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# DYES FROM ANTIQUITY TO SYNTHESIS

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Dyeing and painting activities have accompanied the development of human culture since the early beginnings. The art was developed by trial and error using natural dyes available from vegetable and animal sources, and different cultures, in many cases totally unrelated and unconnected among them, were able to build up similar techniques for extracting the active principles and applying them to textiles. Although the addition of new dyes from the New World significantly enlarged the palette of colours available and added new natural sources for the same, the available base materials lasted until the second half of the eighteenth century when synthetic dyes came into the market and essentially replaced the ones that had been used for thousands of years.

**Key words:** Animal dyes, Dye and dye stuff, Primitive method, Synthetic dye, Vegetable dyes

## INTRODUCTION

The use of dyeing and pigmenting materials was probably born out of the necessity of prehistoric man to adorn and beautify his objects of daily use, of graphically representing the nature around him, as well as serving religious purposes. The knowledge and use of colour began with the dawn of civilization and dyeing is as old as the textile industry itself. The earliest dyes were probably discovered by accident, and may have been noticed from the stains from available berries, fruits and nuts used as food and later from blossoms, leaves, stems and roots of shrubs, bark and twigs of trees, insects, and other living entities. The art of dyeing seems to have independently developed and been practiced among primitive people of almost every region in the world. Primitive man almost exclusively used dyestuff

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of vegetable or mineral origin. The primitive dyer went into the forest or the field and collected the plants that had been found to possess colouring properties. He then extracted the colouring matter by macerating or boiling the plants with water and employing the resulting solution as the dye bath.

Eventually, additional substances (mordants) were found to be needed in order to make the colour permanent and it was noticed that the use of different salts led to different colours and shades[a]. The shade produced was also affected by the composition of the water used in preparing the extracts, so that in certain cases a given shade became associated with particular areas and people. Trade in dyestuff began as soon as the sources of one area were recognized as superior to those used in another.[1]

Archeological findings, accounts in the Bible and in works of classical antiquity, attest to the fact that the preparation and use of dyestuff is definitely a very old human activity. Dyed textiles are mentioned in several places in the Bible, for example, in Exodus 26:1 it is written: "Moreover thou shalt make the tabernacle with ten curtains of fine twisted linen, and red and purple and scarlet." Unfortunately, as pointed out by Ziderman[2], it is not easy to identify the dyes that were used in biblical times; the biblical terms did not identify precisely the dye colours, let alone the dye substances. In addition, often translators used different terms to refer to a particular colour.

The Egyptians, the Chinese, the Greeks, the Roman, and many other cultures were well familiar with the art of dyeing. Examination of a number of ancient Egyptian mummies bandages has shown that dyeing was practiced in Egypt at about 2500 BC. The colour of all the dyed bandages was yellowish and had been produced with the yellow colouring matter of the safflower. According to Pliny[3] (the Elder, 23-79 AD): "In Egypt they also colour cloth by a remarkable process. They first thoroughly rub white fabrics and then smear them not with colours but with chemicals that absorb colour. When this has been done, the fabric shows no sign of the treatment, but after being plunged into a cauldron of boiling dye they are drawn out a moment later dyed." (Pliny was obviously talking about the use of mordants). Greek mythology includes Ariadne, the goddess of spinning and weaving, the daughter of Idon, the dyer of wool. Historic classics of the Chinese mention the dyeing of silk in various colours as back as 2600 BC.

Pliny's writings[3] provide valuable information regarding the art of dyeing in those days. He wrote very explicitly, "Moreover, we know that clothes are dyed with a wonderful dye from a plant, and, to say nothing of the fact that of the of the berries of

Galatia, Africa and Lusitania, the *coccum* (insect)is specially served to colour the military cloaks of our generals. There one stands on land to harvest dyes as we harvest crops". Pliny listed of materials employed and stated that certain mordants were applied to the fabric prior to the dyeing proper. He also wrote that at the time when the Romans first visited England, some of the Britons wore a coarse cloth; that they practiced both the spinning and the weaving of flax and wool; and that they were acquainted with the art of dyeing woolen yarn and cloth. Woad was chiefly used for this purpose and dark blue was the favorite colour.[4] In two of his epigrams the Roman poet Martial (Marcus Valerus Martialis, c. 40 AD - c. 104 AD) makes sarcastic remarks about the use of a dye for colouring the hair: "My caustic remarks reddens the hair of the Germans: with my aid you may surpass your slave's tresses" and "if you desire Octogenarian to change the colour of your venerable hair, accept these Mattiac balls. But to what purpose, for you are bald?".[5]

The purple dye was used in Crete as early as 1600 BC; for dyeing wool Heriod (about 600 BC) recommended oak bark, Theophrastus[6] (c. 371-287 BC) oak galls, while Pliny wrote[3]: "The shell of the walnut is used for dyeing wool, and the nuts while just forming supply a red hair dye; this was discovered from their staining the hands when handled" (Purple dyes are explained in more detail below).

Mordants enabled a wide range of colours, especially when used with madder, and as said, there were no substantial differences between the dyeing techniques developed by the different cultures.

By the end of the seventeenth century dyers in Holland had already developed the techniques for block printing on cotton on a large scale, using various mordants, thus combining printing and dyeing as well as producing a wide variety of shades in many different patterns. The process was cheaper than having to weave the same patterns in the material and soon it spread through neighboring countries. This technological advance was accompanied by a large increase in the area devoted in Europe to the cultivation of dye plants, particularly *madder*; its excellent fastness and relatively low price made it the most important red textile red dye. It was used, among other things, to dye the red uniform jackets and trousers (made of cotton and wool) of the eighteenth and nineteenth century armies.[7]

Synthetic inorganic pigments such as *Egyptian blue*, *soot*, *antimony yellow* and *cobalt blue* had been made since antiquity, and in the eighteenth century people began to synthesize organic dyes as well, but not of the crucial aniline type. In 1704 Heinrich Diesbach, a colour maker, accidentally first produced *Berlin blue* (Prussian blue) by allowing ferric chloride to react with potassium hexacyanoferrate II, and 1740 Ludwig Barth reacted natural indigo with concentrated sulfuric acid and produced the semi-synthetic dye *powder blue*. Introduction of two sulfo acid groups made the insoluble indigo water-soluble, which was easier to use. Since Berlin blue is a pigment, and powder blue semi-synthetic, yellow picric acid (2,4,6-trinitrophenol), first produced in 1771 by Peter Woulffe (1727-1803), may be regarded as the first truly synthetic dye. Picric acid was used to dye wool, silk and leather.[7]

In 1548, Gioanventura Ventura Rosetti, an officer of the Venetian Army (Director of the Arsenal in Venice) known as Plichto, published in Venice the first edition of the earliest known book devoted exclusively to professional dyeing.[8] This book included details of dye recipes and techniques employed in Venice, Genoa, Florence, and elsewhere in Italy, as well as the most complete record of the dyers craft at the time when the first South American dyewood was becoming available in Europe.

