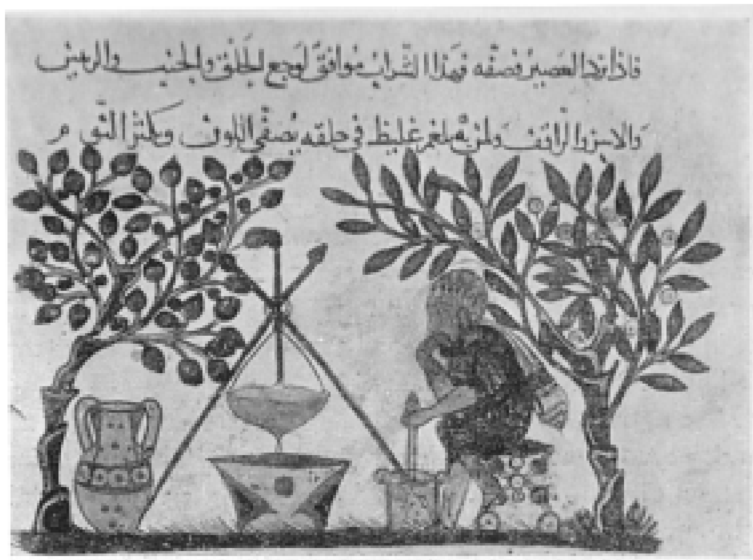

A MEDIÆVAL CHEMIST
FROM THE MATERIA MEDICA OF DIOSCORIDES, WRITTEN AND ILLUSTRATED BY ABDALLAH IBN AL-FADL, 1222 A.D.

MEDIÆVAL DYESTUFFS

BY CHARLES E. PELLEW

THE source and properties of the dyestuffs used in the Middle Ages were very much the same as those used by the ancient Greeks and Romans—with only two important exceptions. In the first place, from about the tenth century the use of Tyrian purple, which for many hundreds of years had been the most famous and most highly valued of all coloring matters, had practically disappeared from the world; and, in the second place, while the famous blue dye, indigo, was very rarely used, and was considered a great curiosity, the dyers had learned how to get exactly the same shades from the impure form of the same coloring matter known as woad.

No great and fundamental change in the ancient art of dyeing really took place until well on in the sixteenth century, when, with the development of the ocean trade route around the Cape of Good Hope, the importation of indigo and other dyestuffs, as well as textiles, from the Far East became general. At about the same time the splendid red dyestuff, cochineal, as well as fustic, dogwood, and other wood dyes, were brought to European dyers from Central and South America. After this, few very important developments were made until the wonderful discovery of the first aniline dyestuff by the young English chemist, Perkin, in 1856, completely revolutionized the whole art of dyeing, and in a few years rendered obsolete all the discoveries and improvements of the previous two thousand years.

A good general idea of the limitations of the old dyers can be obtained by studying some of the fifteenth and early sixteenth century tapestries, preserved in the Metropolitan Museum.

It will be noticed, first, that the range of colors employed is not at all large, and second, that there is great difference in their resistance to the fading action of light. For while, as a rule, the blues and the reds stand out bright and strong, almost as though they had been dyed last year, the yellows have either faded out, or have darkened to dull brownish shades. The greens, too, in almost every instance, have a very distinct blue cast, due to the fact that the old dyers produced their greens by first dyeing blue with woad, which is fast, and then topped their yarns to shade with yellow. In course of time the yellow has faded out and allowed the blue to come through.

This lack of fastness in the yellows continued long after the period of which we are talking, although fustic, made from *Morus tinctoria,* Osage orange, and other American dyewoods, was far better than any European or Eastern coloring matter. Indeed, really fast yellow dyes have not been known until within the last fifty years.

1. YELLOW. The only yellow dyes in regular use by the mediæval craftsmen had been passed on to them by the ancient Greeks and Romans.

(*a*) *Saffron.* This consists of the stigmas of the *Crocus sativus,* a rather large violet-flowered crocus which grows wild in Greece, Asia Minor, and other Mediterranean countries, and has long been cultivated in Austria, France, Spain, and formerly in England. Spanish saffron has generally been considered the best, and it can still be bought, although since the war at an extremely high price, in our New York drug stores, agreeing exactly with the detailed description given by Pliny, nearly nineteen hundred years ago, of its physical and chemical properties.

It is hardly ever used, nowadays, for dyeing textiles, but the cheap bright yellow cakes and cookies dear to school children on the Continent in normal times were all stained with this, and being quite harmless it is sometimes used to color medicines and beverages.

