COMMON COMMODITIES AND INDUSTRIES

DYES

A. J. Hall.

DYES

Frontispiece

TWELVE-COLOUR PRINTING MACHINE

PITMAN'S COMMON COMMODITIES
AND INDUSTRIES

DYES

AND THEIR APPLICATION TO
TEXTILE FABRICS

BY

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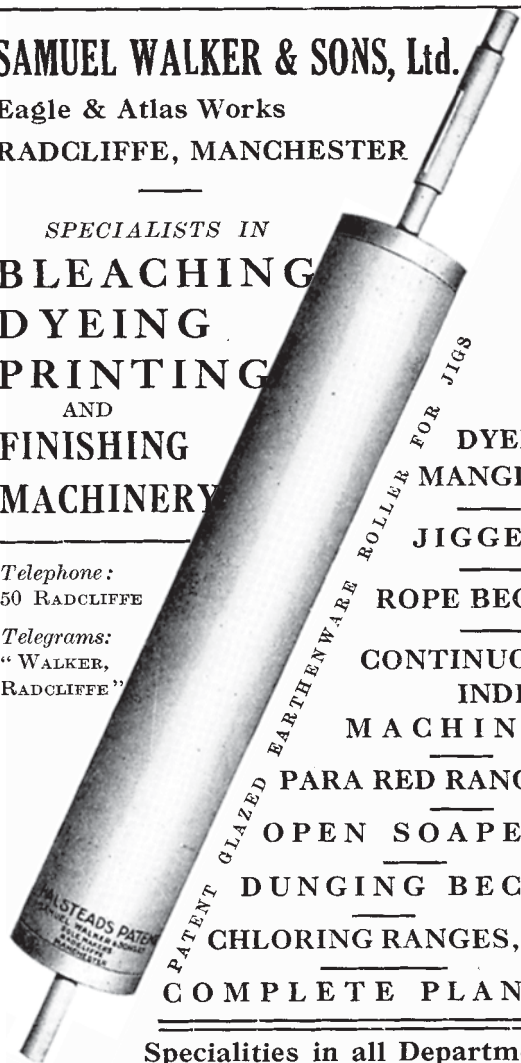
PREFACE

IN the following pages, an attempt has been made to give an account of Dyes and their application to textile materials.

It may be said, without exaggeration, that hundreds of books have been written on the same subject, so that this book is not claimed to be a *complete treatise*. On the contrary, the writer has tried to give a bird's-eye view of the dye and dyeing industries in their development and as they exist to-day.

This book is written for the non-technical reader, and the author has therefore endeavoured to make it interesting and clear, rather than detailed and tedious. He will be completely satisfied if the reader finds this book *interestingly instructive*.

In conclusion, I wish to express my sincere thanks to Messrs. James Farmer, Norton & Co., Ltd., Manchester; Samuel Walker & Sons, Ltd., Manchester; The Hooley Hill Rubber and Chemical Co., nr. Manchester; Mather & Platt, Ltd., Manchester; S. H. Johnson & Co., Ltd., Stratford, London; Livingston & Sons, Ltd., London; The Longclose Engineering Co., Ltd., Leeds; S. Spencer & Sons, Manchester—manufacturers of world-wide reputation, and who have supplied me with illustrations of their machines.

<div align="right">A. J. HALL.</div>

TIMBERSBROOK,
    CONGLETON.

ILLUSTRATIONS

CONTENTS

DYES

CHAPTER I

THE DEVELOPMENT OF THE DYE INDUSTRY

ALTHOUGH clothes have been made from cotton, wool and silk during at least 3,000 years, satisfactory methods for dyeing them have only been discovered during the last century. For it was not until the so-called " aniline dyes " became available that the dyeing of fabrics in a wide range of fast and bright shades became possible.

In very early times dyeing was chiefly carried on by utilizing mineral pigments and various coloured extracts, which were obtained from plants and certain kinds of wood. The well-known purple of the Ancients was derived from a coloured secretion present in certain molluscs which are found in large quantities along the shores of the Mediterranean Sea, while the wrappings around Egyptian mummies were frequently dyed red by means of the safflower and brown with the aid of iron salts. But the number of colouring matters available was quite small.

As facilities for travel increased the art of dyeing spread from Asia and Egypt to Western Europe, and at the beginning of the fourteenth century a flourishing dyeing trade, largely in the hands of Jews, centred around Florence. In fact, no fewer than 400 dyehouses existed there.

That the Jews should have become so skilled in dyeing is somewhat interesting, for there is a curious Persian

1

legend which credits Christ as being familiar with dyers, and as late as the seventeenth century, a dyehouse in Persia was called Christ's workshop, and Persian dyers, although Mohammedans, considered Christ as their patron.

