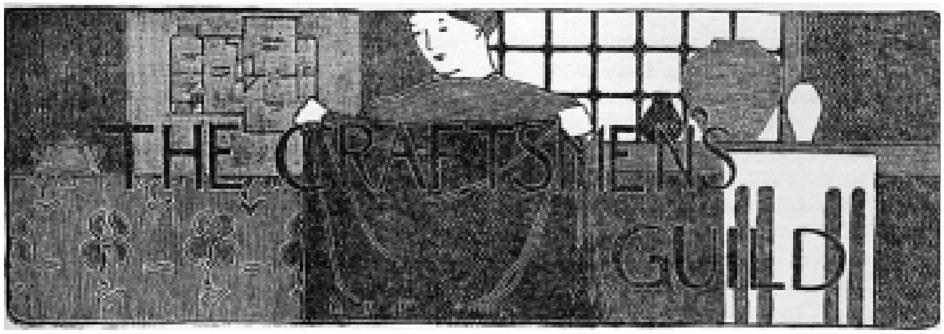

APPLICATION OF MODERN DYESTUFFS TO ARTS AND CRAFTS WORK: GENERAL INTRODUCTION: BY C. E. PELLEW: PROFESSOR OF CHEMISTRY, COLUMBIA UNIVERSITY

ONE day about ten years ago, soon after the completion of the new buildings of Columbia University, the chemical laboratories were thrown open for inspection to several thousand specially invited guests, as well as to the general public. We of the Chemical Department took our station in the most interesting part of our respective domains, and, for my part, I spent most of my time showing the visitors who drifted into the Industrial Chemistry laboratories the equipment and work of the new dyeing and calico printing room. About the middle of the afternoon a very intelligent looking woman came in and glanced around with an air of considerable interest, explaining at the same time that she was the instructor in dyeing and weaving at a small but widely advertised institution in one of the southern states.

Immensely to my surprise, in a minute or two, with an air of great scorn, she turned to me and remarked: "I see that you use here those horrid artificial dyestuffs." Being rather proud of my collection of four or five hundred dyestuffs from the great German dye factories, which I had been working over, night and day, for weeks, and had at last got fairly classified and arranged, I answered: "But, surely, madam, what dyestuffs would you expect me to have?" Whereupon, with a still more superior air, she replied: "I take great pains to teach my students nothing but the dear old natural dyestuffs known to and used by their ancestors. In fact, at our college we firmly believe Mr. John Ruskin's statement that 'there has been nothing discovered of any interest in the tinctorial art since the days of the ancient Greeks and Romans.' "

This, indeed, was a staggering blow. As soon as I recovered myself, I asked her if she used indigo. "Oh, yes, of course, but the natural indigo, and without any horrid chemicals to spoil it." "Well, what vat do you use to dye it with?" "We always use the *woad vat,* just as they used to in the good old days." "Good heavens," said I. "You have gone back, then, with a vengeance to the days of Boadicea and the old Romans." And I hinted, as delicately call it, a red or blue dye, according to the reaction of the bath, obtained from a moss which grows in hot, dry countries. Saffron, too, was used for yellow —and probably they knew of some simple vegetable browns.

But the dyestuff of all others on which they prided themselves was the "Tyrian purple," obtained with enormous difficulty and expense from the juices of a class of shellfish (gasteropod molluscs) found widely distributed, but in small numbers at any one place, in the ocean waters of tropical and, to a less extent, of temperate, localities.

This dyestuff, so valuable that to this day it stands as the symbol of wealth and luxury—"purple and fine linen"—has been carefully investigated of late years and found to produce rather dull, and, to our modern minds, not very interesting, shades running from bluish purple to dark crimson. Curiously enough, it has been discovered of late years that exactly this same "Tyrian purple" dyestuff, extracted from the same class of shellfish and applied to the fiber in very much the same manner as in ancient times, has been, from time immemorial, manufactured and used by the native Indians upon the coast of Nicaragua, without, however, any particularly beautiful results.