An infusion of saffron in hot water gives a bright golden-yellow solution, which readily imparts its color to textiles that are boiled in it. The shades produced, while pretty, are distinctly fugitive to light, and not fast to washing; but it has one great advantage over all other natural dyestuffs, in that it is a "direct cotton color"; *i.e.*, it dyes cotton directly, without the necessity of previous treatment with alum, sumach, or other chemicals known as mordants.

This same very important property is possessed by a great class of modern dyestuffs made from coal tar, and is the reason for the general introduction of "Diamond Dyes" for cotton, "Easy Dyes," and the like, for household use.

(*b*) *Persian Berry*. This is another ancient coloring matter, obtained from the buckthorn and other shrubs known to botanists as *Rhamnus*, occurring both wild and cultivated in southern Europe and Asia Minor. The berries, picked before they are ripe and dried, have a characteristic yellowish-green shrivelled appearance and were in common use as a dyestuff until displaced by coal tar dyes in the last half century.

This coloring matter was generally used to give bright yellow shades upon cloth previously treated or mordanted with alum. While much faster than saffron, those colors always darken and turn brown with prolonged exposure to light. When, however, copper salts are used instead of alum, the color produced is a very fast shade of olive green. It is doubtful, however, if this was known to the ancient dyers.

(*c*) *Iron Rust*. Perhaps the earliest of all dyeing processes is the production of orange and reddish brown shades by dipping cloth in iron springs, and then exposing it to the air. This was probably discovered at an early date wherever such springs exist. For instance, at Kobe, in Japan, they still make, as they have for hundreds of years, very pretty dyed towels and other fabrics in this way, bringing out interesting patterns, sometimes quite elaborate, either by stencilling with a resisting paste, or by tying knots with string or tape over the parts where they wish the final color to come out white.

Where these iron springs do not occur, the same colors exactly are produced by using iron salts made by dissolving iron in some acid solution.

At present, the simplest and cheapest salt to use is copperas or sulphate of iron, to be bought for a few cents a pound at drug or department stores. Besides this, there is needed, to fix the iron in the cloth, an alkaline solution, made, for instance, by dissolving a few spoonfuls of soda in some hot water. In colonial days our ancestors used for their homespuns an iron solution made by soaking old horseshoes, nails, etc., in home-made vinegar, and for alkali an infusion of wood ashes. The ancient Egyptians, as shown by analysis, seem to have used lime-water instead of ashes or soda.

When the cloth or yarn is dipped into the iron solution and then wrung out, little change in color is to be seen. On dipping into the alkali bath the iron salt is "set" as a greenish deposit all over and through the fibres; and when it is taken out, loosely wrung, and exposed to the air, the color gradually changes to a soft permanent shade of orange or orange brown. The color thus formed is absolutely fast to both light and washing. It is not suited for either silk or wool because it makes the fabrics harsh and rough, but it is still used for cotton and linen in various parts of the world. Up to quite recent times, the shades of "Nankin" and "buff" in summer calicoes and linens were colored in this way; and the brown sails of the fishermen off the Irish coast and in the Mediterranean are heavily laden with this iron rust or iron buff dye.

The dark shades can be readily recognized without any chemical tests, because they are very apt to rub, and the presence of the mineral matter makes the cloth hard to cut and to sew.

2. Black. At a very early date it was recognized that when cloth dyed orange or brown with this iron rust dye was treated with various vegetable extracts, the color could be easily changed to gray or even black. This is due to the presence, in these extracts, of the peculiar astringent substance known as tannin or tannic acid, which is found in the leaves (sumach, oak, maple, etc.), bark (chestnut, hemlock, etc.), unripe nuts (walnuts, butternuts, etc.), twigs (hazel) and other parts of many common plants. Tannin, for instance, is found in the skins of many grapes, and in red wine is abundant enough to cause it to turn black when mixed with a mineral water containing a little iron.

The Japanese, for many long years, have availed themselves of this property to make curious, and often extremely pretty leaf patterns upon their textiles dyed at the Kobe iron springs. They take the fresh leaves from trees growing on the grounds, such as the cutleaf maple, pine, gingko tree and others, place them between two pieces of muslin, and with wooden mallets beat the juice out of them. When the cloth thus prepared is dyed in the iron spring, the leaf figures appear dark gray upon the orange background. The ancients used to get blacks, just as dyers did up to the last century, by using strong tannin infusions from gall nuts, little excrescences on the twigs and leaves of oak trees in warm countries, the most valuable in those days, as now, coming from Asia Minor—"Aleppo gall nuts" they call them to this day.

