Are natural colorants good for your health?

Brian Glover and Jeffrey H Pierce

The world has become increasingly aware of environmental issues through discussions about the greenhouse effect, ozone layer depreciation, water pollution and waste disposal. The role of the chemical industry in introducing contaminants into the environment has been much criticised. But how far can this be justified? Brian Glover and Jeff Pierce discuss the issues as seen by one of the world's major colorant manufacturers.

Much of the blame for the declining standard in our global environment has been placed upon the door of industry. The degree to which this is totally justified can be questioned, but the popular perception is that industrial practices and in particular the chemical industry has somehow or other altered the natural balance within the world. There is a perception that chemistry is somehow 'fiddling with nature'.

This in turn has led to returning to a traditional or 'more natural' way of life: biological farming, natural foods and the belief that all things natural are good for you. As part of this trend there is now a lobby for using natural colouring matters to dye textiles.

One of the criticisms made by chemists, however, is that very often the environmental studies do not follow the prescribed logical and analytical analysis that is typical in the chemical industry. Unfortunately, the world at large does not wish to join the self-indulgent scientists in analysing their problems. They are more interested in macroscopic issues and general situations. These comments are made in order to explain that this article is not a detailed scientific study or defence of synthetic dyestuffs. It is meant simply as a means of highlighting the issues and raising some fundamental questions as to the public perceptions and traditional practices both within the public and manufacturing domain.

Global consumption of dyestuffs

The global consumption of textiles is estimated at around 30 million tonnes, and this is expected to grow at 3% per annum. The coloration of this amount needs around 700 000 tonnes of dyes, with a value of some £2.5 billion per annum [1,2].

In other words, we as an industry are putting vast amounts of synthetic colorant into the environment. The reasons for doing this is that people demand coloured textiles for aesthetic appeal, decoration and even for utilitarian purposes. Unless there is a revolutionary and totally unpredicted change in human behaviour, the majority of textiles will continue to be dyed because it is unlikely that the human race will *en masse* turn to totally untreated and undyed fabrics, or adopt massive global recycling of clothing.

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Some natural products

Just how safe are natural products. The following is a quote from *Food for free*, a guide to edible plants of Britain [3]. In the appendix on poisonous plants the comment is made:

> Below is a full list of those British plants generally regarded as poisonous to humans when eaten in moderate amounts. There are some others which it is not wise to eat because they can be damaging in large quantities, for instance, scarlet pimpernel and bracken. Both of these have been eaten safely in the past, but the former can cause anaemia and the latter contains small quantities of a carcinogen.

Clearly, being a natural product does not necessarily mean being a safe product. This can be clearly demonstrated with the natural favourite tobacco, where 2.5 g of tobacco contain a lethal dose of nicotine.

The reality is of course that in any group of products some will be good for you and others bad. A balanced view has to be taken. Let us consider the chemical group, steroids. These as we all know are 'bad for you' because athletes who 'cheat' take them to artificially change their body; indeed the Olympic movement has banned their use. However, there are many different steroids. Let us consider a few of them. Cholesterol is the well known middle-age killer which would support the argument that steroids are harmful. However, the following are closely related structures:

- cholic acid is a bile acid used for digesting fats
- oestrone is a female sex hormone, not to be confused with testosterone, a male sex hormone
- digitoxigenin is for some people a heart stimulant or, depending on dosage, can be a lethal cardiac poison
- cortisone is beneficial in the treatment of rheumatoid arthritis.

As can be seen, different properties are exhibited by closely related structures, demonstrating that you cannot condemn a whole family of products simply by the behaviour of one or two of its members. It

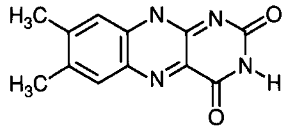

Figure 1 Vitamin B_2 (riboflavin)

is therefore wrong to classify all synthetic dyestuffs as being harmful to the environment *per se*, simply because of problems associated with one or two products in the past.

We are all brought up to believe that vitamins are good for you. Our daily bowl of cornflakes contains these vital elements, as proudly described on the packet. Let us just consider a couple of typical vitamins: vitamin B_2 (riboflavin), a complex heterocyclic product with a structure not too dissimilar from disperse dyes or vat dye precursors (Figure 1), and vitamin B_{12}. The latter can only be obtained from animal meat. A lack of it results in anaemia; it is a cobalt complex and animals on land deficient in cobalt suffer wasting and nervous disease and eventually die. This is overcome by spraying grazing land with cobalt sulphate or administrating it orally. On the other hand, dyehouses using cobalt metal complexes are under severe restrictions regarding their effluent discharge. Simply on a molecular calculation vitamin B_{12} contains 4% cobalt, a 1:1 metal-complex dye such as CI Acid Violet 78 contains around 4.6% combined cobalt and chromium, a 1:2 metal-complex dye contains around 3.5% chromium, and copper phthalocyanine has a molecular content of copper of around 5.4%. For a dyehouse, the consent levels set for the amount of these chemicals permitted in effluent has been set at a few parts per million only.