By the end of the twelfth century crude methods of dyeing fabrics in several colours were known throughout France, England and Germany, for various documents exist which give us information about the state of dyeing at that period. Coventry was then noted for its blue dyed cloth, and a much used phrase was " Coventry true blue," in reference to the colour adopted by the Puritans as distinct from the scarlet badge favoured by the followers of Charles I. We also learn that in Germany no one could become a dyer without serving as an apprentice for five years to a master dyer and working daily from 4.0 a.m. to 7.0 p.m. This apprenticeship which was further followed by a practical test—Meister-Stuck—appears in these days so exacting that one is inclined to wonder what was the status of the master dyer.

Until the nineteenth century the art of dyeing progressed slowly. The discovery of other countries, such as the discovery of America by Columbus, the development of the earth's mineral resources, and an increased knowledge of the working of metals and their compounds, all contributed to extend yet simplify the dyers' efforts. Yet at all times the dyers were working with substances they little understood, and, therefore, over which they had but little control. Moreover, the natural colouring matters were generally so impure that it was extremely difficult to get fabrics dyed in colours that were really bright and pleasing. The dyeing of a million yards of fabric so that no portion of it should fail to match a standard pattern would present

little difficulty to a modern dyer, but it is a feat which would have been almost impossible a century ago. In fact, the difficulties of the dyers of those days would be comparable to those of a doctor whose drugs are so impure that he is obliged to prescribe for a patient suffering from stomach ache a medicine containing not only drugs suitable to that distressing complaint, but also those which would give relief for dropsy, gout, eczema, and other diseases besides. But in 1856 a discovery was made which within a few years resulted in completely revolutionizing the dyer's art.

It would be unfair to mention the discovery which led to the foundation of a progressive dyeing industry, such as we have to-day, without referring to the early pioneers whose efforts made this discovery possible. For nearly all modern dyes are derived either directly or indirectly from coal tar, and this substance was, of course, unknown until coal gas was used as an illuminant.

It was a Scotchman—William Murdoch—who first made the manufacture of coal gas a successful industry, and after experiments in the lighting of the Lyceum Theatre, 1803, and Golden Lane, 1807, the lighting of London with gas on a large scale was carried out about 1813. In making coal gas large quantities of coal were distilled in iron retorts and in the process of purifying the gas a tarry fluid called coal tar was obtained. At first this, of course, had no particular value except for fuel, and as a cheap preservative for timber. In 1826, however, Faraday succeeded in isolating benzene from compressed oil gas, and later this same liquid was shown by Mansfield to be present in considerable quantities in coal tar. Mansfield also further showed how benzene and a similar substance, toluene, could be separated in a pure state from the tar.

Other chemists at about the same time were able to

isolate a few other substances such as aniline and naphthalene present in coal tar. Then the Swedish chemist, Mitscherlich, produced nitrobenzene from benzene, and later Bechamp indicated how nitrobenzene could be converted into aniline. All these substances later became useful in the manufacture of dyes. So that coal tar was shown to have possibilities if a means for realizing them could be found.

In the Easter vacation of 1856, however, Perkin, a young English chemist, while still a student at the Royal College of Science, attempted to prepare artificially quinine, and in the course of his experiments treated some aniline with potassium bichromate—a strong oxidizing agent. The immediate result, taking into account the object of the experiment, was not satisfactory, but from the black tarry substance obtained it was found that a purple or mauve colouring matter could be extracted. Perkin followed up this work by showing that the colour could be used for dyeing silk, and the dyeings so obtained were remarkably fast to light.

The firm of Messrs. Pullar, of Perth, was established even in those early days, and Perkin sent some specimens of the dyed silk to them. We can imagine his pleasure when he received the following reply—

" If your discovery does not make the goods too expensive, it is decidedly one of the most valuable that has come out for a very long time. The colour is one which has been very much wanted in all classes of goods and could not be obtained fast on silks, and only at great expense on cotton yarns. I enclose you a pattern of the best lilac we have on cotton—it is dyed only by one house in the United Kingdom, but even this is not quite fast, and does not stand the tests that yours does, and fades by exposure to air. On silk the

colour has always been fugitive : it is done with cudbear or archil, and then blued to shade."

As a result, Perkin made larger quantities of the colour, patented the method of manufacture, shortly afterwards left the Royal College of Chemistry, and together with his brother and father commenced to manufacture the new dye on a commercial scale at a works situated at Greenford, near to Harrow. The first aniline dye was then produced commercially by separating benzene from coal tar, converting this by means of nitric acid into nitrobenzene (a liquid having the odour of almonds), converting this into aniline, and finally oxidizing this to a dark solid from which a mauve dye could be extracted by means of solvents, such as methylated spirit. The new dye was called mauveine, and for many years was used for colouring postage stamps.

