act 1990 places a duty of care on the body that disposes of controlled waste and prevents the removal of waste by contractors unless they have a waste management licence. This would presumably apply to plant wastes resulting from the production or use of natural dyes.

Disposal of plant wastes to landfill would, under current legislation, be subject to the landfill tax. Alternative methods of disposal, such as composting, animal feed, and as an energy source, could be possible but feasibility studies would be needed in order to assess factors such as environmental impact, potential market outlets, economic viability and technical requirements.

2.2.3 Air pollution

One of the major concerns in the paint and printing industries is pollution by volatile organic solvents (VOS). As yet there are no EU regulations relating to specifically to VOS but it is likely that there will be. Legislation in the US has prompted the development of vegetable oils in inks as alternatives to VOS derived from petrochemicals. The plant oils also perform as well as if not better than their synthetic equivalents, and their extra cost is, thus, not a major deterrent to use. The EU is funding some research into environmentally friendly inks that is concerned with the use of vegetable oils.

Most inks use non-aqueous solvents. Any natural dye used for ink pigmentation would need to be compatible as a direct substitute for a synthetic pigment, ie, compatible with a non-aqueous solvent. Alternatively, if legisative or environmental pressures were strong enough, water-soluble natural dyes could be used in the production of inks without VOS.

As mentioned above, the revival of commercial woad production would need to take account of the odour pollution that could be caused if fermentation was practised.

2.3 Health hazards

Any synthetic dye is usually screened at some stage for its safety to human and animal health. This has resulted in the withdrawal of several dyes as their hazards become recognised, for example, the benzidine dyes which can cause bowel cancer. Chrome colours cannot be used on articles for use by children or on things that come into contact with food. Carbon black, the most widely used printing ink pigment, is thought to be a potential carcinogen. Natural dyes used in food are screened for safety but the information is not known for most of the natural dyes used in craft dyeing, and with potentially wider use. There is a tendency to assume that natural products are safer and better than synthetic products because they are natural. The safety of natural dyes needs to be proved if they are used more widely and in commercial processes.

2.4 Other environmental problems

The paint industry is a major user of VOS, which have environmental concerns dealt with above, but the refining of the major pigment, titanium oxide, used in paints also raises environmental problems. It is unlikely that natural dyes could be used as a substitute for titanium oxide but this is a major opportunity for pigment development.

2.5 New chemicals

Any new chemical has to have a potential market big enough to cover the costs of development, production and registration, plus the costs of compiling the information needed for registration. Chemicals with a small niche market would need to be able to command a high enough price to make them financially viable products.

A modification to the EC Directive in 1976 required the collection and publication of information about the toxicity and hazards presented by new chemicals. The European Inventory of Existing Chemical Substances (EINECS) controls the transport of chemical substances in the EU. Natural products, a definition that is likely to include plant-derived dyes extracted with water, or in dried and ground plant material, are included in the Inventory. Plant dyes or dye-containing material extracted in other ways, eg, with organic solvents or subjected to more than just water extraction, are likely to be outside the Inventory. As such they may well have to be registered under the Notification of New Substances Regulation 1993 and incur the costs of registration plus hazard assessment. The maximum fee currently payable for notification seems to be £6090 plus VAT for 1 t or more of a chemical substance. Substances that have passed through the notifiction procedures each year within the EU are published on the European List of Notified chemical Substances (ELINCS). A company will still need to notify of a substance is if not on EINECS but already notified on ELINCS by another company.

Several chemical companies belong to and fund the Ecological and Toxicological Association of the Dyestuff Manufacturing Industry (ETAD), based in Basel, Switzerland. This was established to research the ecological and toxicological effects of chemical products and share information and methodology, and defray the costs of gathering the technical information required.

3. Uses of natural dyes

3. Textile dyes

3.1 History

The use of dyes to colour textiles is generally considered to be about 2000 years old. The dyes used were derived from natural sources and some, such as Tyrian purple, were particularly prized and an important part of the local economy and world trade at the time. Dyes were obtained from flowering plants, fungi, lichens (eg, crottle), insects (eg, kermes, cochineal and lac), shellfish (eg, Tyrian purple) and earths (eg, ochre). The social history associated with dyes is extensive but not covered in this review. Most plant species will produce a dye but relatively few produce strong, bright colours, especially in the primary colours. Those that did were highly prized.

3.2 The dyeing process

Dyes are substantive or adjective. Substantive dyes are absorbed and fixed by chemical bonds within the fibres without further chemical treatment. However, most natural dyes are adjective dyes. These need the use of chemicals, called mordants, to help promote absorption and fixing, and prevent “bleeding” and fading of the colours.

Mordants form chemical bonds between the dye molecules and the proteins of the fibres. They can also change the colour produced by the dye. Indigo and a few other dyes do not penetrate the fibres and the molecules gradually become detached from the outer surface. Historically many naturally occurring substances were used as mordants, such as crab-apple juice, tannins, urine and wood ash. Compounds with metallic ions are also used; the more common ones are salts of aluminium, chromium, copper, iron and tin. Mordants are most commonly used on the fibre before dyeing (premordanting) but they can also be used during (simultanous mordanting) and after dyeing (after-mordanting).

3.3 Dye assistants

Chemicals known as assistants may be used in addition to dyes and mordants, for example, to change the pH and hence the colour, to brighten colours, help absorption of the mordant metal, or slow the rate of pigment absorption. These include potassium hydrogen tartrate (cream of tartar), oxalic acid, tannic acid, acetic acid, formic acid, ammonia, sodium sulphate (Glauber’s salts), sodium chloride (salt) and sodium carbonate (washing soda).

3.4 Fibres

All natural dyes colour natural fibres to a greater or lesser extent, depending on the fibre and its structure (eg, fine or coarse). Wool and cotton are the fibres most widely dyed by craft and traditional dyers. Cotton takes up dyes differently to wool. Natural dyes are equally good at colouring silk and they do not harm the fibroin or insoluble protein of each silk filament. Many plant dyes are unsuitable for flax but others work effectively on this natural fibre.

There is relatively little information available about the effectiveness of natural dyes on synthetic fibres. Most craft dyers use natural fibres, although there are some reports of good results of natural dyes on nylon and polypropylene (Dyer,1977). Commercial dyers usually use reactive dyes on cotton and other cellulosic fibres, a process that produces relatively large amounts of unfixed dye that need to be treated in some way to prevent discharge into the environment. The basic feedstock for cellolosic fibres is wood pulp, a renewable resource.

Dye assistant or auxillary compounds called carriers are required to dye polyester fibres with the water-insoluble dyes used. The carriers loosen the bonds between the polymers and allow the dye to penetrate and colour the fibre. Natural fibres do not need carriers because they have a relatively open structure. Many of the dye chemicals are toxic and carcinogenic. It would be an advantage if natural dyes could be used on polyesters and other synthetic fibres without the use if carriers and mordants, but that seems unlikely.

3.5 Processes and machinery

In craft dyeing the dyes are extracted from the plants by soaking in water, alkali, alcohol or other organic solvent. Heat may also be required. For some dyes a multistage process may be needed, the dye(s) not wanted being extracted first by using sequences of different solvents. Alternatively, fibre may be dyed with the whole plant extract and then treated with a mordant to change the colour of one of the dyes.

Craft dyeing nearly always uses the vat process and this is the traditional way in which natural plant dyes have been used. Other techniques are also used by industrial dyers.

