# Dyes and Dyeing.

Graduating Thesis

of

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Certain chemical bodies possess the property of only transmitting or reflecting certain constituents of white light, while others are absorbed. In other words, such bodies have a particular color, more or less characteristic. These bodies occur amongst the so called chemical elements, and the color of the element may be totally different according to the form and state of aggregation under which it is observed. Certain elements always form colored compounds; with others, the coloration of the compounds may be regarded as an exception, and if not caused by combination with a color giving elements depends on the constitution of the compound.

The colored carbon compounds come under the latter classification. The number of organic compounds containing besides carbon, hydrogen, oxygen and nitrogen is very large and the greater number of them are colorless. On the other hand, some compounds of carbon with these elements possess color which surpasses that of any other element, both as regards intensity and character.

The colored carbon compounds often differ little, or not at all from the colorless ones in their percentage composition, and it is this fact

which renders it certain that it is the structure of the compounds which causes in one case color, in the other none.

In plant and animal life both colorless and colored compounds are formed and the latter have been employed since the earliest times, as dye materials. Natural dyestuffs have for many years been the subject of chemical investigation, but their study furnished little as to the general nature of colored carbon compounds; and it is only since dyestuffs have been prepared synthetically that we have gradually come to understand the constitution of the greater number of these substances.

The color of compounds depends on the presence of a certain group of atoms, which is termed a color giving group or chromophor. The introduction of a chromophor produces a more or less intensely colored body, which is, however, not a dyestuff. The dyestuffs are formed by the introduction of one or more radicals capable of imparting salt-forming properties which are either acid or basic. Such groups as $NO_2$, $N_2O_2$ are chromophors. Compounds containing only the chromophors are called chromogens, but they become dyestuffs on

the introduction of a salt forming group such as OH or $NH_2$.

A real dyestuff is a body which possesses, besides color, the property of communicating color to fibres, doing this by reason of a peculiar affinity between the coloring matter and fibre. The property of dyeing belongs principally to compounds possessing a more or less marked acid or basic character. It is probable that these properties depend on a partly acid, partly basic character of the fibre, which in the one case is developed by the color acid, and in the other by the color base.

But few of these coloring matters have the property of being fixed on the fibre. This is done by the use of substances called mordants. There are many substances used as mordants, such as alum, sodium silicate, chromic hydrate and acids. Most of the mordants are added to the solution of dye before the cloth is immersed in it. In some cases as in printing the mordant is placed on the cloth and the dye applied after.

Among the methods proposed for fixing basic aniline dyes, there is only one that

has found general acceptance. This is the formation upon the fibre, of insoluble tannin compounds. If the solution of any basic dye is mixed with a solution of tannin, a precipitation takes place, but it is neither complete, nor has the lake properly required by the dyer. To produce a good fast dye, the cloth must be saturated with a solution of tannin and then be dyed in the color solution. In calico printing another property of the tannin lake or compound with the mordant, is brought into play. These compounds are readily soluble in certain solvents, especially in acetic acid. The printer therefore mixes the color and tannin in their due proportions, adds acetic acid as a solvent, thickens with starch, adds sodium acetate to take up any acid liberated from the dye, and prints this mixture upon the cloth. On steaming, the acetic acid dissolves the tannin lake, enables it to penetrate into the fibre, and then escapes along with the water vapor, leaving the color lake in an insoluble condition upon the fibre. But this method does not work well, since there may be

readily an excess of tannin upon the fibre. On washing the pieces after the steaming process, a portion of the lake already fixed is dissolved under influence of this excess of tannin and is precipitated by the lime in the water upon the white and other colored portions of the cloth to the great damage of the design. Tannin, however was rendered perfect by using a metallic salt, the most eminent of which is the salts of antimony. The dyer introduces an antimony bath between the tannin and the color bath, and produces upon the fibre in the first place an antimonial tannin compound, which is carefully freed by washing from any excess of either ingredient before immersing the cloth in the color solution. The lake is not soluble enough in acetic acid to quickly penetrate into the fibre, so the goods is passed into a tartar emetic solution before washing. This causes the excess of tannin to be rendered insoluble. At the same time antimony is introduced into the colored lake adhering to the fibre and enables it after washing to resist soap

at the boiling point, and are thus cleared and brightened. This is especially important when the design includes alizarin and cerulene shades, for which raising with soap is indispensable. The formation of antimony-tannin lakes of the basic colors would rank among the most perfect methods of dyeing and printing if it were possible to render the brilliant shades produced capable of resisting light. Until this is done alizarin and cerulene though more difficult to fix, yet being perfectly fast, will be prefered to the more brilliant shades.

