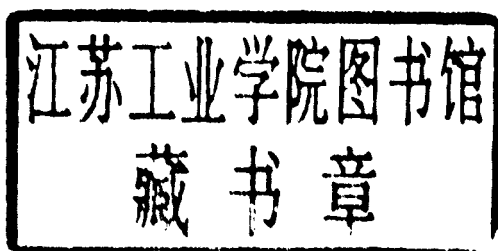




# The Colour Science of Dyes and Pigments

**K McLaren**

Second Edition



Adam Hilger Ltd, Bristol and Boston

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*British Library Cataloguing in Publication Data*

McLaren, K.

The colour science of dyes and pigments

1. Colour

I. Title

535.6 QC495

ISBN 0-85274-490-0

First published 1983

Second edition 1986

Consultant Editor: **Professor W D Wright**

Published by Adam Hilger Ltd

Techno House, Redcliffe Way, Bristol BS1 6NX, England

PO Box 230, Accord, MA 02018, USA

Printed in Great Britain by J W Arrowsmith Ltd, Bristol

# The Colour Science of Dyes and Pigments

## Foreword

The number of books on colour which are being published each year is a clear indication that the subject is very much alive and that it is being studied in ever-increasing breadth and depth. Certainly no one can read this book by Keith McLaren without being struck by the vitality with which he treats his subject and by the breadth and depth of his own understanding of it. He takes us from Stone Age man to microprocessor robot, and en route deals with the physics and chemistry of dyes and pigments, the visual processes by which their colour is perceived, the instrumental and computer techniques available to industry for the measurement of colour and the prediction of the results of colorant mixture, and finally with those knotty problems that have been with us for so long, the specification of colour differences and the measurement of colour appearance.

In all these fields Mr McLaren writes with the authority born of experience and I cannot think of anyone better qualified to cover the subject so effectively. After extensive industrial experience in the Dyestuffs Division of Imperial Chemical Industries, he moved to Instrumental Colour Systems where he has been very actively involved in the development of colour measuring instruments and their efficient use by industry. He has been a leading figure in the Society of Dyers and Colourists and his contributions to its activities have been recognised by the award of the gold medal of the Society and the research medal of the Worshipful Company of Dyers. In further recognition of his 'outstanding contributions to the study of colour fastness and colour measurement of textiles' the Society also elected him an Honorary Fellow in 1970. Internationally, he has played a very important part in the work of the Colorimetry Committee of the Commission Internationale de l'Eclairage, especially in the discussions leading to CIE recommendations on uniform colour spaces and colour difference equations. At the time of writing this Foreword, he is just completing his two-year term of office as Chairman of the Colour Group (Great Britain).

Now through this book his influence will extend to a still wider audience of colour scientists and industrial colourists, to the great benefit of us all. We have much to thank him for.

**W D Wright**

## **Preface to Second Edition**

Developments in colour science and technology have continued at a rapid rate since the typescript of the first edition was completed. The span of these developments ranges from the elucidation of the molecular structure of the visual pigment, rhodopsin, to the adoption of instrumental shade sorting by the garment industry of the UK. It was therefore thought more appropriate to issue a second edition rather than a second printing, especially as it permitted the inclusion of many items which, for one reason or another, were omitted from the first.

**K McLaren**

## Preface to First Edition

Colour has fascinated Man since the dawn of civilisation as it was people of the Old Stone Age who painted lifelike figures of animals in many shades of red, yellow, brown and black on cave walls. During the Bronze Age the art of dyeing was discovered and since then pigments and dyes have provided most of the colours of the man-made world. This world of colour involves many different branches of science.

It is, of course, the *chemical* structure of the colorant which governs its colour which appears as a result of the interaction of light and matter – *photo-physics*. Such interactions are also capable of destroying not only the colorant (fading) but also textile fibres (tendering). This is the realm of *photochemistry*. Light absorbed by any one of the four pigments in the retina of the eye results first in a change in cell potential followed by a signal being sent to the visual cortex in the brain – *neurophysiology*. How the brain interprets these neural signals brings us into the realm of *psychology* and the fusion of this with physics, *psychophysics*, has provided us with a method of measuring the million or more colours the eye and brain can perceive. The science of colour measurement has also made it possible to predict how much of which colorants would have to be mixed together to match any one of these colours to an accuracy which at least equals that of the professional colourist.

