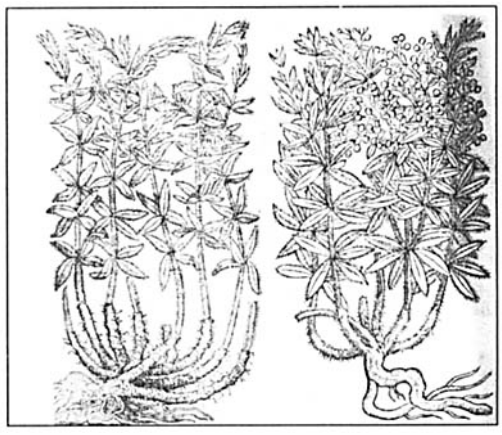
Doing what comes naturally in the dyehouse

Brian Glover wonders whether there a place for natural colorants?



Madder plant

The words 'natural dyes' are emotive. Just to mention the phrase in the company of colourists immediately polarises the conversation. On one hand there is the 'natural is good' argument, which implies that synthetic chemistry is an 'unnecessary evil'. On the other hand there is the 'synthetic chemistry is sensible, and natural is a green fringe diversion' argument.

What I aim to achieve in this article is to blur the edges between the two positions and hopefully demonstrate that, from a dyer's perspective, it is more important to consider coloration in general rather than be over concerned about the source of the dyestuffs. The situation is not clearly separated anyway in that:

- A naturally occurring product, carbon, is used widely in pigment printing and dyeing, but with a synthetic binder
- Natural dyes require synthetically produced mordants whose manufacture can raise environmental issues such as pollution.
- Synthetically manufactured and naturally produced indigo behave virtually identically.
- Pesticides can be used in the cultivation of vegetable dyes.
- Dyes produced by biotechnology or biosynthesis are neither wholly natural nor wholly synthetic in origin.

I would certainly disagree strongly with anyone who argues that natural dyes are environmentally or socially 'better' than their synthetic equivalents. Both natural and synthetically derived products can, for example, be carcinogenic. The workers involved in the cultivation and harvesting of natural products can, just like those in chemical plants, be exposed to hazardous working conditions and hardships such as exposure to pesticides, unsafe equipment and social deprivation. Extracting natural colouring matters often involves industrial operations, consumes energy and creates waste products, as does synthetic chemistry and possibly even biotechnology. In application there are hazards and problems with all colouring matters, and high consumption of energy and water; all dyeing processes produce effluent.

My premise is that it is not the source of the colorant that dictates whether it is intrinsically sound or suspect, environmentally good or bad. It is the attitudes and methods adopted by those involved in colorant production and by ourselves.

Historical developments

In the beginning there were only colorants derived from natural sources. Some chemistry was involved but essentially the colorant itself was obtained from a plant or an animal. With Perkin things started to change, and change quickly. Large numbers of chemists started to study the synthesis of colorants. Anthraquinone-based products were synthesised as purer versions of their natural equivalents. In my view there were three important breakthroughs that radically changed the industry to one in which synthetically produced colorants became the norm. These were:

- The discovery of the diazo reaction and the synthesis of azo dyes, products that do not exist naturally.

Preparing natural dyestuffs from natural sources

- The ability to fuse unsaturated cyclic compounds together to produce vat dyes.
- In the 1950s the synthesis of disperse dyes for dyeing the newly emerging synthetic substrates.

Why did these advances take place? What was it that caused the interest from the scientists in the first place, and then the success of their inventions and discoveries?

It was because the existing natural colorants were failing to satisfy the demands of the market place to such a degree that there was considerable commercial attraction to search for new synthetic colorants. The benefits of the synthetically produced colorants over the existing natural counterparts were such that in the industrialised world synthetic dyes took over the industry in all but a few segments. They were stronger, brighter and more reproducible; they had better fastness; they were cheaper and were readily available, as they were not dependent upon harvests and international sea transportation. In summary, they allowed people to make more money. The race down the synthetic route was frenetic with few taking time to question safety and health issues until it was too late. This is a legacy still carried by the colour-making industry.