These colors, to be sure, are fast to light and to washing, and are so-called "developed" colors, dyeing cotton and linen as well as wool and silk without mordants. But in the first place they do not compare in shade and beauty to whole series of modern dyestuffs, and are in no respect superior as regards fastness to light and washing, while so little of the dyeing material could be obtained that probably one day's demand at the present time would completely exhaust the whole world's supply of these particular animals.

These and a few others of still less importance were the dyes so glowingly referred to by Mr. Ruskin and his followers.

Very considerable advance had been made in the art of dyeing, naturally enough, since the old Roman days, at the time when Perkin's discovery took place. Indigo, for instance, had been introduced, and was largely and intelligently used. So, also, was madder used in very large amounts, producing exceedingly fast and beautiful shades, varying from the brilliant scarlet of the Turkey red to browns, dark purples, and blacks of the chrome and iron mordants.

Logwood, and other wood dyes from the West Indies, Central and South America, were known and used for considerable ranges of colors; and logwood, by the way, of all the dyes known fifty years ago, is the only one which would be missed at all at the present day.

Cochineal and lac dyes, the latter probably occasionally used by the ancients, were in constant use. The red coats of the English soldiers, to this day, are dyed with cochineal on a tin mordant. But this is not because the color is as fast, or as beautiful, as that produced by many modern dyestuffs which will give the same shade and at much less cost—but because of some "perpetual contracts" with specifications made a hundred years ago or more, which are still adhered to.

The great problem with these old dyes, as probably some of my readers may have experienced, is, first, the difficulty of getting them pure and of uniform quality, and, second, the troublesome and complicated methods necessary to produce the required color on the fibers. In the '50's the dyeing industry of the whole world was in the hands of ignorant, opinionated, rule-of-thumb dyers, who worked by secret, highly treasured formulæ, passed down as precious heirlooms from father to son. The range of colors was comparatively limited, and to obtain fast and true shades required a great deal of skill and experience, far beyond the power of any amateur to obtain.

And to ignore the enormous facilities that modern chemistry has placed in the hands of every one interested in artistic productions is to deliberately close the door to opportunities never before offered to any age—however intelligent or highly civilized—or however endowed with the sense of or the desire for beauty.

Before, however, taking up the modern artificial, so-called "coal tar" or aniline dyestuffs of the last half century, it may be of interest to mention briefly two dyes, the iron or rust dye and manganese brown or bistre, both of which were known to our grandfathers, and one, at least, to our colonial ancestors, if not to the ancients. These dyes are still occasionally used, in special classes of commercial work, and are of some value for simple dyeing of vegetable textiles, cotton, linen, jute, etc., which may have to stand very heavy exposure.

The iron or rust dye was of great importance in the pioneer days, in the west and elsewhere, for dyeing "homespuns," rag carpets, and the like, in the absence of more elaborate dyeing agents, and also, on the sea coast, for staining sails and nets. It can best be applied by soaking the thoroughly wetted material in a bath made by dissolving in hot water some ferrous sulphate (copperas or green vitriol), with, if necessary, the addition of a few drops of acid (diluted sulphuric or acetic acid or even vinegar), to keep the bath reasonably free from sediment. After soaking for a few minutes the material is wrung out, by hand or through a wringer, and then immersed for a moment in a bath of some alkali, cooking or washing or even caustic soda, or, as in our ancestors' days, of wood ashes strained or settled fairly clear of dirt and charcoal.

This alkali bath need not be at all strong—a spoonful or so of soda to the gallon until exhausted—for it is only needed to decompose the small amount of iron salt retained by the material.

Directly the fabric has been wet through by the alkali it is taken out, wrung loosely, and shaken out and exposed to the air, when, in a few minutes, the color will change from a dull light green to some shade of rather dull but pleasant orange, or orange-yellow, varying in depth with the strength of iron salt in the bath.

As with other colors developed in the air, in this way, it is better to build up the deep shades by dipping repeatedly in one bath after another, rather than to use one very strong bath of coloring matter, in this case of copperas, and get the full shade directly.