This book gives an overview of all of these scientific and technological aspects of colour, but does not attempt to give a comprehensive account of any. The number of references which have not been mentioned are many times greater than the number which have.

Many individuals have, directly or indirectly, helped in the writing of this book and I would particularly express my thanks to four of them: to the late Deane B Judd whose many publications on colour widened my horizons beyond those of a colour chemist; to W D Wright without whose encouragement this book would never have been started and whose detailed comments after reading the original manuscript resulted in many improvements; to my chairman, A C Perry who provided me with the opportunity to write it; and to my wife, Patience, who converted my badly written manuscript into an acceptable type-script.

**K McLaren**

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# 1

## A Brief History of the Development of Colouring Matters

### 1.1 THE DEVELOPMENT OF PIGMENTS

The idea of using naturally occurring materials solely on account of their colour first arose during the Old Stone Age when Neanderthal man dominated Europe between 180 000 and 30 000 bc. Towards the end of this period these peoples began to bury their dead and the excavation of several of their burial sites has revealed that red ochre (anhydrous ferric oxide) had been placed on the cranium and breast of the corpse. After Neanderthal man had become extinct, his European successor, Cro-Magnon man, used much larger amounts of red ochre in burial rites and caves have been discovered where large quantities – several hundred kilograms – had been stored. It is generally accepted that Stone Age man associated the colour of red ochre with that of life-giving blood and the importance of red as a colour is clearly shown by the fact that whenever a language has developed to the stage at which colour-names are devised, the first is always a word for red (Berlin and Kay 1969).

Cro-Magnon man, however, made a much more important discovery: the art of painting as displayed in the famous cave paintings of Lascaux in the Dordogne region of south-western France. Remains of charcoal in the oil lamps used by these painters have been carbon-14 dated at about 15 000 bc. They blended yellow and red iron oxides, soot, black manganese oxide and white porcelain clay to give the desired colours and mixed them with cave water which has a naturally high calcium content ensuring good adhesion and great durability. The paints were then applied to damp, smooth cave walls with brushes made from macerated twig tips and bundles of bison hairs to depict deer, horses, cattle, ibex and bison (Leroi-Gourhan 1982).

For the next ten thousand years, no developments concerning pigments and paints occurred but with the first civilisations of Mesopotamia and Egypt, artists were able to produce a much wider range of colours. The colours most conspicuous by their absence from the Cro-Magnon cave paintings were blues and greens but both became available to Egyptian painters. The most famous blue pigment used by the Egyptians was ultramarine. This was derived from the

mineral haüyne (sodium/calcium aluminium silicate) which is mainly responsible for the colour of the gemstone lapis lazuli, both being mined in Afghanistan in 4000 BC. Three green pigments were used — terre verte which was derived from glauconite (potassium/aluminium/iron/magnesium silicate), malachite (copper carbonate/hydroxide) and chrysocolla (copper silicate). Bright reds and yellows were also missing from the pigments used by Stone Age artists but the Egyptians used orpiment ( $\text{As}_2\text{S}_3$ ) a bright lemon-yellow mineral and realgar ( $\text{AsS}$ ) a bright red. They were also the first to make pigments which did not occur naturally — white lead (lead carbonate), red lead ( $\text{Pb}_3\text{O}_4$ ), lead antimoniate (yellow) and, most important of all, Egyptian blue which was made by heating malachite with sand, chalk and soda.

The following Greek and Roman civilisations, though exploiting to the full the pigments known to the Egyptians, appear to have added only one of their own, the bright red cinnabar ( $\text{HgS}$ ), and it was not until the twelfth century that another pigment was produced. This was a blue pigment, indigo, and in many ways the history of the development of blue pigments is the most fascinating of all and worthy of special consideration.

