Principles of textile dyeing

The dyeing of textile fibres is carried out in an aqueous solution, known as the dye liquor or dye bath. True dyeing can only take place if the coloration is relatively permanent, which means that it cannot be removed readily by rinsing in water or by normal washing procedures. Moreover, the dyeing must not fade rapidly on exposure to light. Many plants and animals can produce coloured products, but only a limited number of these can be used to dye textiles.

The colour of dyestuffs is due to the presence of chromophoric groups or chromophores. Some examples of these chromophores are the vinylene group ($>C=C<$), the carbonyl group ($>C=O$), the thiocarbonyl group ($>C=S$) and the nitroso group ($—N=O$). These groups belong to systems of conjugated double bonds. Basically the chromophoric structure determines the colour of the dyestuff. However, other functional groups influence the selective absorption of light, which in fact causes a certain colour. Functional groups that modify the light absorbance are called auxochromes. Examples of common chromophoric groups are the hydroxyl group ($—OH$), the carboxyl group ($—COOH$), the amino group ($—NH_2$) and the sulphonic acid group ($—SO_3H$).

The process of bonding the dye molecule to the fibre is one of adsorption; the dye molecules concentrate on the fibre's surface. Chemical as well as physical forces play an important role in bonding the dye molecules to a fibre. Fibres and dyestuffs are both organic compounds and contain sufficient polar groups to attract each other and form primary (covalent) bonds and secondary bonds (by means of van der Waals forces, dipole association and hydrogen bonding). These secondary bonds can occur between the dyestuff and the fibre surface if they are close enough to each other. In any dyeing process, whatever kind of dye class is being used, heat must be supplied to the dye bath; energy is used in transferring dye molecules from the solution to the fibre as well as in swelling of the fibre to make it more receptive.

The hydroxyl, the amino and the carboxyl groups of, for example, mordant dyestuffs are able to form complex compounds with certain metal ions. Metal salts able to form these complexes are aluminium, iron and tin salts. The metal ions are bound to the fibres and form insoluble complexes with the dyestuff molecule and are thus bound together to the fibres. Complexes can be formed with either one or two dyestuff molecules. The former is achieved when dyed in an acid dye bath, the latter in an almost neutral dye bath. Both methods of dyeing have been applied in the past with natural dyestuffs.

Wool and silk are both complicated proteins which have carboxyl and amino groups available for bonding dyestuffs to the fibres. Mordant dyestuffs are very suitable to dye these fibres. Linen and cotton, being cellulose fibres, have less favourable bonding possibilities and are thus more difficult to dye with mordant dyestuffs.

Direct dyes are bound to the fibre by secondary bonds. They are often large linear, flat, water-soluble molecules such as crocetin in saffron. Direct dyes diffuse into the fibres, which are swollen by hot water. The flat shape of the molecule promotes an easy diffusion. Direct dyes are very suitable for cellulose fibres because of the many polar hydroxyl side groups of cellulose, which form hydrogen bonds with the polar groups of the dyestuff molecule. The fastness against washing and light of these dyestuffs is relatively low.

Vat dyes are dyestuffs insoluble in water without sufficient auxochromic groups in the molecule. The groups, which cause the water solubility, are formed by reduction. After diffusion of the so-called *leuco*-form of the dyestuff into the fibre, the *leuco*-form is oxidised again into its original water-insoluble form. Because of the absence of auxochromic groups, the dyestuff is mainly bonded to the fibre by van der Waals forces. Due to these properties vat dyestuffs are suitable to dye protein fibres (wool and silk) as well as cellulose fibres (linen and cotton). Vat dyestuffs have a high lightfastness; the relatively good fastness to washing is due to the limited water-solubility. However, fastness against rubbing is low.

In all dyeing processes evenness is an important quality which can be attained by controlling the dyeing conditions and by agitation of the bath to ensure good contact between dye liquor and the textiles being dyed (Tímár-Balázsy and Eastop 1998: 67–82).

Classification of dyestuffs

The classification of dyestuffs can be determined on the basis of chemical constitution of the dyestuff molecule and according to the method of application of the dyestuff. Classification according to the dyestuff molecule can be based on the chromophore structure, as with anthraquinones (madder etc.) or flavonoids (weld etc.), or the derivatives of one dye, as is the case in indigotin and 6,6'-dibromoindigotin. In the dyeing industry the dyeing characteristics are of great importance. Certain functional groups (OH or NH_2) on the same basic dyestuff molecule may give different colours when applied. An example of this is the group of indigoid dyes. Among the natural dyestuffs only the blue and purple dyes, indigo and Tyrian purple, belong to this group. After the development of synthetic dyestuffs in the 19th century a whole series of dyestuffs with different colours was developed, forming a dyestuff class with the same characteristics as indigo such as high lightfastness.

Dyestuffs can also be classified according to their method of application. In the case of natural dyestuffs only three groups are of importance:

- Dyestuffs which are soluble in water, but form metal complexes on the fibre. They can only be applied with the help of water-soluble metal salts (mordants) and are therefore called mordant dyes.
- Dyestuffs which are not soluble in water and need to undergo a chemical process to make them soluble in water and which become insoluble on the fibre after dyeing. These are vat dyestuffs.
- Dyestuffs which dissolve in water and can be applied as such. These are direct dyestuffs.