Copper phthalocyanine is one of the classic synthetic colouring matters. It does not exist in nature. However, its complex structure can be seen to be very close to natural colouring matters such as heamatin, which is a vital ingredient in the bloodstream, and chlorophyll, which is a vital ingredient in plants. Heamatin is a metal complex based on iron while chlorophyll is a metal complex based on magnesium. Once again it can be seen that the differentiation between natural and synthetic is blurred. One could still perhaps claim that a chemical found in nature was acceptable rather than one deliberately synthesised. However, in one well known book on natural foodstuffs [4] the following comments are found in the section on permitted colorants:

> *E150 caramel*
> Adverse effects: The safety of caramel has long been questioned. The number of types now available has been reduced to six to meet all the needs of the industry, and work is being carried out to find the safest form.
> *E153 carbon black (vegetable carbon)*
> Adverse effects: Probably few risks when the manufacture is perfected and a plentiful supply of oxygen is available for combustion, but in the United States it is banned in the belief that it may be implicated in causing cancer.

There are also the classical colorants used in textile dyeing history. Tyrian purple is obtained from the rare Mediterranean mollusc *Murex brandaris*. In order to obtain 1.4 g of dye some 12 000 molluscs would have to be slaughtered, and calculations have been quoted in which it is stated that, if Tyrian purple were used for all blue dyeings, it would result in some 200 square miles of land being knee-deep in shells, and an equivalent of the entire UK coastline being used for mollusc beds. This certainly does not sound environmentally friendly and most definitely upsets the natural order of things.

Another classic colorant, cochineal, requires 150 000 dried insects reared on 0.16 hectare of cactus to produce 1 kg of dye. In order to obtain this the dried insects are swept off the cactus leaves into bags where they are slowly, and one could claim cruelly, killed by long exposure to the sun. Again not an environmentally friendly procedure. This argument is reinforced when it is explained that cochineal, a mixture of carminic acid and kermesic acid, has very similar chemical structures to the synthetic dye CI Disperse Red 60 (Figure 2) [5]. In other words, how can the use of this natural resource be justified when similar products can be manufactured synthetically?

Dyeing with vegetable dyes

If it is assumed that the use of colorants derived from dead animals is not acceptable, then the only other recourse for the 'natural' lobby would be to dye fibre with dyes derived from vegetable sources. There is already some interest in this in the craft industries for wool dyeing.

The annual production for wool per annum is around 2 million tonnes. The average depth of shade applied using a synthetic dye is probably about 1.7%. This therefore results in a total synthetic dye consumption of 34 000 tonnes.

To match a depth of shade of 1.7% obtained with a synthetic dye, but using a natural dye, would require 120–240 g of dry dye plant or the equivalent of 500–1000 g of fresh dye plant. This is because the vast majority of the fresh dye plant is in fact water. If we assume on average that 750 g of fresh plant will be required to produce enough dried dyestuff to provide a 1.7% depth of shade, then it is possible to calculate that 1 g of synthetic dye is equivalent to 440 g of fresh dye plant. In other words the weight of fresh dye plant needed to replace 34 000 tonnes of synthetic dye is 34 000 × 440, or 15 million tonnes.

When cotton is considered the figures are even more dramatic. Cotton production each year is some 20 million tonnes, and an average depth of shade using synthetic dyes can be taken as 2%; therefore the total synthetic dye use is some 400 000 tonnes. Using the same factor as for wool, the weight of fresh dye plant needed to replace synthetic dyes would be 176 million tonnes. Furthermore, once the dye was extracted from the dye plant it would leave some 170 million tonnes of waste plant that would need disposal.

What would be the impact of this vast tonnage of vegetable dye plant on land

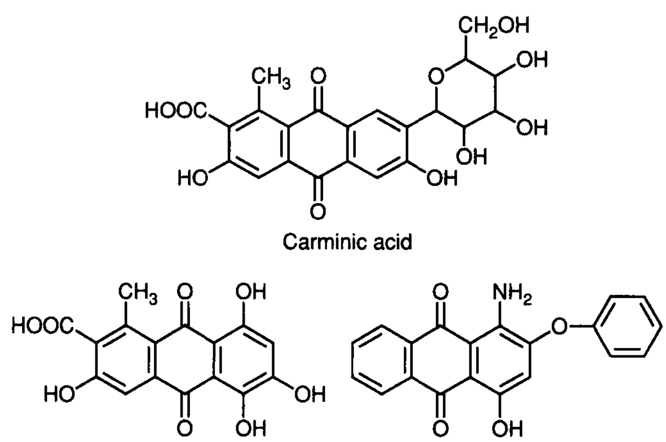

Figure 2 The natural dye cochineal consists of carminic acid with traces of kermesic acid, both with structural similarities to the synthetic dye CI Disperse Red 60