### **Blue pigments**

We have already seen that natural ultramarine had been in use since 4000 BC and that the Egyptians had introduced the cheaper Egyptian blue. Unfortunately, however, the art of making Egyptian blue had been lost completely since the time of the Romans and was not rediscovered until this century. The expense of ultramarine limited its use to small but important areas in paintings and when the dye indigo was first imported into Europe in the twelfth century, its dark blue colour and its insolubility in water led to it being used for hundreds of years only as a pigment, its major defect being its lack of permanence. In the fifteenth century it was augmented by the manufacture of a vitreous pigment containing cobalt called smalt but this, although permanent, was coarse and lacked intensity. In 1704 a very much better blue pigment appeared which was discovered as the result of a lucky accident. Diesbach, a German paint manufacturer, made his own aluminium hydroxide which he used to form a lake† with the dye cochineal. On one occasion, instead of obtaining a white precipitate, it was blue and the cause was traced to the alum containing an iron salt and the caustic potash containing potassium cyanide which reacted to form complex potassium ferri-ferrocyanide which was marketed as Prussian blue. This is still a major pigment though it is only borderline in respect of its permanence.

Prussian blue was not, therefore, an adequate substitute for ultramarine and in the early nineteenth century the French government offered a prize for the development of a method of producing it synthetically. Just as the discovery of Prussian blue was serendipitous, so was that of synthetic ultramarine. In 1787,

† A lake is a pigment prepared by precipitating a soluble dye as a metallic salt or acid complex, sometimes in the presence of an inert substrate, the latter forming an integral part of the product.

Leblanc developed a process for making soda, one stage being to heat sodium sulphate with coal and limestone. On one occasion a blue encrustation was observed on the walls of the furnace. Following extensive research a method of manufacturing this blue substance was discovered which turned out to be similar in composition to ultramarine whose molecular structure has still not been determined although it is closely related to the zeolites and contains sodium, calcium, aluminium, silica, sulphur and oxygen. Synthetic ultramarine then became the standard blue pigment for artists but it has one major defect, its ease of decomposition by acids which limits its use in paints for protective coatings.

In 1901 another important blue pigment, indanthrone, was discovered accidentally but it will be more convenient to consider its origins in §2.3.

The latest and undoubtedly the last stage in the search for the ideal blue pigment was the result of yet another chance discovery. The dyestuff intermediate phthalimide was made by Scottish Dyes Limited by heating phthalic anhydride and ammonia in an enamel-lined cast-iron autoclave. In 1928, several batches of phthalimide were found to be discoloured and from these a dark blue crystalline substance containing iron was isolated, the iron having come from a minute crack in the lining of the vessel. This compound was remarkably stable and was found to have an entirely new structure, phthalocyanine. When the iron atom was replaced by copper a bright greenish-blue pigment having twice the tinctorial strength of Prussian blue and 20–30 times that of ultramarine was produced. It was marketed as Monastral Blue B by ICI in 1935 and has since become the most widely used blue pigment as its only defect is a tendency to “bronze”, i.e. at certain glancing angles its colour may appear brown.

### **Pigments of other colours**

The development of pigments of colours other than blue followed similar lines. The early pigments usually possessed certain technical limitations, or were too expensive, or were poisonous and they were eventually replaced. Even so quite a number of ancient pigments are still important today, though much improved in quality. Among these pigments are white lead, various iron oxides (ochres) and carbon black. The number of available pigments increased exponentially following the discovery of the first synthetic dye as many of them could be converted into lakes: the lake of Perkin’s mauve, for example, was used to print the sixpenny lilac stamp of 1868. Other synthetic colouring matters did not require conversion into lakes. For example, many azo and vat compounds were both dyes and pigments so that today organic pigments outnumber inorganic pigments many times over. Few of those in use during the first half of the nineteenth century were rendered obsolete, however, and they still possess features which have never been imitated by organic pigments.