Dyestuffs are obtained both naturally and artificially. Until the middle of this century nearly all the coloring matters used for dyeing, were either such as existed ready formed in the vegetable or animal kingdom or were producible from natural products by very simple chemical processes. The majority of coloring matters used now as dyes are products of organic synthesis.

The natural dyestuffs may be divided into animal and vegetable. The chief of the animal dyes are cochineal and galls.

Cochineal consists of the dried female of an insect of this name. It lives on a certain species of cactus. The coloring principle of cochineal is glucoside carminic acid. This acid is prepared by precipitating an aqueous decochon of cochineal with lead acetate, and decomposing the lead lake with an amount of sulphuric acid, insufficient for the whole. This solution of carminic acid is evaporated to dryness at a low temperature, and the residue crystallized from alcohol. When obtained in this way, carminic acid forms a purple brown mass which gives a scarlet powder when subjected to friction. It is easily soluble in water and alcohol. It is a weak diabasic acid, forming violet salts. The sodium salts may be crystallized: the other salts are amorphous. On boiling with dilute acids, carminic acid is split up into carmine red and a sugar.

If an ammoniacal solution is allowed to stand, a nitrogenous compound is formed, possessing entirely different dyeing properties. This is prepared on a large scale for dyeing. It is used for modifying cochineal

scarlets, and has a bluer shade than other cochineal colors.

Cochineal is used for dyeing wool and silk. It is seldom used for dyeing cotton. The mordant used is generally stannous chloride. It is boiled with the cochineal, and oxalic or tartaric acid are usually added. Yellow shades are obtained by adding weld, flavine or fustic.

Among the vegetable dyes may be mentioned indigo, lichen-dyes, red dyes from logwood and brazilwood, and yellow vegetable dyes.

Indigo is the product of various leguminous plants. They are cultivated in India, China Java and other parts of the east. Indigo does not exist ready formed in plants, but is produced by decomposition of a glucoside called indican which may be extracted from them by cold alcohol. Fermentation takes place, the indican breaking up and yielding indigo. The liquid becomes green, and then blue. When fermentation is finished, the liquid is drawn off into a tank. This liquid contains the coloring matter in solution.

In contact with the air it is oxidized, forming indigo, which, being insoluble, is thrown down. In order to facilitate the precipitation of the indigo, the liquid is thoroughly stirred. Finally, the liquid is drawn off, the precipitated indigo pressed and dried, and then sent into the market. The indigo thus obtained varies greatly in quality, both as regards the strength of blue coloring matter it contains, and in its freedom from objectionable impurities.

Red dyes from woods: A number of red coloring matters are used in dyeing. The two most common are brazilwood and logwood.

It is not known who first introduced logwood, as a dyeing agent; but its nature, and the art of using it as such, seems to have been but little understood in the reign of Queen Elizabeth for we find her government issuing an enactment entirely forbidding its use. It is now imported in irregular blocks, having a weight of four hundred pounds. The coloring matter probably exists in form of a glucoside, for when trees are first

cut the wood is colorless. The logs are cut into chips which are moistened and allowed to ferment, whereby glucoside is converted into haemo-xylin and this is partly converted into haematein by the air. This is then treated with water and then concentrated to obtain logwood extract. If the concentration is carried on at a temperature exceeding 60°C. the haematein will be converted into a dark purple resinous matter, which injuriously affects the brilliancy of the color. Altho this is called red dyewood, the coloring matter of the logwood is itself not used in practice for producing red shades, but rather violet, blue and black. It does not dye cotton without a mordant and with it, wool acquires a drab tint. The employment of logwood in dyeing depends on the color lakes which it forms with metallic oxides. Logwood is chiefly used for dyeing black in conjunction with potassium bichromate. A solution of logwood is made by pouring boiling water on the wood and filtering. No more should be made at a time than is needed, for

it loses its coloring qualities by standing. The color passes from a rich wine to a yellow-brown and assumes a syrupy appearance. Colors dyed by it after this change takes place, are always wanting in brilliancy; besides it takes a greater quantity of stuff to produce the same depth of shade. This may be caused by a partial decomposition of the coloring matter or of the ingredients of the wood reacting upon the coloring matter. If a little water containing lime is added, it gives a richness of color so that the poorest woods if thus doctored, appear of the best quality. Such wood, however, never produces good light shades.

Alizarin or Madder Red: This is a product of anthracene $C_{14}H_{10}$, of coal tar from which it is now chiefly obtained and by reaction of oxidation. Before 1869 it was wholly obtained from the root of the madder plant. Natural and artificial alizarin are identical when each is perfectly purified. The natural alizarin comes from a glucoside of the plant, ruberythric acid. By boiling with dilute acids, also by a

madder dye.