The production of textiles requires the use of large volumes of water but it has been estimated that the dyeing process alone can use as much as 70 % of all the water needed (Watson, 1991). About 20,000 l of water can be needed to process 1 t of wool from the raw material to the finished textile. Most natural dyes need to be extracted into water, and usually with heat. It is not clear how the current commercial machinery and dyeing processes would need to be adapted to use natural dyes.

Three different principles are practiced for dyeing textiles on a commercial scale.

1) the dye liquor is moved and the material held stationary, eg, raw stock or package-machine dyeing
2) the textile material is moved through the dye liquor, eg, chain warp dyeing, jig dyeing, beck dyeing and continuous dyeing, which is used for most woven materials except for stretch fabrics
3) the textile material and the dye liquor both move, eg, the Klander-Weldon skein dye machine, and jet dyeing.

Chain warp dyeing is widely used in the dyeing of indigo on warp yarns in the forms of ropes or chains. Several chains are pulled through the bath at a time. The technique is useful for dyeing small or test batches, and used widely for material that is easily stretched. Jet dyeing has the advantage of using smaller voumes of dye liquor than several of the other processes.

The major dyeing techniques used are exhaust dyeing (using 1 or 2 above), continuous dyeing (used for most vat dyes), pigment dyeing (using finely dispersed pigments), solvent dyeing (using non-aqueous media and more efficient than aqueous dyeing although with potentially greater operator and environmental hazards). Some dyeing methods are more suitable for fabrics than stock yarn, and vice versa.

3.6 Current R&D

The literature contains reference to the following EC-funded projects concerned with plant dyes.

1) Cultivation and extraction of natural dyes for industrial use in natural textiles production (Contract number AIR2.CT94.0981 (SC)) (Mangan *et al*.,1995). The aim of this project was to carry out research to find out how natural dyes, cultivated in Europe, can be produced and used with economically sustainable and efficient processes, including the development of modern cultivation methods of the traditional dye plants woad, weld, golden rod and madder. Factors examined included soil and climatic conditions, optimal seed rates, harvesting time, optimal fertilisation of plants, efficient weed control and safe preservation procedures. Plant material produced in the field was treated to extract dyes which were then tested by a commercial dye-house where the essential parameters of the dyeing process were examined, including the use of auxillaries, recycling and the safe disposal of waste dyestuff. The contract was due to be completed in mid-1997 although the report had not apparently been published by October 1997. Report NF-AIRID NFI/088 (October 1996) on this project reported that the group had also investigated other plant species other than those named above. “Most gave good dyeing performance when judged by German and internationally-accepted standard tests. However, problems remain to be solved in production of planting material, yield and (in the case of indigo) competition against low cost imports.”

Significant results from the first year of the project (as given in NFI/088) included successful cultivation of madder and golden rod but less success with madder and weld. Propagation of golden rod was also an area requiring more work. The dyes in dried stored plant material were relatively stable except in the case of woad, which does not contain indigo but precusors that are badly affected by the storage technique used. The best method tested was extraction of the precusors followed by the indigo formation. The yield of indigo from woad was relatively low at about 10-20% of the precipitate obtained by hot water extraction but the dye gave a greater range of colours than indigo from *Indigofera tinctoria*. This and the price of imported natural indigo from India, at about 20 ecu/kg, meant that it would not viable to produce indigo from woad on a commercial basis without work to improve yields and precusor content. Experiments to determine methods of composting waste plant material after dye extraction, waste water treatment and microbiological tests of effluents were underway. Ultrafiltration gave a clear waste water fraction and a concentrated dye fraction. Other species identified as possible superior replacements for weld and golden rod included *Serratula tinctoria* (saw-wort), *Chrysanthemum vulgare, Centaurea jacea* (a knapweed) and *Anthemis tinctoria* (dyer’s chamomile).

The conclusions of the first year’s work were:
“The dye producing plants investigated are mainly wild types. Nevertheless, many of them can be adapted to modern cultivation pratices for industrial use at low costs and at a high yield of useful

products. The trials of the different dyes on various textiles were so promising that it is anticipated that the use of such dyes would occur on an industrial basis in the near future.”

(See also 8.4.) (The Non-Food Agro-Industrial Research Information Dissemination Network is a concerted action supported by the EC, DGXII AIR Programme.)

2) European development of walnut trees for wood and fruit production as an alternative and extensive system for agricultural crops (Contract number AIR1.CT92.0142 (SC)) (Mangan *et al*.,1995). Juglone from walnuts has the potential for use in dyeing. The project was mainly concerned with the multiuse of walnut tress as a source of timber, veneer, and fruit, and the secondary products oil, alcohol and colouring. The species’ use in small scale plantations suited to extensive agricultural systems was particularly attractive. Identification of valuable genotyoes and their propagation was also included. The project was due to end in early 1996.

Angelini et al (1996) investigated the potential of weld and madder in Italy as dye crops. The project aimed to test the domestication potential of these species in the Mediterranean area and to assess their value as new industrial crops. Several germplasm sources were evaluated for their agronomic characteristics, and dye content and quality. A range of variation was established for both species for genetic differences in alizarin and luteolin content. Details of the results of the work on madder are given in Angelini et al (1997). (See also 8.5.)

In 1995, an international conference was held in Toulouse, France, to bring together those with an interest in woad. Toulouse University has particular expertise in the extraction of products from trees and plants.

4. Food and drink

4.1 History

The colourants that occur naturally in a food plant have, of course, been the source of the traditional colourant of the prepared food, after the processing needed to produce the food. Such colourants could be viewed as accidental colourants in that they are present only because they or their precusors are present in the food source. Deliberately introduced colourants have become much more important as the manufacture of processed foods has grown. Reasons for their use include the replacement of colour lost during processing, sotage or cooking by the consumer; intensification of natural colours; correction of seasonal variations of natural colour in a product so that a consistent product is presented to the consumer (Jacobson & Wasileski, 1994).

Naturally-derived colours have been used for centuries. By 1906, 80 synthetic “coal tar colours” were being used in the food industry. In 1995 (Ash & Ash) over 30 natural or nature identical colours were permitted for use in the UK (Table 4). “Natural “ colours have an advantage over synthetic colours in that they are perceived as being preferable because they are natural.

Table 4. Name and type of plant-derived colourants permitted for use of food in the UK.

Name	Type	Name	Type
Alkenet extract	P	Cottonseed flour	P
Aramanth	P	Curcumin	P
Annatto & extract	P	Flavoxanthin	P/S
Anthocyanins	P	Gold	M
Barley extract	P	Grape colour &skin extract	P
Beet powder	P	Malt	P
Canthxanthine	P/S	Red beet extract	P
Caramel	S	Riboflavin	P/S
Carbon black	S	Riboflavin tetrabutyrate	P/S
Carmine & extract	A	Saffron	P
Carotene	P/S	Terpene resin	S
Chichory extract	P	Titanium oxide	M
Chorophyll	P	Tumeric	P
Citraxanthine	P/S	Xanthophyll	P/S
Cochineal	A	Paprika	P
		Shellac	P

A - animal; M - mineral; P - plant; S - synthesised

Many foods we eat are coloured naturally through the ingredients used or the preparation and cooking processes used but added naturally-derived colours have been used for several centuries. Before 1906, 80 “coal tar” colours, ie, synthetic colours, were being used in the food industry

4.2 Legislation

The earliest legislation on food ingredients in the UK was the Adulteration of Food and Drink Act in 1860. It was produced because of the wide use of colourants to adulterate food with the intent of misleading the consumer. Cheese was coloured with red lead, pickles with copper sulphate and sweets with mineral salts. “Tea” was sometimes thorn leaves tinted with copper oxide (Jacobson & Wasileski, 1994).