Until the eighteenth century, the technical properties which an ideal pigment had to possess were those making it suitable for artists who inevitably ground their own pigments in whichever medium was being used. During that century,

however, paints became widely used on structures for decorative and/or protective purposes and the pigment's suitability for use in such paints became the most important criterion. Pigments which are far too expensive for domestic paints, such as cobaltous stannate (cerulean blue), are still manufactured for artists' use. Pigments are also extensively used today in printing inks, car finishes, stoving enamels and plastics.

## 1.2 THE DEVELOPMENT OF NATURAL DYES

After the technique of weaving had been discovered in about 5000 BC it was inevitable that attempts would be made to colour fabrics using the wide range of pigments which were available. These early attempts were not particularly successful because the pigment particles were merely held mechanically between the fibres and were removed by rubbing or flexing and particularly by washing. In the fifteenth century pigments were being permanently applied to fabrics by a technique resembling painting, the pigment being first ground with resin or linseed oil. This technique was quite unsuitable for fabrics in general, however, because the coloured areas were stiff and the paint was prone to cracking if flexed. By the end of the seventeenth century linen dyers had discovered how to form basic copper acetate inside the fibre which produced green shades free from these defects. Later other mineral pigments such as Prussian blue and manganese dioxide (which imparted a bronze colour) were formed *in situ* by textile printing methods.

Bronze Age man, however, discovered a completely new class of colouring matters which could be applied to textile fibres with none of the defects which limited the usefulness of pigments: members of this class are called dyes.

Though which dye was the first to be discovered can only be a matter of speculation, it is highly probable that it was one of those occurring in brightly coloured flowers which could be extracted by water alone to give a coloured solution from which the colour could be transferred to one or more natural fibres directly, i.e. by mere immersion. Such dyes are termed 'substantive' and a list of those which have been identified on ancient textiles is given in table 1.1.

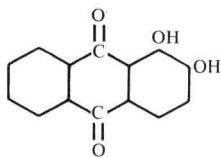
These dyes were, however, very fugitive. If exposed to a few hours of bright sunshine the colour would have faded completely and washing would also

**Table 1.1** Ancient dyes possessing substantivity.

Dye	Plant of origin	Fibre	Colour
Anatto	<i>Bixa orellana</i>	Animal and vegetable	Orange
Henna	<i>Lawsonia alba</i>	Animal	Orange
Safflower	<i>Carthamus tinctorius</i>	Animal and vegetable	Red
Saffron	<i>Crocus sativus</i>	Animal	Silk — golden yellow Wool — orange

remove all of the dye. Archaeological discoveries at Mohenjo-Daro on the banks of the Indus, however, include pieces of red cloth which have been dated at about 1700 BC and the dye used has been identified as madder whose fastness properties are excellent even by modern standards. Though by no means comparable in importance, the discovery of the madder dyeing method must surely rank with the discovery of bronze itself in ingenuity.

Madder occurs in the roots of *Rubia tinctorum* as a glucoside which is hydrolysed when the dead roots ferment under damp conditions. This process generates alizarin (I). Occurring widely in the valley of the Indus are colourless crystals of alum, and Bronze Age man must have noticed the intense red coloration occurring when alum was added to an extract of fermented *Rubia* roots. Bronze Age dyers then discovered that if cotton fabrics were immersed in a solution of alum followed by immersion in an extract of wood ash (which is alkaline) the fabric could be dyed red by steeping it in a hot solution of alizarin.



(I)

The effect of the treatment with alum followed by alkali was to deposit aluminium hydroxide in the fibre which in the dyebath combined with the alizarin to form an insoluble red lake. This pre-treatment is called 'mordanting' and its discovery was crucial to the development of natural dyes because so few have any affinity for textile fibres, and most of those which possess some affinity gave much faster shades on mordanted fibres. Alum remained the most important mordant throughout the whole of the natural dye era but salts of other metals were also used to give different shades or better fastness properties: for example, iron and copper salts were in use by the first century AD, tin was introduced in the seventeenth and chromium in the nineteenth century.