Between 1740 and 1750 Jean Hellot (1685-1766) published two books about dyeing.[9,10] The first one[9] contained the first theory ever published on the fixation of dyes on textiles; although it was entitled "Théorie Chimique de la Teinture Etoffes" (Chemical theory of textile dyeing), the explanation of the phenomenon was mechanical rather than chemical. According to Hellot:

> "Toute la mécanique invisible de la teinture consiste à dilater les pores du corps à teindre à y disposer des particules d'une matière étrangère, et à les y retenir par un espace d'enduit que ni l'eau ni la pluie ni les rayons de soleil ne puissant altérer; à choisir les particules colorantes d'une telle tenuite qu'elles puissent être retenues, suffisamment enchâssées dans les pores du sujet, ouverts par le chaleur de l'eau bouillante, puis resserrées par le froid, et de plus enduits de l'espèce de mastic que laissent dans ces mémes pores les sels choisis pour les préparer...pour que l''atome colorant y soit retenu à peu près comme un diamant dans le chaton d'une bague"
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> "Tr. All the invisible mechanics of dyeing consists in dilating the pores of the body to be dyed in order to integrate particles of a foreign substance and to retain them by means of a coating space so that neither water, rain, or the sun rays may alter them; to select colouring particles having a bond such that they can be retained properly enclosed in the pores of the matter, opened by the heat of boiling water and later closed by cold; and, moreover, coated with a kind of mastic decanted in these same pores by the salts selected for their preparation...., so that the colouring atom be retained more or less like a diamond is held in the bezel of a ring".

For Hellot, the difference between good and bad dyes laid on the fact that good dyes consisted of fine particles that could penetrate the fibers and remain there, while bad ones were simply too large. His books were a summary of the knowledge of wool dyeing; they were complemented by Pierre-Joseph Macquer's (1718-1784) book on silk dyeing[11] and by Le Pileur d'Apligny's[12-14] books on dyeing cotton (1770, 1776). Eugene Chevreul (1786-1891) published his first papers[15,16] about dyestuffs in 1808 and later, after becoming director of the National Gobelin Tapestry manufacture in Paris he devoted himself to a large-scale systematization of dyes. His discoveries, together with the enormous progress of the dye industry, revolutionized the art. Chevreul developed a set of very accurate standards to distinguish between different shades and colours. By mixing different colours in a systematic manner he was able to put together 14,400 shades, which he arranged in colour wheels. They were designed to make it easier for dyers to provide more nuances of colour.[7]

Before the discovery of the New World and its rich potential of dyes, European dyeing technology was based on three primary colours: Blue was obtained from *indigo*, either from woad or the indigo plant; reds were obtained from the *kermes insect*, from the root of the *madder plant*, and from the so-called *brasil wood* imported from the Far East; and yellows were extracted from weld, Persian berries, saffron, and dyers broom. These colours were combined to provide greens, browns, violets, and other compound hues, which could be varied somewhat using mordants. The dyeing methods were still the same ones used in ancient Egypt, the Middle East, and India.

*Madder* was the basis of Turkey red dyeing having been introduced to Europe with the help of Greek technicians in the eighteenth century. The finest and brightest reds, both in the antiquity and in the Middle Ages, were from certain species of *coccus* (hemipterus insects parasitic on various plants) mordanted with alum. The insects were known by several names. In the old times they were called *cocci*; to the Arabs they were known as *kermes*, the source of the English words *crimson* and *carmine*.

Great difficulty was experienced in dyeing a fast green. William Petty[17] (1623-1687) noted that no simple green dye had in his time come into general use, and this situation would remain unchanged for another one hundred years. The best dye was sap green obtained particularly by country people from the unripe buckhorn (*Rhamnus catharticus*) berries crushed in water and the infusion evaporated to the consistency of honey. Otherwise, textiles were first dyed blue and then yellow, or vice versa.[18] The technique and dye depended on the nature of the fabric (wool, cotton, or silk).

In the beginning black was dyed in Europe by two methods. The first one employed logwood or a similar dyewood capable of yielding a black colour on mordanted wool. The resulting black was not very fast, especially to light and exposure. In the second case, the black colour was achieved by forming a heavy deposit of iron tannate in the fiber. The procedure involved spreading a water suspension of iron filings (or copperas) and oak bark over the cloth to be dyed, which was then rolled up and allowed to remain for about a month. The iron permeated the cloth, which was then dyed black by steeping in a suspension of galls or sawdust. A large amount of copperas was used for this purpose.[18]

A particularly costly pigment, used in the old time chiefly by the ladies of the Egyptian court as an eye shadow, was powdered *lapis lazuli*, a natural ultramarine blue. The Egyptians had also produced the cheaper blue pigment *Egyptian blue* (calcium copper silicate) by calcining a mixture of silica sand, chalk, and a copper ore. This was the first synthetic inorganic pigment that like *azurite* (basic copper carbonate) and *cobalt blue* (cobalt aluminate), were also later produced synthetically and used as an artist's pigments. Interestingly enough, the knowledge of the production of cobalt blue was forgotten for over 3000 years, until Louis Jacques Thenard (1777-1857) rediscovered in 1804.[19] Afterwards, cobalt blue became known as *Thenard's blue* .[7]

Other inorganic compounds used in painting were red lead oxide, red ochre, cinnabar red (red mercuric sulphide), yellow ochre (hydrated iron oxide), and orpiment (natural arsenic sulphide), a brighter yellow tone than ochre. Malachite, a material found in nature along with azurite, was used for a greener pigment. Soot and manganese oxide were used as black pigments.[7]

In India the situation was different because cotton had always been the main fiber, in contrast to linen and wool in the Mediterranean cultures. *Curcuma* must have been the main yellow dye because it is the only natural dye that substantively (does not need a mordant) colours cotton. Indian dyers also used *safflower yellow* (the yellow dye from native beriberi varieties), *bastard hemp*, and various other native plants that imparted colour. *Henna* was used for colouring clothes orange, while red was obtained from *madder* and lac dye from insects. Indian yellow, which was produced until 1908, was obtained in Monghyr (Bihar) from the urine of cows that had been fed exclusively on the leaves of a particular type of mango, or from the same urine fermented in the presence of these leaves. The colouring material was precipitated by heating the urine, filtering the suspension, and working the resulting paste into balls. Certain constituents of these leaves were transformed in the cows' bodies and excreted with the urine. Indian yellow (*jaune indien, piuri, purrey*) was then precipitated out of the urine using magnesium salts. Today we know that the principal component is the magnesium salt of euxanthic acid, which in the presence of a mineral acid decomposes into glucuronic acid and euxanthone (1,7-dihydroxyxanthone).[7]

Chinese and Japanese used mainly locally available vegetable dyes. *Gardenia jasminoides* (Ellis) was particularly important in dyeing silks yellow, as was East Indian madder for dyeing red. Red sandalwood was also used. For dyeing black, they had plants containing tannins, from which black could be obtained by iron mordanting. Soot of excellent quality, particularly for the manufacture of Indian ink, was obtained burning camphor oil in lamps.[7]

In spite of all the progress, the basic techniques and colours available to the art of dyeing would remain essentially unchanged from the early beginnings until the second half of the nineteenth century. It took the industrial revolution and the progress in chemistry to improve the dyeing techniques and create an infinite variety of colours, unheard of before. The breakthrough came when William Henry Perkin (1818-1907) discovered the synthesis of *mauveine*. Within a few years the reign of natural dyes would came to an end and a new epoch would dawn in dyestuffs science – that of the truly synthetic dyes.