The use of food colourants now is controlled in the EC by the EC Directive 94/36/EC on Food Colours 1995. Directive (EEC) No 88/593 has specific rules on and concerning authorisation for the use of red fruit juice as a colouring agent in some jams. All food colourants have to be supported by toxicological data before their use is permitted.

4.3 Types and sources of colourants

4.3.1 As in other uses of colourants, the two types “dye” and “pigment”are distinguished. Food coloured by a dye is coloured because the colourant is in solution in a solvent (usually fat or water). A pigment colours by being dispersed though the food. Lakes (a pigment derived from a dye) are also used. Titanium oxide can be added to make a colour opaque.

A colourant has to provide colour (eg, colour hue, tinctorial strength), suit the food being prepared (eg, be soluble in water or fat depending on the food, provide the desired colour at the pH of the food, be stable for foods with long shelf lives), be compatible with the process being used (eg, be in the appropriate formulation, be heat or cold stable) and be safe for human or animal consumption. In addition, the extraction or preparation of a colourant from the parent plant must be economically efficient and present minimal risks to the operator and the environment.

Some pigments found naturally in plants have also been synthesised chemically These are sometimes referred to as natural identical. In this case food colourings obtained by extraction from foods or plants, fruits, etc, would be referred to as “natural”.

It is possible to produce some types of colourants, eg, the carotenoids, by fermentation of yeasts, algae or bacteria, or by tissue culture. These would be classified as natural colours. Although a fermentation plant can be expensive to set up, producing the colourants this way can offer some advantages over extraction from plants, eg, control, no seasonal effect and a reduced waste disposal requirement. Colourants derived from fermentation tend to be more expensive to produce than by chemical synthesis but there are some niche uses and markets, eg, where the customer is willing to pay a premium for “natural ingredients”, where the demand is such to justify production by fermentation (Jacobson & Wasileski, 1994). The most likely markets for pigments produced by fermentation will be those with low fermentation overhead costs or with high synthetic costs. Plant pigments particularly the anthocyanins, may be more competitively produced by cell culture. For some pigments, eg, β-carotene, chemical synthesis is the major production technique; for most extraction from plants still seems to be the most important or only source.

Some synthetic dyes, for example, pyocyanine, can also be produced by fermentation from stock such as ethanol plus inorganic salts. Fermentation may be a suitable way to produce large quantities of bilin pigments contained in algae and blue-greeen algae. These compounds could have some use in confectionaries and frozen products.

Mackinney and Little (1962) classified the majority of colours occurring naturally in foods into five basic groups: tetrapyrroles (chlorophylls from green leafy vegetables and hemes in meats), isoprenoids or carotenoids (carotenes from carrots, tomatoes, and xanthophylls from capsicum peppers and salmon), benzopyrans (anthocyanins from grapes, berries, apples, and flavones and flavanones from nuts, onion skins and tea), betalaines (betacyanin and betaxanthines form beets), and process derived pigments (caramels from honey and syrups, and melanoids from syrups). The last group contains derived food colourants - the result of heat or other processing on food components such as carbohydrates. These are not considered in this review.

4.3.2 Anthocyanins

Anthocyanins are most stable at about pH 1.0 - 4.0. Colour strength is also most intense at lower pH. Compared with synthetic colourants they are less stable with acidity and time, have less tinctorial strength (as much as 100 x weaker colour (Ribboh, 1977) and can give inconsistent colour. They are degraded by heat, light, interaction with ascorbic acid and enzymes, and can form complexes with metallic ions which change the colour (eg, Hrazdina, 1974; Assen *et al*,1969; Assen *et al*,1972). The use of plant cell culture has been explored for the production of anthocyanin pigments (Francis, 1989).

The most widely used added anthocyanin colourants are probably those present in grapes, which have been used since the 1880s. Grape waste from industrial processes, eg wine making, is usually used and is an excellent source of anthocyanins, the main one being enocionina. However the stability of the colourants in food with low pH was less than the synthetic Red No 2 and deteriorated with time. Stability could be improved by flushing with nitrogen. The colourants also introduced a flavour.

Other anthocyanins are used but tend to have more restricted uses. Cranberry promace extract (cranberry juice cocktail), cranberry juice concentrate (cherry pie filling), miracle fruit (*Synsephalum dulcificum*) which produces berries that are very intensely red and contain anthocyanins that are relatively stable at low pH (carbonated beverages), and roselle plants (*Hibiscus sabdariffa*) (apple and pectin jellies) are examples. Red cabbage has been considered but contains relatively small numbers and quantities of anthocyanins. The potential of blueberries has been examined in some detail as the berries have high levels of nonacylated anthocyanins. However, it was considered uneconomic to cultivate primarily for colourant use.

The European elderberry (*Sambucus nigra*) contains the anthocyanins chrysanthemin and sambucin (derivatives of quercetagetin). In the 1700s, elderberries were used extensively for colouring drinks, both in its own right in elderberry wine and somewhat deceptively in “British” wine, “claret” and “Bordeaux” wines. Apparently there were extensive orchards in Kent. In Portugal the problem of adulteration of port with elderberry juice was so serious that the growing of elderberry trees was prohibited there. Today elderberries are used as a source of red food colouring, with about 100ha of trees under cultivation in Germany and a smaller area in Denmark. Fresh, raw elderberries of *S. nigra* can cause nausea and vomiting because they contain two cyanogenic glycosides that cause the release of hydrocyanic acid after ingestion. The related species *S. racemosa* the red or red-berried elderberry has also been recorded as potentially poisonous but may also have potential as source of colourants. (Recent work has suggested that elderberry extract is effective in combatting flu; it contains haemagglutinins that interfere with the virus.)

4.3.3 Betalaines

There are two main group of betalaines that are important as food colourings. The most important betacyanin is betanin (see p xx). Of the betaxanthins, vulgaxanthin-I is the probably of most note. This compound contributes about 95% of the yellow colouring obtained from the major source of both grouups, beetroot (*Beta vulgaris*). The yellow pigment betalamic acid is also present. Both red and yellow water-soluble colourants are plentiful in red and golden cultivars of beetroot and the crops have been examined quite intensively as a source of these colours that could be substituted for synthetics.

Betanin is most stable at pH 4.0 - 5.0. It degrades with increasing temperature, the colour is destroyed by UV and radiation, and oxidation darkens the food and causes loss of the colour (Von Elbe *et al*, 1975). The colours can be made more stable by saturating with oxygen and adding ascorbic acid. Sequestering also appears to improve stablility. Given these characteristics the betalaines appear to be best suited to foods that are not subjected to high temperatures during preparation and storage, are only stored for a short time and have a dry formulation. The use of betalaines also present a possible problem of off-flavours. The typical earthy flavour of beetroot is produced mainly by geosmin. However, the off-flavour disappears in buffered systems. It is possible to mask much of the taste when using concentrated beetroot juice.

Other similar compounds have been investigated for use as colourants. Phytolaccin is the main red colour in pokeweed or pokeberry (*Phytolacca americana*) and is very similar to betanin. (Another source states that the red pigment in pokeweed is thought to be the anthocyanin cyanidin (Cannon & Cannon, 1994)). Neither is as stable as the synthetic Red No. 2 and both have been suggested as colorants for soft pectin gels and firm gelatin gels. Phytolaccin is used to colour wine, pork products and confectionary, as a "natural" colour.