After the color has set, the material should be rinsed in water to remove excess of alkali; and then allowed to dry. Later it should be thoroughly scoured in hot soap to remove any loose color and so avoid the danger of rubbing. The color remaining after this is absolutely permanent—not being affected in the least by special chemical treatment. It will stain to dark shades when treated with vegetable extracts containing tannin, such as used to be made from boiling hemlock or oak or chestnut barks, or twigs and leaves of alders, and the like. These, however, are not particularly interesting.

Manganese brown or bistre is a color of very similar composition, *i. e.,* a metallic hydroxide, but with manganese substituted for iron. It has been used for a hundred years or so for producing various shades of brown upon vegetable fabrics and, occasionally, on wool. For rugs and other articles which must show great fastness to washing, as well as to light, it is still well worth keeping in memory.

The simplest way to develop it is to dissolve in warm water a greater or less quantity, say, as an experiment, two tablespoonfuls to the gallon, of permanganate of potash. This gives a deep purple-colored liquid, in which the material, thoroughly wetted out, is immersed and stirred around. When taken out it is to be wrung as before, shaken out and exposed to the air, when the purple color will rapidly change to a nice, soft shade of seal brown. This process should be repeated until the material is brought to shade, and then it is finished, like the other, by rinsing in water, and scouring with soap.

As before mentioned, the aniline color industry dates from the discovery, by the late Sir William Henry Perkin, of the dyestuff "mauvein," a little over fifty years ago. He was trying, in a very crude, simple way, to make artificial quinine from a strong-smelling oil found a few years previously among the products of the dry distillation of indigo, and named "aniline" from the word "anil," the native name of that substance in the East.

On heating his aniline with bichromate of potash he obtained a dark molasses-like mess, utterly unlike what he was aiming for and apparently of no interest or value. But instead of throwing it away, he made some experiments with it and found that its alcoholic solution would impart a clear, permanent violet shade to silk and wool. With the help of his father he started a factory for the manufacture of it, and, before long, other dyes of more or less similar composition were discovered and, all over the world, chemists began to manufacture and experiment with these new dyestuffs.

During the last thirty years the manufacture of these dyes has been enormously developed, principally by four great German firms, and the number of individual dyestuffs discovered and actually put upon the market amounts not to hundreds but to thousands. The early dyes were of great brilliance and strength, but, unless very carefully used, not of much beauty, and they were distinctly inferior in fastness to the better varieties, at least, of the vegetable dyes that preceded them.

A very serious disadvantage in this respect was that these early "basic" aniline dyes did not fade true. A piece of cloth might be red today—and a few days in the bright sun might change the color to yellow and then to white, or might darken it, throwing it in either case completely out of harmony with its original surroundings.

By 1868, however, a couple of German chemists, Graebe and Liebermann, had invented methods for preparing artificially alizarine, the extremely interesting dyestuff which gives all its value to the famous old dye madder. As in many other instances, this proved the first of a large series of coloring agents of closely related composition. In consequence, from a few years after that date the commercial use of madder has entirely disappeared, and all shades of color on cotton, wool and silk, from the most brilliant reds and yellows to the deepest and richest purples, blues and browns, have been made of unsurpassed beauty and with a fastness to light and washing never before equaled.

Of late years every effort has been made to simplify the dyeing processes, and at the same time to produce colors which would be durable. And at present it is perfectly possible for the amateur, with hardly any practical experience, to produce in a single bath permanent color effects which a few years ago could only have been obtained in a durable form by long and difficult mordanting and dyeing processes.

And yet the fact remains that, in a great many cases, there is good cause to complain of the fastness of the modern dyed fabrics. This is not the fault of the dyes themselves, or of the manufacturer of the dyes, but is owing to the ignorance, or, more commonly, the greed of the dyer. It is possible, now, to reproduce any desired shade on either cotton, wool or silk, in at least six or eight, often in twenty or thirty, different ways, using dyestuffs of entirely different composition, in different combinations, and applied by different methods. Of these, one or two ways can generally be found which will be thoroughly fast both to light and washing. One or two more will probably be fairly fast to light but not to washing, and the rest will be more or less fugitive and unsatisfactory.