In what follows we will describe the different dyes that were used, their preparation and properties, using the arbitrary classification of vegetable and animal dyes.

## VEGETABLE DYES

Some of the dyes originating from plants and trees are produced directly by their physiological activities while others are obtained by their artificial transformation. Normally vegetable dyes are weak acids present in a dissolved state or granular deposits. Those present on the external surfaces of the plant are already coloured; those present in internal parts, not exposed to light, may exist as chromogens, they are not colouring materials but are closely related to the substances that they are. Light, air, ozone, and most oxidizing agents such as chlorine usually decompose vegetable dyes. Substances such as sulphur dioxide change them reversibly into colourless materials. Strong acids change the colour of most vegetable dyes from blue into red and from red into yellow. Alkalis have a similar effect, changing reds to blue, blues to green, and yellows to red or reddish-brown. Neutralization of the acid or base usually returns the original colour.

*Indigo*, long regarded as the most important of all dyestuffs, has a longer history than any other dyestuff. It has been known to the people of Egypt and Asia both as a dye and as a cosmetic for over 4000 years, as proven by some very ancient records, written in Sanskrit, describing various methods of preparation. The celebrated funerary wardrobe found in Tutankhamen's tomb includes a state robe, which is predominantly blue. According to Pliny[3], indigo was a "slime that adhere to the scum upon reeds. When it is sifted out it is black but on dilution it yields a marvelous mixture of purple and red. There is another kind of it that floats on the surface of the pans in the purple dye shops, and this is the scum of purple. People who adulterate it stain pigeons droppings with genuine indigo…" Pliny[3] also tells us that although as a pigment indigo looks black, when it is dissolved it gives a wonderful purple blue colour: "To the eye it is black, but when diluted it gives a marvelous mixture of purple and sky blue."

*Indigo* is a vegetable blue dye of great natural fastness to both light and water. It derives its name from the Greek *indicom*, later Latinized to *indicum*, a word originally used to define all imports from India and later specifically applied to the blue dye of India, replacing the anciently used Arabic word *al-nil*, which meant blue, and which is the ancestor of the modern word aniline.[1] The Greek and Romans seem to have use powdered indigo in paint and cosmetics, until the invention of oil paints. Until the discovery of America, all natural indigo used in Europe and the Near East for dyeing cloth and as pigment in paint and cosmetics came from India. Periplus in 80 AD, recorded that indigo had long been an article of export from India to Egypt. Venetians appear to have been the first medieval people to use indigo, for they very early realized the value of this dyestuff, both from an artistic and a commercial point of view.[1]

Owing to its stability to washing and light, indigo survived long after madder and weld, the other two dyes of antiquity, had been replaced by synthetic equivalents derived from coal tar.

Indigo occurs in certain shrubs (*indigofera*) and in the cabbage-related woad plant (*Isaris tinctora*) and is particularly good for dyeing cotton. It is contained essentially in the leaf of the indigo plant, *Indigofera tinctoria*, a member of the order leguminosae, widely distributed in Asia, Africa, the East Indies, the Philippines, and America. From the very beginning, natives in all countries where the indigo plant grew knew how to utilize its water-soaked leaves to obtain a brilliant blue dye. Garments found in Egyptian tombs, and others, unearthed from Peruvian Incan graves, as well as remnants of miscellaneous primitive cloth, all testify to wide but unconnected knowledge of the indigo plant.[1]

The stalks, pods and twigs of the indigo plant do not contain enough colour to warrant processing. The actual amount of pigment obtained from each leaf is small making indigo dye one of the most expensive used in medieval dyeing. Indigo is present in the leaves in the form of a colourless, water-insoluble glucoside, known as *indican*. In India, and neighboring countries, when the plant was ready for processing, it was cut, placed in vats and macerated in water for several hours to allow fermentation, indicated by the appearance of a yellow film. The liquid, which varied in shade from yellow-orange to olive green, was skimmed-off to beating bats, rendered alkaline, and then exposed to oxidation by air by striking the surface of the slime-like substance with bamboo sticks, for several days. This operation caused a gradual change in colour to dark green and then blue. The supernatant water was taken out and the indigo sludge transferred to a cauldron where it was heated by fire to prevent further fermentation. After cooling, the sludge was filtered and left to rest until it reached the consistency of a paste. The paste was then formed into bars, which, in turn, were cut into the indigo cakes of commerce.[1] As with cochineal (see below), there was much adulteration and the dyer had to rely on his experience and sharpness of observation in judging the quality of the indigo offered for sale.[18]

The people from India also fermented the leaves in water, and the subsequent action of air on the solution precipitated insoluble indigo, which was exported. The Romans do not appear to have known how to bring indigo into solution, and employed it only as a pigment. Already by the fifteenth century dyers in Europe were using honey and lime to reduce indigo to its white form and using the resulting solution for dyeing cloths.

An important detail is that indigo prepared in this manner from the indigo plant or from woad is always mixed with a certain amount of impurities, such as indigo red, indigo brown, and a glutinous substance. Synthetic indigotin is free from these contaminants.

Although this blue-black solid indigo was the subject of much chemical investigation its formula and structure remained unknown until 1865 when the chemist Adolf von Baeyer (1835-1917) entered the picture.[20] Today it is known that the leaves of the indigo plant contain large quantities of indoxyl-β-glucoside (indican), which splits during the hydrolysis to form indoxyl and a glucose sugar. Subsequently, the indoxyl molecules can rapidly undergo oxidation and couple to form crystalline indigotin (i.e., the common indigo blue) as well as indigo brown and isomeric indirubin. Particularly remarkable is the fact that although indigotin has a vegetable origin, its molecular structure is nearly identical to that of the shellfish-derived Tyrian purple, 6,6'-dibromoindigotin.[21]

Indigotin is insoluble in water and has to be converted into a soluble derivative before it can dye. This derivative is known as the leuco form of indigotin (from the Greek *leukos*, white). In chemical terms, indigo is a reduction product of indigotin, which was formerly obtained by adding the indigo to a vat of fermenting woad also containing bran, lime, and a little madder. The cloth to be dyed was dipped in the vat and then exposed to the air, where the leuco indigotin (indigo white) absorbed in the fibers was oxidized back to indigotin. Indigotin precipitated in the fibers, which were thus coloured blue. With synthetic indigotin the reduction to the leuco formed is now carried out much more simply and adequately using alkaline sodium dithionite or proprietary substances such as *Rongalite C* (sodium formaldehyde sulphoxylate). Leuco indigo is an article of the export trade on account of the ease which dyeing can be done with it.[18]

*Indigofera tinctoria* is a leguminous plant, but *woad* (*Isatis tinctoria*) belongs to the Cruciferae. Woad is classified in a group that derives its name from the Greek word *isos*, meaning equal, because it was once thought that this family of plants possessed the virtue of removing skin roughness by applying its leaves to the affected parts. In 1753 Carl Linnaeus (1707-1778) added the word *tinctoria* to describe its dyeing qualities.[1,18] Woad is both a biennial and perennial plant herbaceous in habit consisting of an erect stem varying from 0.6 to 1.5 meters high, with sessile stem leaves and an inflorescence in the form of a corymbose panicle of yellow flowers. The plant has a tap- root, which is woody, deeply seated, and rapidly exhausts suitable nutrient matter from soil.