4.3.4 Carotenoids

The carotenoids are probably the widely distributed group of colourants in nature. In addition to the natural carotenoids, many others have been synthesised. Both types are generally more expensive than the synthetic azodyes. The colours possible are also limited, generally to yellows and oranges. Carotenoid colours tend to be relatively stable, in that they retain their colouring ability throughout a normal shelf-life, but do degrade through oxidation. Loss of colour as they degrade can be offset by increasing the concentration used. Carotenoids are not corrosive and are not usually affected by reducing agents such as ascorbic acid.

Annatto provides a variety of yellow to orange colours and is used widely in foods, particularly for margarines, and milk and cheese products. It is derived from the pulp of the seeds of *B. orellana*. The colour is provided by a range of dyes including tannins and flavonoids but also some carotenoids, of which bixin and nor-bixin are the most important. It is available as refined powders in several different forms (soluble in water at pH 4.0, acid, oil, and water and oil). It is also tasteless. In Europe it is known as E.160.

Saffron was widely used for as a colourant for several substrates but its use today is largely confined to colouring food. As it is so expensive to produce it tends not to be used in the mass-production of food. The major constituent is crocin.

β-carotene is used widely for providing a uniform colour. Apocarotene gives colour to cheese and simulated food products, and canthaxanthin, which is very soluble in fats, is used in icings, meat, salad dressings and products containing tomatoes.

Microalgal fermentation of β-carotene is used for large-scale production in Israel, Australia and the United States (Borowitzka & Borowitzka, 1988).

4.3.5 Others

Chlorophyll is used as a green colourant in food, as well as in other substances (see 1.16). Stinging nettles, spinach, alfalfa and corn are often used as source material.

4.4 Yields

In the US it was estimated that yields of 19 kg/ha of betacyanines and 9.5 kg/ha of betaxanthins could be achieved, assuming a mean total root yield of 19.12 kg/ha and that <0.1% and 0.05% of the weight could produce betacyanins and betaxanthins, respectively. It was therefore considered that beetroot could be an economically viable source of colourants.

At the other extreme, it takes about 140 stigmata from saffron crocuses to produce 1 g of the dyestuff. In cooking, the dried stigmata are used entire.

It is not easy to compare the yields achieved by extraction from plant material with those obtained in fermentation because the units of expression are so different. The highest level found in the references for production of riboflavin, for example, was over 11g/L (Jacobson & Wasileski, 1994). The production method has to be tuned to the organism (microalgae, bacteria or whatever) being used and it seems that the best methods have still be developed for many of the colourants.

4.5 Post-harvest handling and processing

High colourant yield, stability, low cost and a formulation suitable for the intended use are all desirable characteristics of the extraction processes. Anthocyanins can be extracted from a preparation of the parent plant material by using sulphur dioxide, although further refining is necessary using this method. Extraction with methanol and ion exchange gives a purer extract and a powder formulation. Wet formulations of anthocyanins can be freeze-dried to produce a stable powder. Peonidin can be extracted from mature cranberries under low temperature and pressure. It would also be possible to spray dry anthocyanins by using a carrier agent. Peonidin can be produced as a relatively stable powder by combining a spray dry extract with maltodextrin. A powder formulation is an advantage for anthocyanins because of ease of handling and transport, long storage potential and use in powdered food products.

Betalaines can be obtained by pressing the juice from the blanched and chopped roots and filtering it. Much higher extraction rates, eg, of about 70% recovery of betacyanine, can be achieved by using a continuous diffusion process.

The collection of saffron is still very labour-intensive, and because of this the crop is not likely to survive much longer in Europe. The stigmata need to be collected before the flower wilts which means that newly open flowers have to be picked every day over the flowering period of the crop. The stigmata are separated from the flowers and then roasted over charcoal fires. All this is done by hand.

Chloropyll is extracted commercially in a multistage process, consisting of primary extraction with petroleum ether followed by repeated extraction with acetone, petroleum ether, methanol and water. Subdued lighting is essential throughout. The two forms, chloropyll a and b can be separated by their solubility in water; a is soluble, b is not.

The following forms of certified colour additives were used in the US (1982):-

Powder	pure dye represents about 88-93%; dusty to handle and thus appropriate for dry mixes
Granular	88-93%; not dusty
Plating colours	88-93%
Cut blends	22-85%
Wet dry blends	<90%
Pastes	4-10%
Aqueous liquid colours	1-6%
Non-aqueous liquid colours	1-8%; used in fatty foods

4.6 Current R&D

Manufacturers are constantly looking to improve colourant performance, and especially to find good replacements for synthetic colorants. Ways of improving the colour stability of anthocyanins outside their normal pH range, or the identification of a natural red colour that gives good colour across a wide pH range, would be particularly attractive. As the results of such research are potentially very valuable, there is usually little public mention of activity until patents have been secured.

The literature contains reference to the following EC-funded projects concerned with plant dyes.

1) Biomass production system for the biosynthesis of carotenoids (AIR2.CT94.1283 (SC))
The project aimed to improve the biosynthesis of carotenoids through the development of a new, environmentally friendly, cost-effective production of natural carotenoids. The integration of two production systems were studied, photobioreactors, producing astaxanthin using *Haematococcus*, and raceway pond systems, producing beta-carotene using *Dunaliella*. The project was due to finish in mid-1997.

2) Extraction of useful food and cosmetic ingredients of vegetable origin (Contract number AIR2.CT92.0818 (SC)). This project was concerned with finding combinations of improved environmentally friendly processes in order to obtain new ingredients for use in the food, cosmetic and other allied industries. The research examined ways in the relatively low extraction rates achievable by traditional extraction techniques could be increased by introducing the use of processes such as enzymatic pre-treatment and solvent-free extraction processing. Vegetation of marginal land in semi-arid climates was the main target of the work. The contract was due to finish in early 1997.

A meeting was held in 1996 in Brussels for the EC (DGXII Agri-Industry Group) on elderberry (*Sambucus nigra* and *S. racemosa*) (P. Bacon, pers. comm.). However, although this genus has uses in food colouring, the discussion was mainly about medicinal and pharmaceutical uses.

5 Inks and paints

5.1 History

Writing inks were first used in about 2600 BC by the Chinese and Egyptians. They probably consisted of carboneous materials like lamp black or soot mixed with animal glue or vegetable oil. Carbon black is still a major pigment and vegetable oils are used widely in printing inks.

Inks, paints and varnishes are generally referred to as types of surface coatings.

5.2 Source

The pigments in modern inks are almost all synthetic. The two exceptions are Dragon’s blood (a mixture of dracorhodin and dracorubin obtained from *Doemonorops propinqus* grown in Sumatra and Borneo) and chloropyll. The former can be used for preparing halftone plates for multicolour printing. Chlorophyll is obtained from green plant material, often stinging nettle, spinach, alfalfa or corn. For extraction method see 4.4. Natural indigo prepared in a powder form was used as a paint.

5.3 Types of inks and paints

5.3.1 Paints and printing inks both consist of of a thin layer of a curable liquid applied to a substrate. In the case of inks, the substrate is usually metal foils, paper and plastic films, and textiles, which are serviced by a very specific part of the industry. Paints are applied to a wide range of surfaces, including metal, wood, stone, brick, etc.

A printing ink consists of colouring material in a carrier which forms a fluid or paste that can be printed on a substrate and dried. The colourant is usually a pigment, dye, toner or combination of these. The composition of a printing ink is usually highly specific to its use and its properties dependent on the substrate and application method involved. It needs to have the correct characteristics of flow, adhesion, stickiness, drying time, penetration, colour intensity and so on.