More brilliant shades of black were later made by the action on iron rust, not of tannin but of logwood extracts made from the Central American dyewood. But this had the disadvantage, common to the tannin black and to the iron rust itself when dyed upon wool or silk, of making the fabric harsh and stiff and more or less brittle. This is why old rugs and tapestries that have had any rough usage always first show signs of wear in the blacks. The black patterns will often be found worn down to the warp while the other shades of wool are hardly damaged at all.

3. Reds. (*a*) *Animal Dyes. The Grain Dyes.* For many hundreds of years, in widely separated parts of the world, the principal red dyes were obtained by grinding up in hot water small granules about half the size of a pea, the exact nature of which for a long time was unknown. The Greeks and Romans freely used one of these kermes, and the ancient writers tell us how these "berries" came from oak trees growing along the shores of the Mediterranean, but omitted further details.

Travellers from the Far East again reported that in India they used similar grains or berries which gave fine red shades much stronger and richer than the kermes, and which came from the *lac-tree,* a peculiar kind of fig tree, also the source of the well-known gum, shellac. And a very few years after the discovery of America, the early adventurers were bringing back from Central America and Mexico great quantities of a brilliant red dyestuff, also in the form of berries, coming this time from a cactus plant. To this dyestuff, much the most beautiful of the three, was given the name of *cochineal.*

All three of these dyestuffs turned out to be formed in the same way. They were composed of the dried bodies of small insects which live on those different trees and which, at the proper seasons, are collected by the natives and dried. They are very small, it taking some 70,000 of the dried insects to make one pound of cochineal. But they can be bred in enormous quantities, one acre of cactus plants producing from 250 to 300 pounds.

These dyes were used on cotton, wool and silk, and also on leather, the shades depending on the chemicals employed for mordanting. A chance discovery by a Dutch chemist in the seventeenth century led to the general use of tin salts when cochineal was employed, this combination giving brilliant and comparatively fast shades of scarlet. The red coats of the British soldiers up to quite recently were dyed in this way. The shades of the kermes, which was the only one of the three generally used in the Middle Ages, can be recognized on the backs of old morocco-covered books, the real morocco leather consisting of goatskins dyed by the natives of northern Africa with this ancient dyestuff.

(*b*) *Vegetable Dyes. Madder.* The reds, however, that have come down to us from the Middle Ages without loss of color are due to the vegetable dyestuff, madder. This is the root of a perennial plant, the *Rubia tinctorum,* a native of Asia Minor, but cultivated for hundreds of years in Italy, France (Avignon, Alsace) and Holland. It was known as a dyestuff to the ancient Egyptians, as well as to the Greeks and Romans, and all of these knew how to fix it on cotton and wool with the aid of mordants, and recognized that when they used iron salts the shades were dull and brown, while alum gave brighter reddish shades.

The Egyptians also learned how to make paints, the so-called lakes, by boiling metallic solutions, alum, copperas and the like, with the dyestuff, and these same madder lakes have been used for fine permanent pigments up to very recent years.

It is worth noting that Sir Joshua Reynolds, who was an indefatigable experimenter, gained much of his fame as the great fashionable portrait painter of England by his wonderful flesh tints. And yet, even before his death his pictures were found to be fading, and now it is perfectly easy to go into any collection of old masters and pick out one after another of Sir Joshua's portraits by the washed out, pallid, unwholesome, anæmic complexions of his unfortunate subjects.

He used for his flesh tints a ground of ochre (natural iron rust) to give a tan color, and then brightened this by covering it with bright madder lake. Now nothing can be faster or more permanent than either of these two paints when used separately, and Frans Hals and other old masters whose flesh tints are perfectly fresh to this day, probably used exactly the same formula. But while these painters worked carefully and conscientiously, turning out only a few pictures a year and spending plenty of time on each, so that each layer of paint dried thoroughly before another was put on top of it, Sir Joshua, at the height of his success, was turning out a finished portrait (at a thousand or fifteen hundred guineas apiece) every three or four days, and slapped one moist color on top of another without regard for consequences.

Hence it happened that the iron salts of the ochre, not having been dried at all, slowly combining with the red madder lake, completely saddened and deadened its shade, and this simple chemical reaction has ruined almost every picture he painted.