To prepare the blue, the selected leaves were quickly crushed or ground to pulp and left to drain until they had attained the correct consistency. The resulting product was hand rolled into balls weighing about one-and-a-half pounds, which were then placed in trays and transported to the drying ranges, which consisted of roofed open-air structures beneath which a series of frames were arranged in tiers. The dried balls were then ground into a fine powder and the entire mass spread on the floor of a shed, where, by frequent sprinklings with water the powder was reduced to a paste, which was watered and turned over many times during several weeks. Fermentation was at first vigorous, the woad steaming and becoming quite hot and at the same time giving off an objectionable smell that only the trained labourers seem to endure. The final dark clay-like mass was then thoroughly dried and sifted into wooden casks ready for market.[1] The stench of the fermentation process was so revolting that Elizabeth I banned woad mills within a radius of five miles from any of her country residences. The liquid expressed from the leaves was similarly objectionable and there are numerous records of complaints that it fouled the streams into which it was allowed to run.[1,18]

The dyeing vat was prepared by first making an aqueous suspension of woad and then adding various mordants, for example, wood ashes or alum. The liquor was heated for about three hours, with or without the addition of other ferments (e.g., bran and madder). Blues of different depths were preparing by immersing the cloths for different times, as many times as necessary. Afterwards, the cloth was hanged in the open air so as to oxidize the dyestuff, and the pieces were then washed. The skimming of the woad vat (called woad flowers) was sold to painters for use as pigments.

Although woad gave a much smaller yield of indigo dye than indigo, and a lighter blue color, it was extensively cultivated in England and other European countries until imports from India made it uneconomical. The European growers did not renounce to this crop easily and political influence was used to retard the unavoidable as long as possible. In 1557 imported indigo was denounced in England as a "newly invented, harmful, balefully devouring, pernicious, deceitful, eating and corrosive dye." The king of France, Henri IV, also condemned it, ordering that those using it should be subject to the death penalty. In Nuremberg dyers were required to take an oath that they would avoid using it. Today these condemnations would look even more unusual because both plants contain the same active dyeing principle. Obviously this fact was not known in the sixteenth century; not only that, some people did not believe on the vegetable origin of the colour as attested by the fact that in 1705 England letters patent were granted to mine it.[1] The reason for this misconception may be the fact that indigo was imported from India in the form of rock-hard lumps.

*Madder* is another ancient dye that is obtained from the madder plant, *Rubia tinctorum*, which was cultivated for at least two thousand years over large areas of the near East (particularly in Persia, and Turkey) and later in Europe. In England the center of madder trade was located in Norwich. The name for madder, in the various languages, and its connotation, red, clearly indicates the colour content of the plant. It appears in Arabic as *al zan*, in Greek as *erythrodanon*, in Roman as *rubia*, and in German as *rote*.[1] It was probably first used in India, but the historical record shows that it was also well known to ancient Persians and Egyptians, and considerably later, to the Greeks and Romans. Ancient Hebrew law permitted the culture of madder solely for household consumption and strictly prohibited its growth for commercial purposes. About 450 BC, Herodotus tells us that in his time "*rubia* was used to brighten the cloaks of Libyan women." According to Pliny[3]: "There are also two kinds that are known only to the avaricious herd, as they are very profitable articles of trade. First comes madder, which is indispensable for dyeing woolens and leather (rubia tinguendis lanis et coriis necessaria); the most esteemed one is the Italian, and especially that grown in the neighborhood of Rome."

*Madder* is also mentioned in the Saxon Leechdom (a medical work illustrating monastic medicine) of ca. 1000.[1] In the middle Ages it was used in a large scale for the dyeing of wool, and an example of its importance is the command given by Charlemagne (724-814) that the women's workshops on his rural estates should be well furnished with wool, linen, woad, ladder, wool combs, teasels, soap, and other ancillaries for the weaving and dyeing of textiles. Leggett[1] mentions that the instructions, which preface the several prayers and offices in the missals, called the rubric, received this name because monks in the middle Ages wrote them in red ink.

*Madder* plants belong to the order *Rubiaceae*. The genus *Rubia* comprises about 40 species native to the Mediterranean region, the tropical areas of Africa and the warmer sections of Asia and the Americas. The species *Rubia tinctorium* is found in southern Europe and Asia minor, where it grows as a perennial evergreen shrub, one to ten meters high, with a rectangular prostrate stem with lanceolate leaves, surrounded by whorls of tiny yellow flowers that produce dark red, smooth, fleshy fruits that turn black when they are fully mature. The colour imparting substances are present in the cortex of the long, slender roots of the plant; they consist of hydroxyanthraquinones, some of which are free and others present as glucosides. Most of these glucosides hydrolyze during the dyeing process and yield the free dye and the sugars glucose and xylose. A notable exception to this is rubiadin, a C-glycoside that does not undergo hydrolysis.[7] The two most important hydroxyanthraquinones are alizarin and purpurin. Alizarin is produced from the hydrolysis of the glycoside rubierythric acid and purpurin from the decarboxylation of pseudopurpurin. The most valuable roots come from *Rubia tinctorum* (*foliis senis*) or dyers root, and Rubia peregrina (foliis quaternis), both of which grow in the Near East, the Caucasus and in Europe.[1]

With different mordants madder can yield very different colours, all fast to light and soap: red with aluminum, orange with tin, reddish brown with chromium, purple and black with iron.

Already by the year 1500 detailed instructions for cultivating *madder* (*Rubia tinctoria*) had been published in Holland, and for the next 300 years the Dutch retained their position as the most advanced growers in the world, meeting little competition until the Revolution in France; then the French government sponsored its cultivation in Alsace and Provence and the Dutch quasi-monopoly was broken.[1]

Discovery of the chemical constitution of *alizarin* by Karl Graebe (1841-1927) and Karl Lieberman (1842-1914) in 1868-1869 signaled the beginning of the end of the madder industry. Synthetic *alizarin* came into the market a few years later and the trade in the natural product expired after a very short interval. Today madder is cultivated, in rather limited quantities in few countries, solely to supply a demand of artists for natural colours, and for some physicians who believe it has some especial medical virtues.[1]

Until the advent of synthetic dyes in the second half of the nineteenth century yellow colouring matters also were very limited in number and not of the same tincture value as indigo and madder. The principal varieties were saffron, safflower, and annatto. All three remained in use throughout the period and still find limited employment.