The increasing use of non-petroleum carrier oils, usually a vegetable oil substitute such as soybean oil or oilseed rape oil, has been driven by the need to reduce the emission of volatile organic solvents (VOCs), the desirability of rapid, safe biodegradation, and the advantages of using inks that can be safely and effectively removed (de-inked) from waste paper for re-cycling.

5.3.2 The most important properties are:-
Drying - the process that transforms the fluid ink into a rigid form. This is achieved by absorption, solvent evaporation, oxidation, resin precipitation, drying with other various forms of energy (eg, radiation, infra red, radio and microwaves), etc.

Rheology (printability) - concerns the viscosity, yield value (the point at which the ink starts to flow under pressure) and thixotrophy. Flexographic and rotogravure inks need to have a low viscosity, yield value and thixotrophy, whereas letterpress and litho inks can be more viscous. Printing with low press speeds needs inks of high viscosity, and vice versa. The degree of pigmentation can affect yield value and thixotrophy. (Thixotrophy - the property of becoming temporarily liquid when shaken or stirred, etc, and returning to a gel on standing (Concise Oxford Dictionary).)

Colour - Inks currently use dyes, usually made insoluble in some way, and inorganic pigments to produce the required colour. The most commonly used pigments are black pigments, principally carbon black, used in very large quantities in newsprint and publication, and white pigments, the most popular of which is titanium oxide. The major types of dyes used are anthaquinone, azo, phthalocyanine, triphenylmethane and vat dyes. All are synthetic.

These properties are obtained by different mixes of various oils, driers, solvents, resins, pigments, dyes and waxes. Linseed oil is the major oil used as a binder in printing inks, although soya and rape seed oil are used increasingly.

There are four classes of inks - 1) letterpress inks, 2) lithographic inks, 3) flexographic inks and 4) rotogravure inks. The first two types are usually oil inks or paste inks, and the latter two, solvent or liquid inks.

Letterpress inks are usually based on a mineral oil, although vegetable oils are increasingly used. Litho newsprint inks are based on rosin or other resins dissolved in petroleum fractions.

Table 5. Types of inks currently used in printing

Ink	Type	Composition and comments
Rotary heat-set publication and commercial inks	L	Based on natural or semi-natural resins
Sheet-fed commercial inks	L	Resins dissolved in vegetable drying oils (linseed, soya, chinawood, tall oils) and diluted with hydocarbon solvents; commonly used in commercial printing
Document-reproduction and business form inks	L	Jet-dot method printing inks based on glycols, water and dyes
Folding-carton inks	L	Similar to document inks; need to be quick drying
Corrugated and Kraft-liner container inks	L	Resins dissolved in ethylene, dipropylene or triethylene glycols
Metal container inks	L	Oleo-resinous and heat-set varnishes in drying oils
Plastics inks	L	Oleo-resinous varnishes
Stamp pad	M	Dyes (usually induline black) used as the total ink has to soak into the pad
Ball-point ink	M	Strong dye solutions and pigment dispersions in vehicles containg oleic acid and castor oil or a plasticiser; need to be slow drying, free of particles, high tinctorial strength
Steel-die inks	M	Need to contain a drying oil
Electrostatic inks	M	Powder pigment dispersed in a resin; particles need the proper electrical properties, size range and be free-flowing
Ink jet inks	M	Soluble dye colourant in a suitable resin-solvent vehicle; need to be stable, fluid and free of particles

5.4 Ink manufacture

Inks are usually made by 1) mixing the pre-dispersed pigments with the vehicles, solvents, oils and other ingredients, or 2) mixing the dry pigments or resin-coated pigments with the other ingredients and then grinding them in an ink mill.

5.5 Printing processes

The printing process being used dictates the specification of the ink, as shown above in 5.5. The surface and type of substrate and its end use are also important in determining the type of ink. They are so specialised that each use needs to be considered separately. The biggest requirement for ink would appear to be carbon black for newsprint.

5.6 Current R&D

Considerable effort is being spent in improving ink quality, particularly for the increasingly specialised specifications that are needed, but the author has been unable to identify any work on the use of natural pigments in inks. It seems that no work is currently being done and, according to one source at least, if it was being done it would be commercially sensitive and would not be publicised.

6. Other uses (cosmestics, etc)

6.1 Cosmetics

6.1.1 History

Many of the better dyes and pigments have been used for cosmetic use for centuries. A common name of annatto (*Bixus ocellana*) is the lipstick plant. Natural indigo from *Indigofera tinctoria* was used by the Romans and Greeks in a blue crayon for eyeshadow while the powdered form had other cosmetic applications, such as body painting. In Venice in the late 1500s, saffron was used as a hair dye, applied in a mixture with sulphur to hair pre-treated with dried caul, egg yolk and honey. The hair was gradually dyed yellow with the action of the sun.

6.1.2 Current use

Rosemary, henna and chamomile are still used in hair colouring preparations and there has been a move towards the development of more natural hair colourants by some of the major cosmetic manufacturers. For example, Wella (a German-based company) has produced a series of natural herbal colour granules containing henna (*L. inermis*), Roman chamomile (*Chamaemelum nobile*), catechu (*Acacia catechu*), sedre (*Phus latus rhamnaceae*), indigo (*Indigofera tinctoria*) and sage (*Salvia officinales*) in various proportions to acheive a wide range of hair colours. Chamomile and sage grow widely in Europe, especially in the Mediterranean region. The other plants are not native to Europe and not generally cultivated here.

Woad has a very small and specialised hobby use for body painting by those who re-enact the ancient Briton way of life. It is, apparently, rapidly washed off the body by sweat.

7. Markets - type and size

7.1 Tables 6, 7 & 8 show the production and trade statistics for dyestuffs and pigments, and printing inks in the UK for 1991 (Anon, 1992)and 1992 (Anon, 1993), respectively. They do not permit the easy quantification of the volume and value for natural dyes and pigments but the total value is probably about £9-12 million (1991 prices) per year for all markets.

7.2 Natural products are far exceeded in production and value in the UK by the synthetic dyes and pigments, and overall the UK is a net exporter of all colourant types. Annual output looks to be relatively stable. There are only a small number of manufacturers of each type of colourant; in 1989 only 17 natural colours were listed as being available in The Colour Index International.

7.3 The UK imports more colouring matter and tanning extracts of vegetable origin than it exports. However, the products imported are of considerably lower unit value than those exported.

7.4 The major UK market for plant-derived colourants is food and drink. In 1995, there were 49 companies listed as supplying colourants in the UK (European Food Trades Directory), of which about 17 supply natural colourants.

7.5 Estimated global production of textiles has been estimated at about 30,000,000 t (Glover & Pierce, 1993), with an estimated growth rate of 3% per year. The consumption of dyes to colour these textiles is an estimated 700,000 t, with a value of about £2.5 billion per year (1988 prices). Dyes represent <1.0 % of total world sales of organic chemicals. Elsewhere, the global annual sales of dyestuffs was estimated at £7 billion in 1989 (Watson, 1991), with prices for dyestuffs ranging between £20,000 and £50,000 per ton.

7.6 More than 8000 chemically distinct dyes, the vast majority of them synthetic, are commercially significant worldwide. The largest volume dye by far used in the world is indigo, predominantly synthesised. In 1976, the estimated world demand for indigo was 13,000 t/year (Chemistry Week, 3 March 1976). At least 30 different processes for the manufacture of synthetic indigo have been identified.