Now, the honest manufacturer has a deep-seated sympathy with the aspiration of the fair sex to buy a new gown whenever the old one gets at all faded. Too permanent colors have little or no attraction for him. And when, as is generally the case, it costs a little more, even a minute fraction of a cent a yard, to turn out goods that are durable instead of goods which look exactly the same, but will only last a few weeks or even days after they have left the retail counters, it is almost impossible to get him to use the better grades of dyestuffs.

In other words, if the manufacturer calls for cheap and nasty dyes, they can be furnished him in abundance. But it is equally possible, with a little care in the selection and application of the dyes, and a little greater expense, to produce colored fabrics which are absolutely durable, as well as of any shade that may be desired.

As an illustration, one of my friends in one of the great dye importing houses heard me patiently enough, when I asked him for the names of some thoroughly fast dyes, and said that he could furnish me with all that I wanted. But he laughed in my face when I suggested that there might be a good market for those, if only they were well known, and asked point-blank: "Who would buy them? The only people who have the sense and money to pick and choose fast and durable materials are the particular ones who have money enough to throw them away, long before they are worn out, because they are so tired of them."

And as for art work, rugs, curtains, and the like, he quoted the case of one of the famous weaves of Indian blankets, lately taken up by some enterprising eastern manufacturers, whose motto was the common one of their tribe: "Manufacture cheap and sell dear." In order to sell dear they were advertising extensively that they were using the old patterns, the old weaves and, above all, the same fine old vegetable dyes of these world-renowned blankets; and they quoted from travelers and scientific men to show that such blankets were in existence, hundreds of years old, with colors still fine and true.

And to manufacture cheap these same people were sending to the dye houses letters, one of which my friend had on his desk at the time, asking for competitive bids on fifty-pound lots of the basic aniline colors—the cheapest, strongest, crudest dyes of the whole list, some of which would be completely spoiled by twelve hours' exposure to the direct sunlight.

Before closing this introductory paper I ought, perhaps, to call the reader's attention to some of the effects produced by the discovery of the coal tar dyes in many departments of human interest and activity far removed from the dyeing or textile industry itself.

For instance, in the late '50's and

early '60's the most vital problem before the civilized world was to explain the closely related subjects of fermentation and putrefaction, on the one hand, and infectious and contagious diseases on the other. It was recognized by many brilliant investigators that the solution lay in the study of the "floating matter of the air." It was also believed that some living "germs," of dimensions so small that they could barely be observed, and could not possibly be identified by the most powerful microscopes of the day, would be found to play an important part in both disease and decomposition. Closer and closer came the observations, only to be constantly blocked by the impossibility of distinguishing such minute, colorless objects under the microscope. Until finally, in 1867, the famous Dr. Robert Koch, pursuing his studies on the causes of blood poisoning in army hospitals, found that the recently discovered basic aniline dyes had the property of staining and brilliantly coloring the various micro-organisms, moulds, yeast plants, and, above all, bacteria, without leaving any color at all in neighboring tissues and cells, of either animal or vegetable origin. This at once changed the whole situation, and, almost immediately, began the large and important series of investigations and discoveries which have resulted in the triumph of antiseptic surgery and the discovery of the causes and proper treatment of so many of the most dangerous and dreaded diseases, such as tuberculosis, cholera, typhoid fever, and the like, as well as the great range of illnesses coming under the general classification of "blood poisoning."

Thanks, largely, to the investigations carried on for the manufacture of these artificial dyestuffs, chemists have made enormous progress in the study of organic chemistry, and have not only gained far closer knowledge of the composition of various organic bodies, but have also learned new methods and reactions for building them up, and forming them from simpler substances.