Until 1869, when alizarin was synthesised (an event of extreme importance in the development of synthetic dyes), madder remained one of the most important natural dyes for cotton and linen especially when applied by the Turkey red dyeing method. This involved up to twenty separate stages of scouring, mordanting, dyeing and aftertreating which lasted for a total of about a month. Only fibres of the highest quality could withstand such processing and this fact, together with the high fastness obtained, resulted in Turkey red dyed fabrics acquiring the reputation of being virtually indestructible. Greece was the centre of Turkey red dyeing in the seventeenth century and the methods used were not known to the dyers in western Europe. Weavers were therefore forced either to import dyed yarns or to send their yarns to Greece for dyeing. The French discovered the secrets of this method in the middle of the eighteenth century and established Turkey red dyehouses in Rouen and other towns. One stage

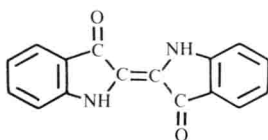
involved exposing the dyed cloth to sunlight and the area surrounding the site of one such dyehouse at Mulhouse-Dornach is still known as 'La Mer Rouge'.

The Turkey red dyeing process produces in the fibre a complex of alizarin containing both aluminium and calcium, its formula being  $\text{CaAl}(\text{OH})(\text{Az})_2$  where Az represents the alizarin molecule (I) minus two hydrogen atoms (Kiel and Heertjes 1965).

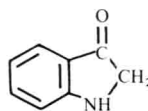
From the early beginnings in the Bronze Age, dyers discovered many natural dyes from the plant and animal kingdoms – Brunello lists about 300 (Brunello 1973) but in this brief history mention can be made of only those the author considers to be the most interesting, namely indigo, kermes, cochineal, logwood and Tyrian purple.

### Indigo

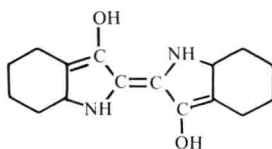
Amongst the most ancient textiles ever discovered are those which have been dyed blue with indigo (II) whose precursor, indoxyl (III), is contained as the glucoside indican in the leaves of two separate species – *Isatis tinctoria* which grows widely in Europe and is commonly called woad and *Indigofera tinctoria* which is indigenous to India. When the dead leaves of these plants ferment, indican is hydrolysed to indoxyl which is readily oxidised by air to indigo. This



(II)



(III)



(IV)

technique was used by the Ancient Britons to obtain woad which they used to stain their bodies. Fermentation also causes reduction of any indigo which has been formed to pale yellow leuco-indigo (IV) which is soluble in alkali and possesses substantivity for all natural fibres. Like indoxyl, leuco-indigo is readily oxidised by air to indigo and, after immersion in the dyebath, the fibres are squeezed and allowed to oxidise in air when the characteristic blue colour is formed. The operation of reducing indigo in an alkaline solution was carried out in large vats and this method is termed 'vatting'. Indigo was the only natural dye which required vatting and was one of the few whose fastness properties were not improved by mordanting.

*Indigofera* leaves contain much more of the glucoside of indican than *isatis* leaves and in India, where indigo dyeing originated, fermentation was not

capable of reducing all the indigo formed by air oxidation. The separated indigo was therefore vatted by a chemical method using arsenic sulphide ( $\text{As}_2\text{S}_3$ ) and wood ashes. There are no records to indicate how this unusual method was discovered. One possibility is that as arsenic sulphide was used as a bright lemon-yellow pigment, orpiment (auri-pigmentum), it might therefore have been used with indigo to produce green pigments which might have become alkaline accidentally, the disappearance of the blue component then being observed.