7.7 Within the EU, the sales of dyes (all types) for textile dyeing have declined recently (Anon, 1994). About 9% of manufacturing employment in the EU is in the textiles and clothing industries (2.7 million people in 1992). Overall production is declining, as the gap between exports and imports widens. The EU textile industry is relatively modernised with a high proportion of shuttle-less looms and still has a strong competitive position in technical textiles, eg, geotextiles. The critical factor for textile production is the price volatility of raw materials, including those based on petrochemicals. Natural dyes could reduce dependency on petrochemicals and help dampen the price volatility of the raw materials but their impact is unlikely to be great as they constitute a relatively small part of the current costs.

In Italy, the dyeing industry are interested in finding alternatives to synthetic dyes because of the high pollution load of modern textile dyeing processes (Angelini *et al*, 1996). The use of textile products in 1996 was about 30 million t; the use of natural dyes was less than 1 % of total dye use.

7.8 Dyes are part of the speciality chemicals sector. The main driver for research and development in this sector has been environmental protection, especially in the area of minimising toxicity from solvents and pigments based on heavy metals (Anon, 1994). The use of natural dyes would appear to be less hazardous but would be likely to bring their own problems of pollution by mordants, disposal of plant wastes, and so on.

7.9 Ilker (1987) estimated that the world food colour market was growing at abouit 10% per year. The total world market for food colourants was estimated by Klaüi (1989) to be in the region of $320 million in 1987. About $120 was for natural colours, consisting of $35 million for natural extracted colours, $35 million for synthetic (nature-identical) colours and $50 million for process derived colours. The market for β-carotene was estimated at $50 to $100 million per year (Borowitzka & Borowitzka, 1989), most of which was produced synthetically. The selling price of synthetic β-carotene is about half that of microalgal β-carotene.

About 50% of the riboflavin used in the world annually is produced by a combination of fermentation to produce the ribose that is then a reagent in a chemical synthesis of the riboflavin (Florent, 1986).

7.10 Opinion on the future development of demand for food pigments was conflicting. Francis (1984) predicted that interest in natural colours would have waned by the mid-1990s because of the increasing acceptance of synthetic colours. Paulus (1989) asked 43 experts in the EU what the future use of food colourants would be. They predicted that by 2000, 50-75 % of the synthetic food colourants in use in 1989 would be replaced by natural pigments. On current performance, one would have to conclude that the experts quizzed by Paulus showed more prescience than Francis.

Table 6. Production and value statistics for dyestuffs and pigments in the UK

Year	Total Sales	Output 1985=100	Sales £million	Exports £million	Imports £million
1986	956	109.3	717	503	246
1987	1082	110.3	871	580	274
1988	1206	117.0	954	622	306
1989	1333	121.5	1071	696	354
1990	1354	115.5	1097	732	377
1991	1240	115.4	1009	735	357

Table 7. Annual sales of dyestuffs and pigments by UK manufacturers, 1991.

Product type	Number of enterprises	Value (£million)	Weight (tonnes)
Natural dyes & synthetic blended dyes for food, drinks & cosmetics	4	3.3	-
Finished synthetic dyestuffs & preparations for dyeing	7		
Gross sales		344.4	58,480
Net sales		305.1	49,844
Inorganic pigment colours, pure or reduced dry & in pulp form	7		
Gross sales		30.3	12,361
Net sales		27.0	10,888
Titanium oxide	6	331.8 *	237,118*
Zinc oxide	4	8.0	12,204
Vegetable tanning & dyeing extracts		0.7**	1,180**

* 1990; ** 1989.

Source: as above

Table 8. Exports and imports of dyestuffs and pigments by UK manufacturers, 1991.

Product type	Exports £million	Tonnes	Imports £million	Tonnes
Synthetic organic dyestuffs & preparations (excluding food & drink dyes)	438.9	70,195	138.7	28,254
Food & drink types	18.1	2,878	16.9	942
			82.0	15,593
Colour lakes	2.7	871	1.6	316
Colouring matter of vegetable origin	3.7	513	6.8	1,709
Colouring matter of animal origin	0.6	179	1.0	136
Tanning extracts of vegetable origin	1.5	772	3.4	4,360
Inorganic pigment dyes	237.8	181,170	82.4	88,921
Retail dyes	6.0	1447	2.4	579
Other	26.1	24,002	22.7	23,570
Total	735.1	-	358.0	

Table 9. Annual sales of printing inks by UK manufacturers, 1992.

Product type	Number of enterprises	Value (£million)	Weight (tonnes)
Black news and sack inks	4	24.6	-
Gravure and non published inks	4	13.7	4.7
Flexographic inks	4	44.4	13.9
Screen process inks	5	38.6	5.8
Lithographic inks	8	83.9	20.0
Letterpress inks	7	9.9	-
Others	6	23.5	4.3

Table 10. Imports and exports of printing inks, UK, 1992.

Ink type	Export (£million)	Export (t)	Import (£ Million)	Import (t)
Black ink	19.7	7,454	12.1	4,013
Paste (heatset, metal decorating, etc)	14.9	3,992	15.4	5,106
Gravure*	0.6	394	3.3	2,169
Others	36.1	7,945	21.6	6,746
Total	70.7	-	49.2	-

* 1991 figures

8. Market requirements

8.1 Textile dyes

8.1.1 Quality

Synthetic dyes are consistent and their behaviour predictable. Natural dyes need to match the colour consistency, range and strength, and colour fastness of the current synthetic dyes to substitute for the synthetic products. Quality (eg, intensity of colour, hue) of the product dyed naturally is likely to be variable (depending on the dye concerned) and many natural dyes are not colourfast, eg, to light or washing.

However, part of the attraction of natural dyes is their inconsistency. Colour inconsistency and lack of colour fastness can be a fashion benefit, eg, indigo-dyed denim, and such specialised markets may provide a niche for natural dyes. Consumer demand for “environmentally friendly” textiles could increase the use of natural dyes but such demands in fashion tend to be fickle and relatively short-lived. To be effective, the demand would need to be across all the major consuming countries in Europe and North America.

8.1.2 Price

Natural dyes would need to be competitively priced compared with synthetic dyes, ranging from about £20,000 to £50,000 per ton of product. The price of a natural dye would be set by the prices commanded by the synthetic dyes but the cost would have to take into account the generally lesser tinctorial strength compared to the synthetic dyes, and the relatively low yield of dyes in plant material, plus any processing costs.

As an illustration of the effects of comparative production costs, *Indigofera tinctoria* has a high yield of indigo (20%), of which about 60% is pure indigo. It is still cultivated for the production of indigo in parts of Africa, India and Asia where up to four crops of the plant tops can be taken each year. Woad has a much lower concentration of indigo-producing dye, about 5%. It can also produce four crops of young leaves, totalling about 2.5 tonnes of plant material per hectare, from which about 125 kg of dye can be produced. If indigo dye is sold for £20,000 per t then the gross value of indigo produced from woad would be about £2500 per ha. The traditional cultivation of woad was labour intensive, as was the processing, and the resulting gross margin is likely to be small. Higher yielding varieties, modern production and processing techniques would probably increase the gross margin.