*Saffron*, the principal yellow dyestuff of the Greeks and Romans, was obtained from the pistils of the *Crocus sativus*, order of iridaceae, and native to Greece, Persia, and Asia Minor. It was formerly cultivated in England near Saffron Walden, Essex, and in Spain, where it was probably introduced by the Moors. Saffron is mentioned just once in the Bible (Song of Songs, 4:14) and the inference is to a fragrant plant. Saffron was a ordinary crop in England until towards the end of the eighteenth century, the growers being known as crokers .[1]

The name saffron is derived from the Arabic word of *za faran*, meaning yellow. In addition to being used as a dye it was also utilized as a spice and as component of medical prescriptions. The Romans also used it to perfume the air in baths. In the early days of Greece it was, at one time, the official colour. The Egyptians were well acquainted with saffron, and Homer frequently refers to it in his writings. It was long cultivated in Persia and from there it found its way into China because of nomad Mongols.[1]

Manufacture of the active material continuous to be very simple: The stigmas of the flowers are dried in sieves over charcoal stoves, about 150,000 of them being required to yield one kilogram of the dyestuff; this contains the colouring matter in the form of a glucoside.

Presently, saffron is used chiefly in cookery, medicine and perfumery; only small amounts of it are used for dyeing cotton.

*Safflower* is an isolated botanical species of the thistle, *Carthamus tinctorius*; a plant belonging to the Cynareae, order Compositae. The origin of the Latin name is probably derived from the old Hebrew or Semitic root *qrtm*, which in the verb form means to cut, nip, truncate, as in the process of collecting the flowers of the plant. The plant probably originated in Southern Asia and from almost prehistoric days it has been cultivated in China, India, Persia, and Egypt, where its first use was for food and medicine. It was introduced into the American continent after the discovery of the New World. Safflower provided a basic yellow stuff, similar to true saffron and was often used as a substitute for saffron. There are numerous references showing that for many centuries the Chinese used it to obtain rose, scarlet, purple, and violet shades on silk, and that the Egyptians used it to secure a brilliant scarlet on linen.[1]

*Safflower* is an annual or biennial herb, 60 to 90 cm in height, with bright reddish orange flowers. The dye is located in the floret heads; the inflorescences are picked when fully mature and dried in the sun to yield an orange coloured fibrous mass, resembling saffron. The dye contains a water-soluble yellow and a water-insoluble red component, the two yielding an orange hue. About two thirds of the yellow component can be easily removed by soaking the dry mass in water. The insoluble reddish residue can be used with various acids and alkali to give a variety of shades varying from yellow through orange and pink, but the colours, although bright and beautiful, are not very fast. The dye is a very weak dyeing agent, requiring from 0.25 to one kilogram of extract per kilogram of fabric to be dyed, to obtain shades of colour varying from pink to crimson. In spite of this disadvantage, safflower is still cultivated in India for purposes of dyeing. In the dyeing process (normally of cotton) the textile is immersed into the dye solution and then the dye precipitated into the fibers by means of an acidic solution, such as vinegar.[1]

*Annatto* is obtained from shrubs or small trees known as *Bixa orellana*, believed to be native to India or Brazil but now commonly found throughout the tropics. The colouring matter, known as *Orleans* or *bixin*, is obtained from the pulp of the fruit. The latter is first macerated in water and the solution filtered and evaporated to the consistency of a paste. In this form *annatto* is used as a colouring agent for such foodstuffs as butter, margarine, and cheese, but before the discovery of suitable synthetic dyes it was also employed as a direct or substantive dye for cotton. It is interesting to note that the chemical constitution of *bixin* is closely related to the yellow colouring matter, *crocetin*, of saffron.[18]

In 1517 Francisco Hernández de Córdoba (1475-1526) landed in Mexico at the site of the pre-Columbian town of Kimpech and in 1540 the Spaniards founded there a new town, the modern Campeche. In the forests around Kimpech they discovered that the wood of certain trees soaked in water gave a solution that could be used to dye fabrics dark blue, purple, or black. This wood was known as Campeche wood or campeachy wood, which was changed later to the more generally used name of logwood. Logwood trees, *Haematoxylon campeachianum*, belong to the Leguminae; they occur native in much of Central America and have long been cultivated in Cuba, Jamaica, and other parts of the Caribbean region. The use of the wood as a dye source was introduced into Spain in the middle of the sixteenth century.

The colouring matter of logwood, *haematein*, is obtained from the heartwood. When freshly cut, this wood contains haematoxylin, a colourless substance, which on exposure to the air is quickly oxidized to the dark purple haematein. Haematoxylin is in fact the leuco form of haematein. To extract the dye, the wood is first cut into small chips, which are heated in steam under pressure and then left in heaps to ferment slightly and allow transformation of haematoxylin into haematein. The mass is subsequently treated with hot water and the haematein is obtained by evaporation of the solution.

In dyeing with logwood, various shades can be produced by the use of different mordants, but the most valuable is black, which is obtained with a mordant of iron and tannin. Nowadays logwood has been almost completely replaced by synthetic black dyes, nevertheless, it is still unrivaled for producing beautiful black shades on silk and is commonly used for that purpose. It is also used as a stain for biological work, particularly in histology, and as an indicator.

*Brasil* wood comes from the leguminous tree *Caesalpinia braziliensis*. It contains a leuco compound, *brazilin*, very similar to haematoxylin in constitution. Exposure to air causes the oxidation of brazilin to the corresponding colouring matter, *brazilein*. Brasil trees grow in both the Old World and the New and were therefore well known to the Europeans.

*Brazilein* is still used to some extent, but mainly in mixed with other dyes to produce variations of shade.

### Animal dyes

Animals possess various colouring and pigmenting materials that serve to dye the skin and different appendices of the body, or play an important physiological role. Several animals have the faculty of secreting coloured materials for defensive purposes. Some of these substances are soluble in water, most of them are soluble in alkalis, and a few are soluble in alcohol, ether or chloroform. Most of these substances are neutral and destroyed by chlorine.

Purple occupies a special place among dyes. Until the advent of aniline dyes, after 1856, there were three ways to obtain to purple dyes: (1) from shellfish, (2) from mixtures of blues and reds; the cheapest route to purple was to blue the fiber with an extract of *Indigofera* and then redden it with either an extract from madder or from the cochineal beetle. Shades were dull and the red tint tended to fade and, (3) from lichens, a method intermediate in exclusivity and cost.

***(a) Shellfsh***

Archaeological evidence indicates that shellfish were first used as a source of purple dye in Crete. The manufacture of purple textiles became one of the pillars of Phoenician economy for over 2000 years, with production sites on shores throughout the Mediterranean province wherever the seashells required were found to breed. Shellfish purple became known as Tyrian purple because the best quality came from Tyre; it was the most highly prized and expensive dyestuff of ancient times. It is the only dye described at great length by Pliny[3] and other ancient writers, who relate that the Phoenicians intensively searched for purpura shellfish on every coast and when found in quantities, as at Tarentum, promptly established trading stations and subsidiary factories.[1]

According to Ziderman[2] the collapse of the industry in the Levant was brought about by Byzantine Imperial exploitation and then by the Islam conquerors in 638 who destroyed the dyeing installations. A restricted center for purple silks continued sporadically in Constantinople, and may even have survived until the city fell to the Turks in 1453.