What has caused the resurgence in interest in and a reappraisal of natural colorants? There are a number of influences. Today we have a much greater awareness of health and safety and of our environment in general. The need to improve and protect the environment is understood as is the need to conserve vital resources.

Commercially the colorant manufacturing industry has changed, with profitability falling to such an extent that the industry has had to contract, certainly in Europe and the USA. Synthetic chemical manufacture is a very controlled operation and therefore a costly one, especially where potentially hazardous intermediate products or processes are involved. Raw materials are also increasing in price, and in the longer term become more difficult to source as other industries change or natural resources become depleted. For example, the steel industry uses less coke, and therefore less anthracene, a by-product from the coke industry and a building brick for dyes, is available.

W H Perkin

There are some natural dyes that have remained important, such as indigo. Using modern agricultural techniques (for example, germination, cultivation, hybrids and agricultural chemicals) it has been possible to increase plant and colorant (indigotin) yield in the same way that wheat and barley yields have been progressively improved. Further work is being done and improvements can be expected. There is interest in expanding this work to other plants that yield colorants.

The European Union set-aside policy is causing people to look to new, non-regulated crops, such as flax, which is grown for linseed oil. In the past natural colorants have not been an attractive cash crop. However, due to the EU's Common Agricultural Policy, land in Europe cannot be used for food, and other cash crops are being sought. Natural colorants could be one option, but I would suggest that any major investments in this area would have to be made against a background of political expediency, that can change suddenly.

Finally there is biotechnology and biosynthesis. This topic is too large to be included in detail within the scope of this article. However, the level of activity and investment is increasing as society looks for cleaner, more efficient and potentially cheaper alternative raw material sources, or the ability to recycle materials. Some success has been reported in synthesising colorants by this route using processes that are reproducible. But it will be some years, even by the most optimistic of predictions, before we can expect to see any large-scale commercial production of colorants by this method. I will therefore concentrate on the conventional natural colorants, but bearing in mind that biosynthesis could be a way for the future.

Limitations of natural dyes

The limitations of natural dyes that caused their demise at the turn of this century still exist. They can be summarised as:

- Colour yield, dyeing efficiency and cultivation efficiency
- Shade range
- Process complexity and reproducibility
- Availability
- Effluent
- Unsuitability for synthetic fibres
- Toxicity.

Let us consider these in greater detail, concentrating on natural dyes of vegetable origins, since using colouring matter extracted from animals, specifically bred and killed for the purpose, does not fit well with the concept of concern for the environment.

Cost efficiency of natural dyes

Natural dyes are tinctorally weaker than synthetic dyes. Taking typical commercial strengths of products, the average depth of shade for synthetic dyes on cotton is 2%, i.e. 100 g cotton will require 2 g synthetic dye. To dye the same depth of shade with a natural dye will require 140–280 g dry dye plant. This in turn will require 500–1000 g fresh dye plant.

Natural indigo is cultivated in India, where, according to government statistics, 1 tonne of dye can be obtained from 77 hectares. To put this into perspective, if all world production of cotton and wool were dyed with natural dyes, and assuming the same plant yields for all dyes, 462 million hectares of land would be needed. This is equivalent to 31% of the world's currently available agricultural land. The process also produces organic plant waste, and 176 million tonnes of it would be produced just to dye cotton with vegetable dyes each year. A waste management system needs to be in place in order to avoid methane production, potential ozone depletion and a build up of phosphates.

There is also the need to use, and pay for, the mordants that are often needed with vegetable dyes. This results in a major price differential between the costs of dyeing with natural and synthetic dyes. It has been calculated that:

- To dye 1 kg wool on average costs £0.17 with synthetic dyes and up to £18 with vegetable dyes
- To dye 1 kg of cotton costs on average £0.20 with synthetic dyes and up to £44 with vegetable dyes.

Primitive dye works – indigo dyeing

So, to produce vegetable dyes requires land, cultivation (with the possible use of pesticides), harvesting and extraction techniques. The process is not cost free and is not without environmental impact. Finally the cost of dyeing with vegetable dyes is on average higher than with synthetic.