If the amount of plant material harvested from *Indigofera tinctoria* is the same as for woad, and it is probably greater, then about 10 t/ha is produced per year, resulting in about 300 kg of dye, equivalent to about £6,000 per ha. Labour costs and the costs of meeting legislative requirements would be less where *I. tinctoria* is currently cultivated than for woad cultivated in Europe. Even allowing for greater transport costs, it is likely to be more profitable and more efficient to produce natural indigo from *I. tinctoria* than woad.

Indigo from *Indigofera* can be imported from India at about 20 ecu/kg (see 3.6), giving an upper price limit for indigo from woad of about £15,300 per t.

8.1.3 Costs

No comparison of the total costs over the product lifecycle for synthetic dyes and their natural equivalents has been found in the literature. It is difficult, therefore, to give a full comparison of the costs incurred between natural and synthetic dyes but it is unlikely that natural dyes would be cheaper.

8.1.4 Availability

Colourant-containing plants are unlikely to be available as fresh material all year round but have a seasonal production cycle. Where the colourant is present in the flowers, berrries or leaves it may be able to preserve the material and retain the colourant. Craft dyers tend to use fresh or dried material. Alternatively the plant material could be processed to extract the dye in a form easily stored, transported and used.

8.1.5 Ease/compatibility of use

Any plant-derived dye would ideally need to be compatible with the dyeing plant and handling/waste disposal facilities. Deviation from this would probably increase the cost of using natural dyes above that of using synthetics.

8.1.6 Operator and environmental safety

The general question of environmental safety is dealth with above (pxx). In the EU, the environmental costs in dyeing and finishing were estimated at between 3.5% (Belgium) and 9.2% (Germany) of total costs. It was expected that the costs would increase as environmental policy was strengthened. In addition to any pollution hazards, the dyeing and finishing process requires the largest volume of water in the production of finished textiles.

Metal contamination of effluent from mordants used in processing with most natural dyes, using current technology, would be unacceptable for discharge to sewers (Glover & Pierce, 1993; german ref). It may be possible to re-enginneer the process to reduce contamination levels but this would require research and may require capital investment to put into practice.

Any natural dye would have to comply with legislation, eg, Control of Substances Hazardous to Health, Health and Safety at Work, for operator safety. In addition, the transport in the UK of any new chemical substance in any quantity is governed by regulations that require the registration of the chemical and the provision of environmental and other data packages.

8.1.7 Market potential

Sales of dyes for the textile industry declined in the EU in the early 1990’s. This is probably linked to the decline in manufacture of textiles in the EU because of a declining population and the increase of imports from outside, even although exports also increased but by less. The EU still has a strong position in the production of technical textiles. The textile industry is vulnerable to the price volatility of raw materials. The MultiFibre Agreement and GATT both also affect EU production of textiles. It was thought that short- and medium-term prospects for the textile industry were not good.

Natural dyes are unlikely to be a total replacement for synthetic dyes because the area of land required for production is not available using plants currently available. It was estimated that to provide sufficient vegetable dyes to dye cotton alone, about 462 million ha would be needed, ie, 31% of the world's current agricultural land (Glover & Pierce, 1993).

In addition, synthetic dyes are consistent and their behaviour predictable. Quality (eg, intensity of colour, hue) of the product dyed naturally is likely to be variable (depending on the dye concerned) and many natural dyes are not colourfast, eg, to light or washing. However, part of the attraction of natural dyes is their inconsistency.

It is possible that dyes could be used as a source of raw materials for the synthesis or extraction of other valuable products. For example, isatin, an oxidation product of indigo, was used in 1866 to synthesis indole. Indole is an alkaloid with commercial uses in perfume and other products and several important other alkaloids (eg, tryptophan and heteroauxin) can be derived from it. Alkaloids tend to be used in high value, low volume products/processes. Indole is currently extracted from coal tar distillate and is also present in a number of waste products, so there may not be a viable market for plant-derived indole. However, there may be other chemicals for which plant stock is appropriate.

In the mid 1990's, polyester, nylon, polypropylene and acrylics together accounted for 65% of total fibre use in textiles in the EU. Generally speaking, natural dyes are not good for dyeing synthetic fibres, with current current processes, and their potential use for textiles is linked closely to the type of fibre being dyed. Some natural dyes may however be sufficiently versatile to be used on synthetic fibres.

In summary, it is likely that natural dyes will occupy a small niche market at best for textiles. Such a market would be driven by consumer demand primarily, although legislation changes could also have an effect. Within the EU, it seems that the most influential country for naturally coloured textiles is probably Germany.

8.2 Food and drink

Quality

8.2.1 Legislation

The use of food colourants is controlled in the EC by the EC Directive 94/36/EC on Food Colours 1995. Directive (EEC) No 88/593 has specific rules on .... and concerning authorisation for the use of red fruit juice as a colouring agent in some jams. All food colourants have to be supported by toxicological data before their use is permitted.

8.2.2 Market requirements and potential

According to the "Panorama of EU Industry 1994" the demand for food products in Europe is nearly static. The market for traditional foods is declining as the demand for prepared products grows. The UK has by far the largest in terms of size of the main European companies. The major environmental concern is packaging. Colourants were not mentioned.

However, the move towards prepared and part-cooked foods could increase the use of colourants. In addition, the development of food industries in non-EU countries could also open up new markets for colourants.

There would appear to be potential for the use of natural food colourants to increase, as manufacturers seek to replace the use of synthetic colourants. There is a presumption by the public that natural colorants are safe and preferable to synthetic materials. However, the safety of any additive has to be determined and accepted. The development of new natural colournts will require substantial data packages on safety and toxicology. Such studies are often expensive and the market will have to be relatively high value and/or volume to justify the cost.

8.3 Inks and paints

8.3.1 Market requirements

The end users of paints and varnishes are rather conservative in that they tend to take a long time to adopt new coatings. The sector as a whole is spending relatively large amounts on R&D and developong new techologies, especially as the sector becomes more environmentally conscious. There is perceived to be a lack of technically skilled staff and growth in production is currently affected by a shortage of raw materials, especially of the most widely used one, titanium oxide. In 1994, the EU's, and the world's, leading producer was ICI with BASF, Herberts and Hoechst(Germany), Akzo (Netherlands) and Courtalds (UK) also as major players. The major environmental factor is the emission of volatile organic solvents and reducing environmental pollution from the refining of titanium oxide. The emission of volatile organic solvents is not yet regulated by the EU, although there are EU Directives covering the use of titanium oxide. Manufacturers have produced water-based gloss paints but the colour is not stable, largely because of oxidation of the oils used.

There are only a few multinationals among the EU companies manufacturing printing inks and a preponderance of family companies, especially in southern Europe. The major environmental concern is the use of non-aqueous solvents but the relatively small number of professional users (compared with users of paint, for example) means that control is easier. In both sectors, there are moves to reduce pollution by waste and by encouraging recycling.

Opinion seems to be that within the EU the sector is recession-proof and growth was expected (about 3.1% between 1993 and 1997). The major concerns were thought to be environmental protection legislation and the reliance of some raw ingredients on the price of crude oil (the source).

For the users of ink, the printers, the market is strongly demand-led. The major type of printing currently is photocomposition. Use of inks is thought to have a marginal environmental impact, the main concerns being the need to reduce the emissions of volatile organic solvents from web-off set printing, improve the quality of water discharged and encourage the recycling of waste. There is also some concern about the contact of inks on packaging with food.

8.3.2 Market potential

In the US the estimated annual value of printing inks produced was $1,000,000,000 (1979).