4. BLUE. *Indigo and Woad.* For thousands of years the substance known to chemists as indigo, has been recognized as the most beautiful, most permanent, and most valuable blue dyestuff known to the world. It was known to the ancients who imported it from India at enormous expense (hence the name Indicum, the Indian substance), and used it chiefly as a paint, but occasionally as a true dyestuff, as is clearly shown in some of the specimens of ancient Egyptian textiles in the Metropolitan Museum. But its origin was not clearly known, although in one passage Pliny describes an Eastern shrub with peculiar dyeing properties, which must have been some variety of indigo-bearing plant.

This dyestuff is found in the juices of a large number of different plants, the most valuable of which are known by the name *Indigoferae,* or indigo-bearers. These have been cultivated from time immemorial in India, Java, Ceylon, China and other Far Eastern countries, and have furnished the supply of dyestuffs for the world.

But other plants, carrying the same dyestuff, are found in Central and South America, and beautiful specimens of indigo-dyed yarns and textiles, both cotton and wool, can be seen at the Museum of Natural History, in the collection taken from prehistoric tombs in Bolivia and Peru.

Another source of the same dye was brought to the attention of civilized Europe by Julius Cæsar, who, when describing his famous expedition to England, mentioned that the warriors there stained their bodies blue with the juice of a plant. Pliny, a half century later, told more about the plant, which he called *isatis*, later known as woad, and remarked that while the men colored themselves in this way to appear more ferocious in battle, the womenfolk dyed themselves almost as dark as Ethiopians, and used this color in the place of clothing!

This woad was later cultivated on a large scale in England and France. Its coloring matter is exactly the same as that obtained from the indigoferae of India or South America, only it is much harder to get it in a pure form. The dried woad from which the dye baths were made, rarely contained more than 25%, or at most 30% of the real dyestuff, whereas the indigo imported from the Far East would run from 60% to 90%, or even 95% pure.

Toward the middle of the sixteenth century the cultivation and trade in woad were seriously interfered with by the general introduction of indigo from Bengal and Java. Immediately a terrific outcry was made by the woad growers against the use of this abominable, foreign coloring matter. They said it was worthless as a dyestuff, that it would stand neither light nor washing, that it was poisonous, even that its use savored of witchcraft! And they had laws passed both in England and France prohibiting its use under most severe penalties.

And yet, as soon as the price was brought low enough to compete favorably with woad, the latter was completely driven from the market as a dyestuff, and only survived at all because in small quantities it was found to be of use in preparing the bath for dyeing indigo. An English chemist, some fifteen years ago, reported that he had found in one of the eastern counties, I think it was Cambridgeshire, a farm where woad was still being grown and prepared for market as it had been for hundreds of years. Since then, I believe the cultivation has disappeared completely. Indigo, which replaced it, has continued up to the present day to be one of the best known and most highly valued of all dyestuffs.

In the various indigo plants, the coloring matter is contained in the juice, which, somewhat like the juice of the milkweed, is white when fresh, but darkens and changes to a fast shade when exposed to the air. They used to prepare indigo by soaking and pressing the juice from the plants, and then these liquors, drawn off into large vats and clarified, were beaten with long paddles by natives sitting on the sides, until the blue dyestuff was formed. This being quite heavy was allowed to settle, the clear water drawn off and the blue mud drained on porous tiling and then dried in the sun.

Of course the purity of the product depended upon the care with which this was done; and, as indigo always commanded a high price, and was sold on its looks and on its label or "chop" rather than on analysis, the first requirement for a successful indigo-dyer was to have a trustworthy purchasing agent who could guess, accurately, the percentage of coloring matter in any given lot.

Some eight or nine years ago, after long and most elaborate experimenting which cost, it is believed, enormous sums of money, the problem of making indigo artificially from coal tar products was at last solved, and two or three great German dyestuff firms, soon followed by French, English and Swiss, began to place synthetic indigo, 100% pure, on the market. Then again the cry was raised that this new indigo did not compare in color or fastness with the old natural product. But, as before with the woad growers, the new product was so much purer and easier to handle than the other, that even without reducing the price much, it soon gained complete control of the market and, in a year or two, natural indigo became almost a curiosity.

The outbreak of the present war brought, to some extent, a revival of the indigo cultivation. But the allied nations determined to rid themselves of the German dyestuff monopoly, once for all. With government assistance, England, France, Italy and Japan have all started great factories where indigo itself, and some new derivatives of indigo, are among the most important products. In this country we have one factory in Michigan, soon it is hoped to be followed by others in the East, engaged in making very considerable quantities of this famous old dyestuff. And it is an easy matter—indeed, I did it myself a few weeks ago—to dye in a few minutes, with indigo made from American coal tar, shades identical in every particular with cloth from ancient Egyptian tombs.