Indigo began to be exported from India to Europe in the twelfth century but as mentioned in §1.1 it was originally used only as a pigment, the first mention of its use as a dye being by Marco Polo at the end of the thirteenth century. It was then being used by Venetian dyers but in virtually every other European country, including England, its use was bitterly opposed by the woad growers and various laws were passed prohibiting its use. This opposition began to crumble when the opening of the sea-route to India in the beginning of the sixteenth century resulted in greatly increased quantities being available at a much lower price. Another factor which undoubtedly helped was that the woad dyers preserved the livelihood of the woad growers, and eliminated the hazards associated with arsenic sulphide, by discovering a better method of vatting. A woad vat was capable of reducing substantial amounts of indigo and this remained a major method for wool dyeing until it was replaced by the use of sodium dithionite in the twentieth century. Cotton dyers, however, abandoned the woad vat in the middle of the eighteenth century in favour of the more readily controlled ferrous sulphate/lime vat whose high alkalinity was not harmful to cotton.

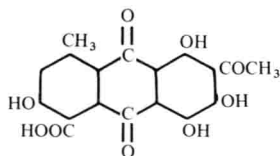
Indigo was probably the most widely used dye during the natural dye era, its importance being indicated by Newton's use of the word as a colour name. The inclusion of indigo as one of the seven named spectral colours has been the subject of much controversy during the present century which has been critically reviewed (McLaren 1985a). The synthesis of indigo in 1880 was another landmark in the development of synthetic dyes.

### Kermes

Kermes is another ancient dye having been used to dye the red capes which the Hebrews discovered when they captured the city of Ai in about 1400 BC. It was the most widely used red dye for wool and silk, madder being suitable only for vegetable fibres.

The dye was obtained from the dried bodies of the insect *Coccus ilicis* found on various species of oak growing in the Middle East. The colouring matter present was kermesic acid (V) which was originally applied on an alum mordant. The word *kermes* is of eastern origin and is the root of *crimson* and the French word *carmoisine*. This strongly suggests that the shade it gave on alum was a bluish-red though the colour of the capes discovered at Ai is described in the Bible (*Josh. VII: 21*) as scarlet. Brunello states that in the Middle Ages only the Venetian dyers knew how to produce a scarlet shade from kermes – by mordanting with alum and tartar.





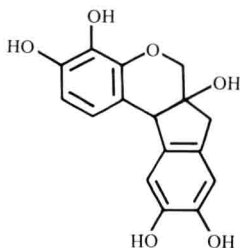
(V)

A dye similar to kermes was discovered by Mexican dyers in about 1000 BC. This was contained in the bodies of the insect *Dactylopius coccus* which lived on the cactus *Rhynchota* and was found being used by the natives when the Spanish entered the country in 1518. The Spanish began to cultivate it and exported it to Europe in 1550 under the name *cochineal* where it rapidly superseded kermes as it contained about ten times as much colouring matter, the glycoside of carminic acid in which the  $-\text{COCH}_3$  group of kermesic acid has been replaced by  $-\text{CO}(\text{CHOH})_4\text{CH}_3$ .

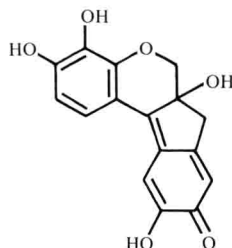
Cochineal certainly gave crimson shades on an alum mordant but in 1607 Drebbel accidentally discovered that salts of tin gave the much coveted scarlet shade which also had a significantly higher light fastness. Cochineal dyed on a tin mordant resisted the onslaught of synthetic dyes for nearly a hundred years. It was used until 1954 to dye the dress uniforms of the Brigade of Guards though this owed more to innate conservatism rather than technical superiority. Its aluminium lake has been widely used as a food colorant since the Middle Ages and is still widely used for such purposes, being one of the few natural food colorants which has been subjected to toxicological testing. It has never been synthesised on an industrial scale.

### Logwood

When the Spanish entered Mexico they discovered that the Mexicans had long been using a dye obtained from a tree growing on the shores of Campeche Bay. The wood from this tree contained the colourless haematoxylin (VI) which oxidised in air to the red dye haematin (VII). When logwood was first exported to Europe, however, there was considerable opposition to its use by the various



(VI)



(VII)