utilisation? For cotton alone 176 million tonnes of plant would be needed to give 6 million tonnes of vegetable dye. Cotton is still dyed with naturally derived indigo in some parts of the world and 1 tonne of vegetable indigo dye is derived from 77 hectares according to Indian government statistics. Assuming all plants give as high a yield of dye as with indigo, which is not likely as indigo is regarded as being one of the most efficient in terms of cultivation, then 6 million tonnes of natural vegetable dye would require 462 million hectares. This is equivalent to 31% of the world's agricultural land today, an area 13.5 times larger than currently needed to grow all the world's cotton. These figures are derived simply by looking at the need to dye cotton with vegetable dyes and totally ignores the need to dye wool, polyester and other synthetics.

In other words, in terms of environmental impact and maintaining the natural order, it is impossible to consider using natural dyes as a viable alternative to dyeing today's textile production.

There are other practical considerations to be made. Nearly all natural dyes require the use of a mordant to 'fix' the dyestuff to the fabric. A typical recipe to dye 100 g of wool would include 15 g of alum, 3 g of potassium dichromate, 2 g of zinc chloride (possibly containing cadmium!), 5 g of copper sulphate and 5 g of iron sulphate. If the liquor ratio used was 50:1 and 50% of the mordant fixed to the wool, the exhaust liquors would contain the levels of metal shown in Table 1. As can be seen, the concentration of metal in the effluent considerably exceeds the consent levels for discharge to UK sewers.

Table 1 Level of metal contamination in exhaust liquors from hypothetical mordant dyeing with natural dyes

Metal	Amount of metal present (mg/l)	Actual UK consent level (mg/l)
Al	340	2
Cr(VI)	100	0.5
Zn	200	10
Cu	260	2
Fe	480	10
Total	1380	10

Apart from the cost of the mordant, the application of natural dyes is time-consuming. In classical Turkey red dyeing there are ten processing steps involving the use of environmentally unfriendly products such as alum, rancid oil, cow dung, soda, ox blood, samac as a tanning agent, gall nuts and chalk.

When the long processing is combined with the high cost of fresh plants, and the tinctorial weakness of the natural dyestuff, not surprisingly the cost of dyeing using natural products is considerably higher than when using synthetic products. General levels are shown in Table 2.

Table 2 Relative quantities and costs of dyeing 1 kg of wool and cotton with synthetic and natural dyes

	Synthetic dye		Fresh dye plant	
	Amount (g)	Cost (£)	Amount (g)	Cost (£)
Wool	17	0.17	7500	15–18
Cotton	20	0.20	8800	18–44

Furthermore, with few exceptions, natural dyes are fugitive even when applied with a mordant, and therefore their fastness performance is generally not adequate for modern textile usage. Their fastness to washing is generally poor, with only a few exceptions have a light fastness better than 4. These are indigo (blue), carminic acid when applied with copper and iron mordant (brown), kermes when applied with a tin mordant (red), madder when applied with a tin or aluminium mordant (red), laccaic acid when applied with a tin or mixed copper/iron mordant (red or brown) and weld when applied with a tin mordant (yellow). This represents a very limited shade range, requiring the inclusion of heavy metals in the recipes, with their consequent unfriendly environmental impact.

Little work has yet been carried out to assess the toxicity of natural dyes, although one or two have been identified as posing potential problems. For example, quercetine is considered to be mutagenic. On the other hand, new synthetic dyes are fully tested for their levels of toxicity, and when introduced have a full set of data on their toxicity and ecotoxicity profiles.

Conclusion

We hope that the foregoing discussion demonstrates that natural dyestuffs do not present a viable alternative to the coloration of textiles in the mass market. There will obviously be those niche segments of the market where people for whatever reasons regard 'naturally' dyed products as being superior. However, for the majority of textile uses natural dyes do not present technically, commercially or environmentally adequate alternatives to the synthetic dyes currently in use.

The widespread adoption of natural products, assuming all commercial and technical objections were overcome, would result in a major shift in the usage of land throughout the world. In reality the area needed to satisfy the demand for colorant production is unavailable, because higher priorities are placed on the growing of food for the world's burgeoning population.

We are therefore exactly in the same position that Perkin was over a century ago when he discovered mauveine, and that Greiss was when he discovered the azo reaction, and with it the ability to make azo colorants. The reasons why the dyestuff industry was created last century, i.e. to overcome the inadequacies of the natural dyes available at the time, are equally applicable today. Synthetic dyestuff production is the only viable way of satisfying the global demand for colorants. The onus is on that industry to establish ethical, responsible and environmentally aware manufacturing procedures, as part of the efforts of the wider chemical industry to meet today's higher standards.

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