Dyestuff classes

Mordant dyes

A mordant dye is a colouring matter that can be bound to a textile material for which otherwise it has little or no affinity by the addition of a mordant, a chemical that combines with the dye and the fibre. Most mordant dyes yield

Kermes

Current terminology

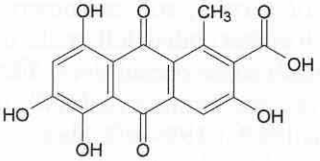
English: kermes grains
French: kermès
German: Scharlachkörner
Italian: chermes
Spanish: grana quérmes
Dutch: kermes

Obsolete terminology and synonyms

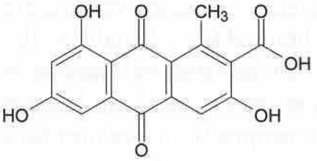
Alkermes, cramoisi, crimson, grain, grain d'écarlate, greyn, kermin, pastel, scarlatum (Latin), vermeil, vermillon, vermilium.

Composition: main colouring matters

Colour Index Natural Red 3.



Kermesic acid (Schweppe 1992: 220)



Flavokermesic acid (laccaic acid D) (Schweppe 1992: 221)

Ratio between the colouring matters: flavokermesic acid (0–25%)/kermesic acid (75–100%).

Chemical properties

The main colouring matter – kermesic acid – is slightly soluble in cold water and soluble in hot water, giving a yellowish-red solution. In concentrated sulphuric acid it gives a violet-red solution, turning blue on the addition of boric acid. Kermesic acid is soluble in ethyl ether as distinct from carminic acid (Dimroth 1910). It is soluble in methyl and ethyl alcohol but insoluble in benzene and chloroform. Apart from kermesic acid, a second dyestuff, flavokermesic acid, is present but in smaller and varying quantities (Thomson 1971; Wouters and Verhecken 1989a).

Source

The dyestuff is obtained from the dried bodies of the female of the insect *Kermes vermilio* Planchon (formerly *Coccus ilicis*) living on the kermes oak (*Quercus coccifera* L.). Resembling bluish berries, they are found adhering to the twigs of the tree and are covered with whitish powder (Donkin 1977; Schweppe 1992: 255–6).

History of use

Since antiquity, kermes has been used in Europe, the Near East and Asia and is mentioned in many early manuscripts and dye books. In France in 1669, Colbert promoted kermes reasoning that it was a 'French local product' (Colbert 1671). The dyestuff was recommended for dyeing the uniforms of officers and costumes of the nobility (Haak 1733) and it was used in Flanders in the Middle Ages for scarlet woollen cloth (Munro 1983). In the northern Netherlands, the first coccid dye to be used was cochineal – kermes does not seem to have been used. It was not introduced until the end of the 16th century following the uprising of the Netherlands against Spain and the consequent migration of many Flemish craftsmen to the northern Netherlands (Hofenk de Graaff and Roelofs 1972; Hofenk de Graaff 1996a).

Kermes is one of the oldest dyestuffs in the world. It is said that the word 'kermes' comes from the Orient, meaning 'worm'. In Sanskrit it seems like 'krmi' and in ancient Italian 'kerema'; the Arabs called it 'Dûd il Quîrmis'. From all these words it can be seen that kermes is of animal origin, nevertheless the Greeks and Romans thought that kermes was of vegetable origin in its appearance (Forbes 1964). The discovery of the real origin of kermes was a lengthy process. The naturalists of classical antiquity were so certain that kermes was part of the kermes oak that they saw the emergence of the insects from the eggs as a phenomenon of decomposition. In Arabian writings dating from the Middle Ages, however, correct conclusions can be found about the development of the insect. But the first systematic description of the insect was given by Quiqueran de Beaujou, Bishop of Senez, in 1551. A hundred years were still to elapse before the real origin of the insect was recorded in the dye books (Born 1936b).

Following the fall of Constantinople – the most important centre for dyeing with Tyrian purple – in 1453, kermes became the principal scarlet dyestuff. In 1464, Pope Paul II proclaimed that in future cardinals' robes had to be dyed with kermes and it replaced Tyrian purple completely: thus 'Cardinal-purple' is not Tyrian purple but kermes!

The discovery of scarlet dyeing with kermes can be attributed to the Phoenicians, who had practised purple dyeing from antiquity and possessed good knowledge of the techniques of dyeing – the earlier Greeks also considered the Phoenicians the most important dyers of kermes. The dyeing of textiles with kermes is also mentioned in the Old Testament – again the Phoenicians are named as kermes dyers. Pliny the Elder, in his *Naturalis Historia*, describes kermes as an important dyestuff derived from the Phoenicians. Kermes was an expensive dyestuff in antiquity and therefore it was only used to dye the clothes of the rich. However, it was relatively cheap in comparison to the almost prohibitively expensive Tyrian purple (Born 1936b). Kermes was so highly regarded in antiquity that it was among the tributes most in demand. Pliny named Africa, Asia Minor, Greece and Spain as the principal countries of origin. From Spain dyeing using kermes spread all over Europe, where due to migration and the establishment of the great Carolingian Empire, a new market had opened up for dyed goods. Kermes was also an important substance in the economics of the early European Middle Ages (Rodon y Font 1966; Edelstein 1966; Munro 1983; Cardon and du Chatenet 1990: 356–7).

After the discovery of cochineal in the 16th century, kermes, Polish cochineal and Armenian cochineal lost much of their importance in Europe: the colour produced from cochineal was brighter than the colour of kermes, and cochineal insects contained a larger amount of dyestuff. Although it was used in the southern Netherlands, kermes does not appear in the statutes for dyeing the expensive scarlet cloth in the northern Netherlands (Posthumus 1910–1922; de Nie 1937; Munro 1983), where madder was the most used red dyestuff. Cochineal did not come into use until the beginning of the 17th century (Hofenk de Graaff 1996a).