Shade range available with natural dyes

It is possible by careful selection of plant extract and mordant to obtain a full shade range with vegetable dyes. But the dyer rarely has the luxury of dyeing a primary colour or only using a single dyestuff. Instead commercial dyeing requires the full gamut of shades, tints, brightness, dullness, tones, subtle nuances and non-metamerism. It also demands colour and light fastness across all hues and fabrics.

A key aspect of the dyeing process is the ability to mix dyestuffs together in the same dyebath using a common application process and produce the full gamut of shades and fastness properties required in a reproducible manner. The cost of getting a dyeing wrong is considerably higher than the profit from getting it right. Reproducibility and compatibility of dyes in admixture across all shades is of paramount importance. Synthetic dye molecules are deliberately engineered to give this universal applicability and therefore are superior in this respect to natural dyes.

Process complexity and reproducibility

Anyone who has dyed wool with chrome dyes understands the difficulties and limitations of using mordants, especially when dyeing mixtures of shades. It was these problems that caused the development and acceptance of metal complex dyes, and the avoidance of mordants for dyeing all but standard shades. Mordants require a two-stage process and pose inherent reproducibility problems. Vegetable dyes, just like the wool and cotton they can be used to dye, exhibit variations from source to source and harvest to harvest.

The land on which the plants are grown will also have an influence. Any gardener knows that the colour of hydrangeas can be influenced by the soil and the water, or by doctoring with tea leaves. The same is true of natural dyes. As in any agricultural situation there will be good and bad years, depending on the prevailing weather. There will be periods when there is a glut of the fresh plants and periods when there is scarcity, such as during the winter months.

In a commercial operation this puts considerable pressure on the standardisation processes and the storage and distribution network required. It would not be acceptable for a bulk dyeing operation to have supplies of natural colorants varying in shade and application performance from delivery to delivery, nor to have availability and price fluctuating according to seasonal and weather patterns. In order to gain wide acceptability the vegetable dye industry would need to follow the same manufacturing, operational and quality procedures adopted by the synthetic dye industry.

Availability of natural dyes

As well as the issues covered above, there is one further aspect to consider. With the current predominance synthetic dyes, sources of vegetable dyes have dwindled during this century. Despite renewed interest in the 1980s and 1990s, products such as Brazilwood and logwood have virtually disappeared. The knowledge and expertise in the cultivation of what were at one time staple vegetable colouring matters has been lost. So to reawaken large-scale interest in and use of vegetable dyes, lost cultivation techniques must be researched if an acceptable shade gamut and fastness properties are to be achieved.

Effluent

No effluent-free dyeing process has yet been developed that has gained widespread acceptability. Vegetable dyes are no different in this respect. Exhaustion and fixation will not be 100% and therefore there will be coloured effluent. More importantly, as nearly all vegetable dyes are applied using a mordant, their environmental impact will be similar, if not worse than when applying synthetic dyes with mordants, e.g. chrome dyes on wool.

A typical mordant used for dyeing wool with natural dyes is shown in Table 1. If the liquor ratio was 50:1 and 50% of the mordant was fixed to the wool, the exhaust liquors discharged to effluent would contain the amounts shown. From this we can see that vegetable dyes do not provide an answer to effluent problems.

Synthetic fibres

Dyes from natural origins do not present an alternative to synthetic dyes for dyeing synthetic fibres. There is every likelihood that natural disperse dyes could be developed but it would require considerable investment of time and money to do so.

Man-made fibres are a very important

Table 1 Metals in effluent from dye mordants

Mordant/ metal	Mordant (mg per 100 g wool)	Metal in effluent (mg/l)	UK sewer consent limit (mg/l)
Alum (Al)	15	340	2.0
Potassium dichromate (Cr(VI))	3	100	0.5
Zinc chloride (Zn)	2	200	10.0
Copper sulphate (Cu)	5	260	2.0
Iron sulphate (Fe(II))	5	480	10.0
Total		1380	10.0

part of the textile industry and in the present situation they can only be dyed with synthetic dyes. The synthetic dyestuff industry will therefore continue to grow and to develop new products that are more environmentally friendly, more efficient in use and ultimately designed to be more universal in fibre suitability, e.g. a single dye type for polyester/cotton blend fabrics.