The technique of purple dyeing was one of the most closely guarded secrets of all time and thus poorly recorded in literature, As the centuries passed, not only were the dyeing processes themselves lost but also the identity of the species of snails that were used.[2] According to Pliny[3] the method or preparing the dye was very complicated, varying with each of the four or five different shellfish harvested for that purpose: "In Murex there is a white vein of very scanty fluid from which that precious dye, suffused with a dark rose colour, is drained, but the rest of the body produces nothing. People strive to catch this fish alive, because it discharges this juice with is life." Pliny pointed out that shellfish supplying purple dyes and scarlet were of two kinds, "the whelk is a smaller shell resembling the one that gives out the sound of a trumpet...the other is called the purple, with a channeled beak...It is most profitable for them to be taken after the rising of the dog star, or before spring time..." Pliny went on to describe in detail the procedure for dyeing wool according to the variety of the shellfish.

The amount of dye extracted from the mollusks was extremely small; for example, in the case of the larger mollusk, *Murex brandaris* or *Turk's blood*, only one drop of glandular mucus could be extracted from a gland located next to the respiratory cavity. Freshly extracted mucus is white but upon exposure to air and light it first turns yellow-green and then attains the permanent colour of either violet or reddish purple. The smaller shellfish, *Murex trunculus*, found along the Phoenician coast near Tyre and Sidon, were first crushed and the crushed mass was salted for three days, following which the batch was boiled for ten days, or until the dye showed the anticipated scarlet hue.[1] The secretion of the shellfish was boiled and the cloth dyed in the liquor. The shade varied according to the proportions of the various species used. The final product could be topped with archil or kermes.

For a long time, Tyrian purple was considered a status symbol. According to Pliny[3]: "The official rods and axes clear it a path, and it also marks the honorable estate of boyhood; it distinguishes the senate from knighthood, it is called in to secure the favor of the gods; and it adds radiance to every garment, while in a triumphal robe it is blended with gold." The high price led to purple clothing being the preserve of the upper echelons of society, particularly during the period of the Roman Empire. It was then known as imperial or royal purple due to its association with the emperor, although it was usually available to anyone who could afford it. In Rome, laws governed precisely which officials; knights and senators were permitted to wear robes adorned with purple stripes. The width of the stripes (*clavus augustus* or *latus*) was, of course, very important, the broader the stripe the greater the importance of the wearer. The word *purpura* was sometimes used as synonym of consulate. Later on, in the time of the Caesars (i.e., Caesar and Augustus), it was decreed that only the Caesar himself was entitled to wear a robe that was all purple, a privilege that was later transferred to the princes of the Church, and that survives today in cardinals' purple. Because of the high price of purple, the Egyptian dyers made a substitute with a mixture of the cheaper dyes indigo and madder. They called this mixture *Egyptian purple*.[7]

The religious and sacred character played by purple permits understanding the role it played in certain Greek legends and in ordinary life as a protecting amulet (apotropion): Perseus (the slayer of the Gorgon Medusa) thrown to the water inside a chest together with his mother Danaë, is covered with a purple cloth, which permits Zeus to recognize and save him. When Teseus went under water to respond to the challenge of Minos and prove his divine origin, he did so covered with a purple mantle provided by Anfitrites to attest his noble lineage, and was thus made invulnerable.

Today we know that several species of whelk-like mollusks, such as *Murex brandaris* and *Murex trunculus*, secrete a few drops of a creamy liquid, which in contact with air and light changes through various shades to dark purple. Like indigo, this compound can be reduced to a soluble leuco (colourless) form that is easily absorbed by the yarn. On exposure to air, this species is reoxidized to the insoluble coloured form, which remains locked into the fiber or fabric. The colouring matter is 6,6'-dibromoindigo. According to Ziderman[2], the naturally occurring precursors of the purple dyes found in the hypochondrial glands of seashells are colourless, water-soluble derivatives of the sulphate ester of indoxyl. The molluscan prochromogens characteristically contain organic bromine, which has been selectively concentrated from seawater against a 30-fold excess of chlorine. Dye formation is an artifact initiated by the autolytic or acidic hydrolysis of the sulphate ester linkage in the prochromogens. Oxidative coupling forms green diindoxyl intermediates, such as triverdin; these may liberate their sulphur constituents as odorous mercaptans, by the action of sunlight or heating to form the dyestuffs.

### *(b) Lichens*

*Lichens*, as well as larger plants, were also utilized for dyeing purposes. One of the oldest references to the use of lichens appears in the Bible: "Fine linen and broidered work from Egypt was that which thou spreadest forth to by sail; blue and purple from the Isles of Elishah was that which covered thee" (*Ezekiel* 27:7). According to Ziderman[2], although the Isles of Elishah have not been unambiguously identified it is believed that they lay either in the eastern Mediterranean or the Aegean Sea, areas in which the lichen *Roccella tinctoria* abounds. In the remote past, peasants of the Near East and Mediterranean area used *orseille*, or *archil*, for simple colouring purposes, when a purple shade was desired. Both Theophrastus and Dioscorides describe how this lichen grew on the rocks of various Mediterranean islands, particularly Crete and Candia.[1]

Lichens are the result of a symbiotic relationship between algae and fungi; they usually have a green, gray, or yellow tint and are often found growing in rocks. The fungus provides the algae with a measure of protection and receives nutrients in return; algae contain chlorophyll and can photosynthesize food from $CO_2$ and water. The main lichen species that have tinctorial potential are: (a) *Roccella tinctoria* (Cape Verde Islands, eastern Mediterranean generally), (b) *Roccella fuciformis* (Sri Lanka, Mozambique), (c) *Ochrolechia tartarea* (Scotland), (d) *Lasallia pustulata* (temperate Europe), and (e) *Roccella montagnei* (Mozambique, Angola, Madagascar); in practice, *Rocella tinctoria* and *Rocella fuciformis* are almost exclusively used.

According to Brown et al.[22] lichen dyes were introduced to Western Europe around 1300 AD, the main source being *Roccella tinctoria* and termed *oricello*. As the industry spread, the name changed to *orchillo* and *orciglia* in Spain, *orchella* and *orseille* in France, and *orchal*, *orchil*, and *archil* in England. By the end of the nineteenth century *orchil* had come to represent any red or purple dye derived from *lichen*.