Alizarin Blue: This is formed from alizarin orange by heating with sulphuric acid and glycerin. A bluish paste of about ten percent solid content. It is soluble in alkali with a greenish blue color. An excess of the alkali causing a precipitate. It is colored red brown by sulphuric or hydrochloric acid.

Alizarin Orange or Nitro-alizarin. In commerce it is in the form of a yellow paste. It dissolves in sodium carbonate solution with yellow-red; in Sodium hydroxid solution with red color; an excess of the caustic alkali precipitates the solution.

In turkey red dyeing, the alumina compound of alizarin is formed by passing the cloth saturated with an alum solution, through a solution of alizarin, the insoluble compound being formed directly on the fibre. Besides alizarin, madder roots contain an oxidized alizarin, which has been gradually formed from the alizarin by the action of the oxygen of the air. This is called purpurin. It is also produced as a side product in the manufacture of

artificial alkalies. Its alumina compounds are also soluble. It dyes wool and etc. It is a color resembling alizarin.

## The Artificial Dyestuffs.

The natural dyestuffs, with few exceptions contain only carbon, hydrogen and oxygen, while many classes of artificial coloring matters contain nitrogenous groups, often of a decidedly basic character.

The raw materials for the preparation of these bodies are at the present time almost exclusively products of dry distillation and the most important of these is coal tar, obtained as a bye-product in the manufacture of illuminating gas from coal. The discovery of the preparation of coloring matter from products of dry distillation, was first made in 1832 by Von Reichenbach, from wood tar.

In 1834 Prof. Runge found in coal tar, a body which readily forms with acid, crystalline salts and possesses the property of imparting to a solution of bleaching powder a beautiful purple color called "blue oil".

Somewhat later Fritzsche investigated

the products which are produced by distilling indigo with potash and found a large quantity of a basic oily compound which he called 'aniline', meaning blue. About the same time Juria found benzene could be converted by certain reactions into a basic compound to which he gave the name of 'benzadame'. Hoffman found that these were the same and afterward it was known as aniline.

It exists in coal tar in a very small quantity, but can be obtained from tar in any desired quantity. It is manufactured in very large quantities from benzene. It has often been reported that the fumes from these dye works are very injurious, but it has been found that these fumes only affect the intemperate workmen. Observation has shown that alcohol reduces the power of the constitution to bear the action of aniline. Applicants for work in these shops are rejected, if on medical examination they are found to have the appearance of drunkards, or if evidence is obtained that they are given to drinking.

The present requirements of the color industry, as raw materials, are benzene and its homologues (toluene and xylene), naphthalene and anthracene, obtained from coal tar. The coal tar of the gas works is first worked up in tar distilleries, and the above bodies obtained are in an impure state. Further purification is carried on in some color works; but this generally takes place in intermediate manufactories, where the crude products are purified and worked up into a higher stage, benzene and its homologues being made into anilines, toluidine and xylidine and naphthalene into naphthylamine.

The crude benzol is first submitted to a careful fractional distillation and benzene, toluene and xylene are separated in as pure a state as possible. The hydrocarbons boiling at a higher temperature find their principal application for solvent purposes, hence they are principally met with under the designation of solvent naphtha. One purpose for which it serves, is the purification of anthracene. Benzene, toluene and xylene are converted into aniline

toluidine, and xylidene by nitration and subsequent reduction. These bases are at present prepared by aniline works in a state of great purity: for instance the aniline employed in the manufacture of blue is required to be chemically pure.

There are a great many different shades and colors produced from aniline, but it will be possible here to mention but a few of the most common colors.

The first dyestuffs prepared and applied on an industrial scale was mauve or aniline purple, introduced by Perkin in 1856. He made it by mixing aniline sulphate with potassium chromate. A black precipitate is formed on standing, containing only a small percent of mauve, which may be extracted with alcohol.

Rosaniline or aniline red is also known by the name of magenta, fuchsine and rosine. Hofmann discovered in 1843 while studying the action of fuming nitric acid upon aniline, that a deep red color was produced. But it was in 1858 that the crimson coloring principle was pointed out to him. He found the action of carbon

tetra chloride on aniline formed a basic substance which when dissolved in alcohol produced a rich crimson color. This led to an industrial discovery 1859 where this was used in printing and dyeing. Soon chemisty found that the formation of color was due to oxidation of aniline and other processes of oxidation were used.

Rosaniline is the starting point of many other beautiful dyes. By heating it with methyl or ethyl iodine, one, two or three atoms of hydrogen are successively replaced by methyl or ethyl, and violet and purple colors are produced.

Aniline Green: This belongs to the rosaniline group. It is prepared by adding aldehyde to an acid solution of rosaniline and pouring the blue liquid thus obtained, into a boiling solution of sodium thiosulphate.