Toxicology

It is important to destroy one myth from the beginning and that is that natural products are inherently safe and that only synthetic products are dangerous. Clearly there are many poisonous products in nature, and natural carcinogens are known. In contrast studies have been carried out that show widely used synthetic dyestuffs are benign. But because natural products have always existed, it is assumed that they can be treated with less caution than synthetic ones.

The issue is one of misunderstanding or ignorance. The chemical industry was ignorant of the potential harmful effects of the products concerned. I do not seek to defend this situation, but, in a similar way, society has been ignorant of many of the potential harmful effects of natural products.

The benefits of pharmaceutical chemistry, a science spawned by the dyestuffs industry, is well understood, although again there have been terrible consequences and painful learning experiences along the way. It is not the actual source of the product that causes the problem. It is the chemical structure of the molecule and its biological impact, whether the origin is natural or synthetic. The attitude, care and understanding of the people using or making the product also play a large part.

Azo dyes need a special mention. These chemicals do not occur naturally and are therefore often regarded with suspicion. Azo dyes can break down into free amines which, as a chemical class, have had toxicological problems. German legislation on dyes is concerned with the amines that form the dyes, and has eliminated the use of dyes that are derived from suspect amines, even though there may be no evidence to suggest that in nature such a breakdown back to the parent amine is possible. On the other hand, there are those who consider the cosmetic removal of azo colour from waste liquors using reducing agents (which will generate the parent amine) or treatment with ozone, when not being able to characterise the reactions taking place, as 'good things' to do. The issue again is more to do with attitudes and misunderstanding.

Conclusions

From a dyer's perspective, I would argue that the actual source of a product is of no consequence. The large-scale commercial dyer requires reproducibility, cost-effectiveness and products that are dependable. Whether these properties are provided by natural, synthetic or biotechnology/biosynthetic in origin is unimportant, provided the products can be used with confidence in mixtures to provide all the customer's requirements. In the business environment there will be no prejudice for or against products based on their source.

Marketing departments or retailers may wish to promote natural dyes where they see a commercial advantage from doing so. In such cases the motivation usually has as much to do with assuaging the consciences of those customers who are willing to pay extra for such products, rather than any environmental awareness of the businesses concerned. Whether major retailers decide to follow the same route will depend upon market forces and whether they are prepared to accept the disadvantages of using natural products. Shade reproducibility and cost would be key issues. There is no denying this market niche exists and could grow but at present it is hard to see it being big enough to be attractive to the commercial dyer.

I believe the most likely scenario will be that any development of vegetable dyes will be based on selected products that are free from most of the disadvantages described for the class as a whole. There is one product that stands out from the rest, namely indigo. It is already widely used in large volumes, the behaviour of the natural and synthetic product is very similar. In use indigo does not require a mordant and there has been continued cultivation over the decades. Furthermore there is a potential marketing appeal in natural denim: a natural fibre dyed with a natural dye. Otherwise I believe the main impact of natural colorants will be limited and restricted to novelty, craft and niche market segments.

Maybe in the future new developments in biotechnology will offer an effective way of combining the advantages of both natural and synthetic dyes on the one hand with commercial practicability on the other. It is likely that natural or biotechnologically produced dyestuffs will be used in increasing amounts. However, it will be purely commercial considerations that will dictate whether or not biotechnological products become a major force in world dyestuff markets. It is likely that emphasis will be focused on key large volume intermediates rather than individual colorants.

Certainly there is a place for natural dyes in the dyehouse, provided these dyes meet the already established selection criteria and satisfy the profile established for the dyes already in use. Natural and synthetic colorants are not mutually exclusive means of dyeing. The dyeing industry is and will remain an 'equal opportunity' consumer. The market place is open to dyes from all sources. The constraints are on the suppliers, manufacturers or cultivators of the vegetable dyes.

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