*Archil*, from species of *Rocella* and *Lecanora*, was imported to Florence from the Near East, and for a considerable time the European trade in it was a monopoly of the Italians; English, French, and German cloth merchants, and dyers were forced to buy it from them in the form of oricello dye paste, called *persis*. The powdered dried plant was mixed with stale urine and lime and used with alum for dyeing silk and wool in violet shades. The dye was substantive; it adhered to wool without a mordant. Another purple dye, *litmus*, was produced from *Roccella tinctoria*, *Rocella fuciformis*, or *Orchrolechia tinctoria*, by heating the lichen to 60-80°C in the presence of aqueous ammonia, sodium or potassium carbonate, and air for four to five days. The product was either dried and ground to a powder or filtered, mixed into a paste with $CaCO_3$ and $CaSO_4$, allowed to harden, fabricated into cubes, and dried.

***(c) Insects***

The finest and brightest reds, both in the antiquity and in the Middle Ages, were made from certain insects belonging to the species of *coccus* (hemipterus insects parasitic on various plants) mordanted with alum. These insects had several names. The ancients termed them *cocci*; to the Arabs were known as *kermes*, from where the words crimson and carmine originated. Medieval Latin writers described them as *vermiculi* (little worms), from where the words and expressions *vermillion*, *grana*, *grain* and dyed in the grain, are derived. To this group, the new discovered (cochineal) parasitic coccus (*Dactylopius*) from Mexico was added in the sixteenth century. A true and permanent scarlet, however, was not discovered until the early seventeenth century, when Cornelius Drebbel (1572-1634) introduced tin salts as a mordant. These sources of red became extremely more important after purple dyes disappeared from the market.[1]

Besides lac dyes of India, *kermes* was the oldest of all insect dyestuffs; it is an oriental shield louse that lives on the leaves and stems of low shrubby trees having prickly leaves; principally the holm oak, *Quercus ilex*, and the shrub oak, *Quercus coccifera*, which grows abundantly in Mediterranean countries, particularly Syria, Lebanon, and Israel. These trees provided for nearly 3000 years the scarlet dye widely used from ancient times until the middle Ages. The insect has been variously called *Coccus arborum* and *Coccus ilicis*, but since antiquity it has been known as *kermes*, an Armenian word meaning little worm. Hebrew and Arab writers frequently mentioned it; in the Bible it is called *tola'at shani*, or worm scarlet.[1] The dyestuff itself consists of the dried and pounded bodies of female scale insects, which are about the size of a small pea. It yields an anthraquinone red dye, soluble in water and in alcohol. The dyestuff found in the *kermes* insect is closely related to the carminic acid found in the Polish, Armenian or American cochineal insect.

The *kermes* berries are hand picked annually at the season when the insects themselves are dead but contain viable eggs; these are killed by treatment with a weak acid, such as vinegar, and then packed in kegs.

*Kermes* was the only dye of insect origin used by ancient and medieval dyers of Western Asia and, although expensive, it was less costly than purple.[1] The bright colour it imparted to fabrics was popular over a very long period, the center of trade in the Middle Ages being Venice. Cloth dyed with *écarlate de Venise* (Venetian scarlet), made from *kermes* and cream tartar with alum as mordant, was highly prized throughout Europe. At a later time *kermes* was used to dye the fez; this use was in itself the basis of a large industry. Trading in *kermes* started to decline when cochineal began to be imported from America and came to an end with the development of synthetic dyes.

*Cochineal* (a New World dye) is a natural, rich crimson dyestuff, obtained from an insect of the same name that feeds on the flattened stems of certain prickly pear cacti (platyopuntias, Opuntia), especially the species called *nopales*; it was used for the production of scarlet, crimson and other red tints, differing from kermes, chiefly in shape. Since the Mexican cochineal (*Dactylopius coccus*) is some ten times richer in dyestuff than kermes, its import into Europe led to replacing the latter in the Old World from the middle of the sixteenth century onwards, for the dyeing of red tints on silk and wool fabrics.[1]

*Cochineal* is the name given to the dried gray to brown, about 0.5 cm sized bodies of the female insect *Coccus cacti* (scale insect). They contain about 10% of a red dye that is an alkali protein compound of carminic acid. The pigmentation is a bitter, water-soluble astringent chemical called carminic acid, which is extremely effective in repelling potential predators; such as ants. Carmine is the aluminum calcium colour lake produced from carminic acid by precipitation with the appropriate salts. It is used in painting as a pigment and for a time it was used to colour lipsticks. Both carmine and carminic acid are still used nowadays as food colours; in some countries it is used to colour sausages, and it is also used to colour a world-famous bitters milk.[7]

There are two principal forms of *cochineal*, one called silver cochineal, having a grayish-red colour with the furrows of its body covered with a fuzz or white bloom; the other, called black cochineal, is dark reddish-brown and does not have a fuzz. *Cochineal* is harvested three times during the seven-month long season; the best crop is the first of the season when the females have not yet been fertilized. During collection the insects are carefully brushed from the cactus plants upon which they feed, into bags or wooden bowls. They are then killed either by being packed in baskets for immersion in boiling water, or by heated ovens, or even by long exposure to the hot sun. This latter method, as with kermes, is considered as producing a superior quality of dye. Under either of these drying methods, the insect bursts open and turns rust-red, indicating that the process is completed. The dried insects have the shape of irregular, fluted or concave, current-like grains of a reddish-brown or violet-brown colour. About 55,000 of these are required to weigh one kilogram and it has been estimated that, on an average, it requires about 150,000 dried insects to produce one kilogram of cochineal dye.[1]

The Spanish word for wood or shield louse is *cochinilla*, a diminutive of cochina or small female pig. The term was applied by the Spanish conquerors to the insect because of some capricious resemblance in shape. The conqueror Hernán Cortez (1485-1547) promptly imitated the Aztec system of tribute and very shortly afterwards the export of cochineal began.[1]

Wool was dyed with cochineal using the same procedure and mordant (aluminum) as that for dyeing with kermes scarlet (aluminum mordant), though the resulting shades differed. The use of cochineal received a great stimulus when it was discovered that pewter in aqua fortis (nitric acid) could be used as a mordant, turning the red dye into bright scarlet. The required tin solution was made by dissolving bars of pewter in aqua fortis; the dyeing kettles were eventually also made of pewter.

Cochineal can also be made to dye a purple colour with chromium mordant, crimson with aluminum, and gray or slate with iron. The cochineal colours are very fast to light, but somewhat susceptible to the action of alkalis.