Aniline Black: The various aniline blacks in use are not strictly speaking dyes. They are in most cases produced during the process of color printing, or by some treatment of the printed goods, are not like the true aniline dyes, in a state fit for

immediate use by the dyer. The black is in many instances an intensely dark green.

In 1862, Lightfoot printed fabrics with a mixture containing potassium chlorate, an aniline salt and copper chloride. By the reaction of these salts in air, black is produced. The permanence of these dyes depends on the amount of coloring matter held in the fibre. In most cases the color holds bright longer in silk and wool, than in cotton.

The chief trouble with these dyes is the crocking or rubbing off, of the color. Malachite green and Victoria blue are especially defective in this. This is sometimes due to too much dye held in the goods, or in case of wool, it is frequently due to insufficient scouring of the wool. The fibre is covered with grease or other impurities and does not allow the dye to enter it.

## The Art of Dyeing and Calico Printing.

The discovery of dyeing is attributed to the Tyrians. In dyeing and dipping their own clothes the English were so little skilled, that their manufactures were usually sent to Holland to be dyed. The art of dyeing woolens

was brought from the Low Countries in 1608.

In dyeing cotton the substance to be employed must be in solution, so as to enter the fibre or pass through its pores, and be made insoluble or precipitated by chemical means. The unripe fibre cannot be dyed, for the fibre is broad and thin, the coloring matter cannot permeate the fibre, becoming fixed. If the cloth is immersed in strong caustic alkali, the fibre will contract in length and become almost circular and has a greater attraction for the coloring matter.

In the dyeing of cotton the mordant is in most cases first fixed on the cloth: but as it must not only be deposited on the surface of the cotton, but be also contained in the interior of the fibre, it is first applied in solution, and then rendered insoluble by chemical reaction.

The first process in the dyeing of wool is to remove all oil from it. This is done by washing in a warm bath not exceeding 50° C. containing a solution of soap and ammonia or soda, or soap only. After being thoroughly washed it is ready for dyeing.

Silk is prepared for dyeing by first

scouring it, or passing it through a hot soap solution, which removes all gummy matters. After washing it is bleached by gaseous sulphurous acid, then passed through a hot solution of tartar, and finally well washed with warm water. Silk and wool act so nearly alike in dyeing processes that they may be treated together.

Dyeing with Aniline Colors. The salts of rosaniline, as well as those of the different violets are mostly soluble in water, and the dyeing of them on wool is a very easy operation. The yarn is simply suspended in a hot and not too concentrated solution of the color, until the shade required is assumed. In dyeing wool the solution is usually hotter than for silk.

The phenol violets are almost insoluble in water, but readily soluble in alcohol. To dye with them an alcoholic solution, mixed with glycerine is added gradually to hot water, in which the wool is to be suspended. The addition of the glycerine increases the solubility of the color and also the alcohol without it would evaporate too quickly, leaving the color precipitated

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on the cloth unevenly.

Silk is best dyed in a soap bath, and the color brightened by immersing it in dilute sulphuric acid.

Alkali Blues are best fixed on silk and wool by adding to a hot solution of the color a little borax or soda.

## Calico Printing.

Calico is a kind of cloth made entirely of cotton, but the term calico printing has usually a broader meaning than simply printing calico. It is applied to the printing of any kind of tissue used for garments, whether from cotton, wool or silk.

A few passages occur in ancient writings which, though vague and general, make it certain that there existed in very remote times, say 2000 B.C., some method of coloring cloth with designs, representing figures of plants and animals, but it is only in Pliny that there is any distinct reference to the dyeing of mordanted cloth, as was seen by him practiced in Egypt. The only remains of ancient textile fabrics, which have been preserved to modern times are the wrapping of mummies. The dyes

used were without much doubt indigo and safflower. The printing on the cloth was probably applied with a pen or brush. Until the end of the last century this was used in France to fill in certain colors.

Printing was formerly done with blocks. These were made by carving the design into the wood. The hollow spaces are filled with felt. The felt is covered with the dye and the block then applied to the mordanted cloth.

The latest patent for printing is the Roller or Cylinder Printer. It is a very complete one and makes printing cheap. In the printing of wool the goods must be cleaned and well scoured. But it always has a yellow tinge, and in order to have the colors stand out they must be in contrast with a perfectly white ground. The wool must then be dyed white. This is done by passing it thru a warm solution of soap to which a little indigo carmine has been added. Thus the yellow and blue, being complimentary colors neutralize each other. The next process is alumming the wool in a tepid solution of alum-

The colors produced on wool by printing are all steam colors. This is not only for fixing the colors, but also to obtain pure, bright shades. Without steaming they are dull.