In the course of some investigations on the same problem that Perkin was originally working on, the artificial formation or "synthesis" of quinine (a problem not yet solved, by the way), some chemists made some new substances resembling that of quinine, although not identical with it. Upon testing the medicinal effects of these compounds, and then pressing their investigations still further, they came upon some active substances with very valuable medicinal properties, such as antipyrin, antifebrin, phenacetin, and the like. These drugs are sought for and manufactured in the same great factories that manufacture the dyestuffs, and the same careful, accurate, painstaking, scientific methods are used for them as for the others.

Associated to a great degree with the last class of substances, and produced by chemists trained in dye factories and laboratories, are the modern "synthetic perfumes." In some cases these have been discovered accidentally, as, for instance, in the case of artificial musk, when a chemist, working out a new nitro compound by well-known reactions but upon substances hitherto not used for that purpose, found that one of his products had a very characteristic musk odor. The substance, thus discovered, during the last few years has almost, if not entirely, driven from the market the natural musk, obtained at great expense and difficulty as a secretion from the little musk deer, in Manchuria.

Other perfumes, such as ionone, the scenting material of violets, heliotropin, and others, were prepared by deliberately trying to duplicate the composition of the natural perfumes.

Flavoring matters, also, have been

produced in large quantities, and vanillin and coumarin, the synthetic flavoring matters of the vanilla and the tonka bean, respectively, have brought another branch of organic chemistry close to daily life. The most curious of all flavoring matters, however, is saccharin, whose wonderfully powerful, sweet taste was accidentally discovered in a new compound, prepared by a young chemist under Prof. Remsen's directions. This compound, in minute quantities, proved to have exactly the taste of sugar, but it is so powerful that four pounds of it are equivalent in sweetening power to a whole ton of dry cane sugar.

Another branch of industry was affected by Perkin's discovery in a way not altogether satisfactory. Up to 1865 or so the various pigments used were, with but few exceptions, of mineral origin and, therefore, very permanent and durable. To be sure, the lead colors, and especially lead white, do have the property of darkening with age, owing to the gradual action of sulphuretted hydrogen. But this action was slow, and not infrequently actually assisted the "tone" of a picture by softening and saddening the original, rather too bright, colors.

Of late years, however, the paint manufacturers have found it far easier, and far less expensive, at the same time, especially for the more valuable and brilliant classes of colors, to dye white, insoluble, inert powders, like china clay, barytes, chalk, and the like, with artificial dyestuffs, thereby producing pigments of any shade and brilliancy.

Unfortunately the brightest and in many cases the most beautiful of these new pigments are comparatively fugitive, and, in the absence of any standards of composition, fixed by some organized body of artists, each manufacturer has been at liberty to select his colors according to shade, and price, and with little or no reference to permanence.

After all, the most important result of the development of the color industry has been the enormous impetus given to scientific and especially to chemical education and research during the last half century. It has opened up a vast field, with immense possibilities, to the active and intelligent student, and every year hundreds of well-trained chemists are sent out into the world to earn their living.

Some go into teaching and help to spread the knowledge of their science far and near. Others, and not the least valuable, go into the industries, improving methods, cheapening and perfecting processes, and helping very largely indeed in the development of natural resources, and the raising of the general standard of living for rich and poor alike. It is little wonder, then, that, not to chemists alone, the discovery of the first coal tar color is a landmark worthy to be held in remembrance and in honor for many generations to come. Nor should we be surprised that dear old Sir William, who died but a few months ago, full of years and showered with honors from every part of the world, should, at the fiftieth anniversary of the discovery of mauvein, have been universally hailed as one of the great benefactors of the human race.

EDITORIAL NOTE.—The foregoing article introduces a series of eight lessons on the art of dyeing, by Prof. Charles E. Pellew, of Columbia University, a chemist who has made a special study of dye stuffs and is one of the best authorities in this country upon the subject. The article printed in this issue merely reviews the subject and forms a foundation for the more definitely technical articles that follow. The second will be a general description and classification of dye stuffs; the third covers the application of artificial dyes to arts and crafts work, and the others are devoted to the dyeing of special materials, such as cotton, silk, wool, paper, wood and leather.