Many attempts were made to breed cochineal outside Mexico; they failed in India where a somewhat similar insect, *Tachardia lacca*, had long been used as a source of the red pigment known as lac. Greater success attended the introduction of the insect into the Canary Islands, Guatemala, Nicaragua, and other Central American countries, the production in Guatemala finally outstripping that of Mexico itself. Later on the century, the Canary Islands became the chief producer of cochineal, exporting in 1869 not less than 2,717,000 kg.[18]

The price of *cochineal* varied considerably but the average was about 10s a pound, high enough to occasion a great deal of adulteration with vegetable refuse, inferior kermes, sand, white lead, and other materials.[18]

The decline of *cochineal* began in 1858 with the introduction of aniline red, but for the next twenty years the new dye merely depressed cochineal prices; the final blow came about 1880 when azo dyes came into the market. Only small quantities are now produced, mainly for colouring foodstuffs.[1]

*Lac dye* is a resinous incrustation produced on the twigs and young branches of various trees by the insect *Coccus* (*Tachardia*) *lacca*, native of Indochina, Siam and Southern India, and closely related to kermes of Asia and cochineal of America. The term *lac* is derived from the Sanskrit *laksha* and from the Hindu word *lakh*; it is the same as the numeral *lakh*, meaning a hundred thousands, and thus illustrating the countless thousands of insects that infest the trees. Lac dye produces scarlet and crimson shades, fast to both light and water, and was known in Asia many centuries before it was introduced in Europe.[1] Lac dye is considered to have reached the biblical lands only by the first century.[2]

The dye itself is derived from the gum-lac or viscous fluid formed in punctures made by this minute larval insect, which bores into the bark of young twigs and branches, and draws its food from the sap of the tree. The insect exudes the resinous secretion over its entire body, becomes enclosed in the exuding juice, and slowly forms a *cocoon*, which hardens into a resin. This substance attains its full size in March. Females constitute the vast majority of the insect population and in fact become trapped within the resin. The females, which are fertilized by the males after their liberation, develop into an organism consisting mainly of the ovary, a large crimson coloured sac. The red fluid in the ovary is the substance that forms the lac dye of commerce. The young lac, which grows on the head of the dead mother, temporarily uses this red liquid for food and eventually crawls out leaving the body of the mother in its resinous shell. This is the stick lac of commerce and for centuries has been gathered in the hilly banks of the Ganges River in India and elsewhere and marketed as a crude produce, which yields 10% red colouring matter. Stick lac is crushed, washed with hot water to free it from colouring substances, and the finished product is known as seed lac. Seed lac is melted, filtered through canvas, and then left to solidify into thin plates called *shellac*.[1]

Modern chemical analysis has shown that lac pigments are composed of a mixture of substituted polyhydroxyanthraquinones called laccaic acids A, B, C, etc., some of which are condensed at the C-2 position with amino acid (e.g., laccaic acid A,3).

Others scale insect reds were also used in antiquity in the Near East. Polish cochineal was obtained from *Margarodes polonicus* scales found on the roots of knotgrass in Eastern Europe; chemically it is a mixture of kermesic acid with its C-2 glucoside carminic acid. Armenian red was prepared from the species *Porphyrophora hameli*, a coccid found on the roots and lower stems of grasses around Mount Ararat. Chemically it has been characterized as carminic acid. Traded since remote antiquity, Armenian red was also called kermes; adding to the nomenclature confusion.[1]

## Miscellaneous Dyes

The *weld* or *woald* plant (*Reseda luteola*) is a member of the mignonette family, *Resedaceae*. The whole plant serves for dyeing purposes. It was anciently known as dyer's rocket, dyers broom, and dyers weed. As a source of yellow dye it has been used since prehistoric times; it was highly prized by the Romans who restricted yellow to bridal garments. However, Romans used weld not only for that purpose but also for the cotton garments of the six Vestal virgins who consecrated their lives to the service of Vesta.[1] In later times it was used in England, in conjunction with woad, to give the celebrated Lincoln green. It was replaced only when old fustic was brought to Europe from the New World in the sixteenth century.[18]

*Weld* is indigenous in much of Europe, west Asia, North Africa, and the Canary Islands, and was introduced into America. It is a biennial plant, 90 to 120 cm high. To manufacture the dye the stems and leaves were cut, dried in the air, and made up into bundles for sale. The yellow colouring matter, luteolin, a flavone derivative, was extracted by infusion in water.[1] Luteolin has been prepared synthetically, but the process is too expensive to be commercial.

Two kinds of wood using for dyeing yellow are known as fustic, from the Arabic word *fustuq* (meaning small tree) and ultimately from the Greek *pistake* (πιστακη), *pistachio*. The one that has been employed by far the longer of the two is paradoxically called "young" fustic; it is botanically quite unrelated to the other variety, "old" fustic.[18]

Young or Zante fustic, often called Venetian sumac, comes from the stem and larger branches of the smoke tree, *Rhus cotinus*, a shrub-size member of the cashew family, belonging to the Abnarcardiaceae, and mentioned by Pliny in his *Natural History*[3]. It is a native of Asia and Southern Europe. The wood is hard, compact, and of reddish-orange colour, thus providing the yellow shade, peculiar to medieval scarlet. Chips of the wood are steeped in water and the solution, which contains the colouring matter *fisetin*, is used with various mordants to produce on cotton and wool shades ranging from yellow through orange to dark green, depending on the mordant used: olive yellow or old gold shade with chromium, yellow with aluminum, brighter yellow with tin, and olive green with iron; in conjunction with logwood it gives black. Young fustic was shipped to cloth dyers either in the form of small size logs or sticks, which after rasping or grinding were used to make the dye, either in the form of chips or as a liquid.[1]

Old fustic, the *bois jaune* of French dyers, is the golden-yellow wood of a large tree of the mulberry family, *Chlorophora tinctoria*, which grows wild in the West Indies and tropical America. Its colouring matter, *morin*, is extracted in the same manner as *fisetin*, and the solution used for dyeing cotton and wool, principally mixed with logwood. Chemically both *fisetin* and *morin* are derivatives of flavone, a compound that occurs naturally as a white coating on the leaves and flower stalks of certain species of *Primula*.

The dyes obtained from this tree were principally used for woolen fabrics, to which it imparted shades of yellow, varying from old gold to lemon yellow. Today, old fustic is used as an extract in combination with logwood, for dyeing wool and cotton various shades of brown or olive.[1]

*Lakes*, although obtained from dyes, are pigments, which are prepared by precipitating soluble red lyes with alum. In the antiquity, the Middle Ages, and later a great variety of *lakes* were in use. Crimson lake was made by boiling pieces of fabric with grain, a substance closely allied to cochineal, and precipitating the colour with alum. Rose-coloured lakes were usually prepared by precipitation of the red extracts obtained from brasil and madder. The main disadvantage of lakes is being very fugitive (unstable), the most permanent being a madder lake.

## Concluding Remarks

Historical records show that that the people of antiquity were well familiar with a series of natural dyes as well as the techniques for their application on different materials. Although they did not have a theoretical explanation of the dyeing process, trial and error led them to develop a reasonable range of colours and their method of application to the different fibers available. The craft would have to wait until the middle of the nineteenth century to begin to understand the science of dyeing and to develop synthetic dyes that would replace the natural ones, cheapen the process, and tremendously enlarge the palette of colours available.

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a. Many of the natural dyes did not have a strong chemical affinity for the textile fibres and had to be fixed to them by previous application of substances known as mordants, which "bite" (Latin *mordere*) or hold them. The action is a chemical one; the resulting enlarged solid complex that is formed within the fibres, does not easily wash out of the textile and makes the resulting dyeing is relatively fast. Mordants are either acidic or basic; the commonest acidic mordant is tannic acid or tannin, while various metallic salts such as alum provide the basic mordants. Metal salts and tannins served as bridging agents between the fibers and the dye

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