8.4 Other uses

The use of natural dyes and pigments for other uses such as cosmetics is likely to be consumer and legislation driven. Where information has been found, most natural colours used are minerals rather than derived from plants. For cosmetics especially, “natural colour” tends to mean something that is coloured in a way reminiscent of a natural object such as a flower of plant, rather than that plant derived dyes or pigments have been used. Cosmetics form a large and relatively price-insensitive market and if it becomes an advantage, or necessary, to use plant dyes and pigments then there is some considerable potential.

9. Plant species as dye crops in the UK

9.1. Colourants can be obtained from many UK plants but relatively few have been used because of the quality of the colourant, its yield and similar factors. UK plants that are currently used commercially as sources of colourants are beetroot, spinach and some berry fruits, mainly for food colourings.

9.2. Very few of the potential dye plants have been developed as a crop, and many of those that were, eg, woad and weld, would need further work. The following are needed: cultivars or selections with a good yield of the colourant, that are compatible with modern agriculture or horticulture, that yield consistently both in terms of quantity and quality, and whose husbandry is known. Some husbandry information is known for those species already grown as garden plants (see Table 9).

9.3. Plant material brought in from abroad for testing and/or breeding would need to comply with the Plant Health Order 1993, and possibly the Wildlife and Countryside Act 1981, which restricts the introduction of non-indigenous organisms.

9.4. The EU-funded project at IACR (Long Ashton) and in Germany investigated the agronomy of woad, weld and madder, including crop husbandry, weed control, performance of genotypes, etc. (See also 3.6.) By the end of the first year's work, reliable methods of cultivation (seeding, fertilser requirements and weed control) had been established for woad and golden rod, as had the best harvesting times, seed production and storage techniques to give optimal yield of the dyes from the plant material. Golden rod has very small seeds that do not give good plant establishment rates in the field conditions tested. Planting out of seedlings raised in a glasshouse gave the best establishment rates. This species is a perennial. Likewise, plants (runners) gave the best establishment rates for madder. Seed production in madder plants varies significantly from year to year in mid-European conditions so that some years no seed at all is formed. If seed is used as a propagation method then it may be necessary for the seed to be grown in a more favourable climate.

9.5. Work carried out in Itay from 1992 to 1995 investigated the the domestication potential of weld and madder in Mediterranean conditions and their potential as new industrial crops (Angelini *et al*, 1996). Germplasm from several sources were assessed for their agronomic characteristics and yield of dyes. There were large variations in yields and in drought susceptibility between genotypes. The tinctorial stength of the dyes produced also varied between genotype, species and harvest date. The yield of luteolin dye from the weld varied in different parts of the plant and with harvest time. Less was obtained from stems than from the flowers and leaves, and yield declined in all parts between flowering and fruiting. Most alizarin in the madder grown was found in the cortex of the roots; very little was present in the stele.

9.6. This type of research on determining and developing robust, high yielding crop plants would be needed for the development of plant species in the UK as industrial crops for dye production.

Table 11. Recognised dye plants capable of cultivation in the UK

Latin name	**Common name**	**Plant type**	**Cultivation conditions**
Alkanna tinctoria	Dyer’s alkanet	P	Very light sandy soil, free from lime, in warm position. Not totally hardy.
Allium cepa	Onion	A	Well cultivated, fertile, friable soil. Sunny position.
Anthemis arvensis	Dyer’s chamomile	P	Well cultivated soil, sunny position, not very tolerant of lime.
Baptisia australis	Baptisia	P	Wide range of soils, including calcareous soils.
Berberis spp	Barberry	S	Well cultivated including calcareous soils.
Betula spp	Birch	T	Most soils; silver birch - light sandy soils.
Calluna vulgaris	Heather	S	Not limy or chalky soils (most spp)
Carthamus tinctorius	Safflower	A	Most soils; transplant after sowing under glass, or sow Feb/Mar, thinning to 6 ins.
Chamaemelum nobile	Common chamomile	P	(A weed of arable crops)
Cheiranthus cheiri	Wallflower	P	Dry, chalky soil. Naturally occurs on cliffs and rocks.
Coreopsis tinctoria	Coreopsis, tickseed	A	Open, sandy conditions but any fertile soil also suitable.
Cosmos sulphureus	Cosmos	A	Fertile soil.
Cotinus coggygria	Young fustic	T	Most soils, sunny position.
Crocus sativus	Saffron	P (C)	Sandy or loamy soil, sunny position
Cytisus scoparius	Broom	S	Most fertile soils, sunny position.
Dahlia pinnata	Dahlia	P (R)	Most fertile soils, sunny position.
Erica spp	Heather	P	Not limy or calcareous soils (most spp).
Eucalyptus spp	Eucalyptus	T	Most soils, expect frost damage in most areas.
Fallopia japonica	Japanese knotweed	P	All soils, very invasive and agressive, banned in US as noxious weed.
Galium verum & spp	Lady’s bedstraw	P	Most soils, especially sands, but not very acid soils.
Genista tinctoria & spp	Dyer’s greenweed	S	Most fertile soils including clays, sunny position.
Hedera helix	Ivy	P/S	Most soils; good tolerance of shade.
Hypericum perforatum	St John’s wort	P	Many calcareous soils, agressive weed.
Isatis tinctoria	Woad	B (P)	Fertile or light calcareous or sandy soils. Sow Mar - Oct, sow or thin to 9 ins spacing.
Juglans nigra & J. regia	Black walnut, common w.	T	Well drained soils, not very frost hardy.
Maclura pomifera	Osage-orange	T	Wide range; thin, chalky soils in UK. Hardy.
Mahonia spp	Mahonia	S	Most well-cultivated soils.
Morus alba	White mulberry	T	Chalky or limy soils, and gravels and sands.
Nymphaea alba	White water-lily	P (R)	Sheltered slow-moving water; tolerant of low nutrient levels.
Phytolacca americum	Pokeweed	P	Most fertile soils; young plants not frost hardy.

Polygonum spp	Knotweed	A/B	P. tinctorium - not frost hardy, needs 10wks hot, sunny weather. P aviculare (common knotweed) - found as a weed in poor ground.
Quercus velutina & spp	Black oak & oaks	T	Naturally in poor, well-drained soils.
Raphanus raphanistrum	Radish	A	Fertile, moist soil
Reseda luteola	Weld	B	Naturally in calcareous, well-drained soils. Plant at or thin to 6 ins spacing.
Rhamnus spp	Persian berries	T	Most soils. Some spp. not cold-hardy.
Rubia tinctoria	Madder	P	Well drained, well-cultivated soil with lime or chalk.
Rubus fruticosus	Bramble (blackberry)	S	Any soil.
Salix caprea & spp	Goat willow	T	Most soils.
Sambucus spp	Elderberry	T	Most fertile soils (see Appendix 3)
Sanguinaria canadensis	Bloodroot	P (R)	Many soil types with high humus levels; need good sunlight.
Scabiosa columbaria	Scabious	P	Limy soils and other soil types.
Serratula tinctoria & spp	Saw-wort	P	Well-cultivated soils, preferably with some lime.
Solidago canadensis	Goldenrod	P	Most soils.
Succisa pratensis	Devil's bit scabious	P	Damp, heavy (even acid) soils.
Tagetes patula & spp	French marigold	A	Most soils, half hardy.
Taxus baccata	Yew	T	Calcareous soils usually.
Urtica dioica	Stinging nettle	P	Fertile soils.

Key : A - annual; B - biennial; C - corm; P - perennial; R - rhizome; S - shrub; T - tree

Sources - Cannon, J & Cannon, M (1994), Goodwin, J (1982).

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