We cannot here follow the development of the Greenford Works, but the manufacture of mauveine and other dyes which were taken up afterwards proved to be as romantic as the circumstances surrounding their discovery.

At first there were great difficulties in applying the new dye for dyeing and calico printing, but these were speedily overcome. So that when the new brilliantly dyed fabrics spread throughout England and the Continent, many colour chemists turned their attention to aniline and endeavoured by all manner of means to obtain other dyes from it. Discoveries of new dyes then followed quickly. The first was magenta, and this was succeeded by various blue, green and violet dyes. Perkin's method for preparing mauveine proved to be superior to all others subsequently devised by competitors, and, moreover, in 1863 it was discovered that the process yielded yet another red dye—safranine —as a by-product.

About 1864, Peter Griess, chemist to a Burton firm
of brewers, found that aniline could be transformed
by a simple reaction—known as diazotization—into a
curious unstable compound, which readily condensed
or combined with other substances derived from coal
tar to form valuable dyestuffs.   Yellow, brown and
orange dyes of this type were speedily manufactured and
were called Azo dyes.   The process discovered by Griess
can be applied so widely that to-day the Azo dyes
outnumber all others put together.

Meanwhile various chemists continued to examine
coal tar more thoroughly.   It was found to be a most
complex mixture of substances (over 200 have been
identified) related to benzene and naphthalene.   Methods
for separating and purifying many of these were dis-
covered and from the pure substances numerous other
compounds could be made by well recognized processes.
Nearly all these products were utilized in the manu-
facture of dyes, and so coal tar became the ultimate
source of a large number of substances which are known
as dye intermediates.

But as yet the relationships that existed between
these various intermediates were not sufficiently appre-
ciated.   Chemists were groping in a darkness which
they intuitively knew could be dispersed if they but
knew how.   In 1865, however, a German chemist
named Kekule came to the rescue.   It had, of course,
been generally proved that each molecule of benzene
consisted of six atoms of carbon and six atoms of hydro-
gen, but no one had succeeded in finding out how these
atoms were arranged or linked together within the mole-
cule.   Then Kekule suggested that the properties of
benzene could be explained by the assumption that
the six carbon atoms were united in the form of a ring
or chain.   Also that one atom of hydrogen was attached

to each atom of carbon. This was all summarized by giving the following formula to benzene—

$$C_6H_6 \text{ or } \quad \text{Benzene}$$
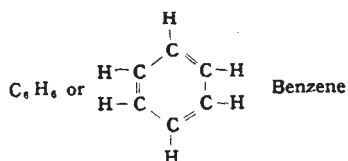
In the same way, in naphthalene which has the composition $C_{10}H_8$ (ten atoms of carbon united to eight atoms of hydrogen), two benzene rings are present, while anthracene—another valuable dye intermediate—contains three benzene rings.

$$C_{10}H_8 \text{ or}$$

Naphthalene

$$C_{14}H_{10} \text{ or}$$

Anthracene
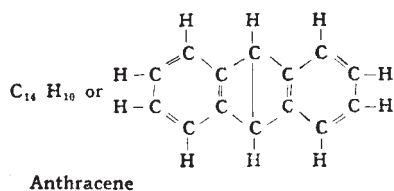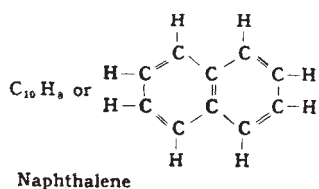
In all these structural formulae, the forces linking the atoms together are represented thus —, or where the force is doubly strong ═ or even ≡ and ≣ for forces three and four times as strong.

Kekule's suggestion was found to fit in with all the

known facts and greatly helped investigators by indicating likely methods by which new intermediates could be prepared. Even to this day Kekule's benzene theory is capable with but little modification of explaining the properties and relationships of tens of thousands of coal tar compounds which have been made since 1865.

The search for new dyestuffs from coal tar compounds continued without interruption. But in 1869 a new method of approach was indicated. In that year Perkin and two other chemists—Graebe and Liebermann—simultaneously succeeded in making from coal tar products a dyestuff (Alizarin) which was identical with madder, the natural colouring matter present in the root of a species of plant which had been cultivated for dyeing purposes from the most remote times. The dye was and still is extensively used for dyeing cotton fabrics in fast purple, black, brown and violet shades, and is also used in the production of the well-known Turkey-red. At the time of the discovery the price of madder was £50 a ton, but owing to the low working costs and efficiency of the process used for manufacturing this dye artificially, or synthetically, as chemists would say, the price dropped to £18 a ton within ten years. In these days madder is no longer cultivated, the cheaper and purer artificial product having killed the industry.

This success encouraged chemists to tackle the synthetic production of indigo, another valuable natural colouring matter. It was a difficult task in which chemists of the highest genius engaged. Nearly £1,000,000 was spent altogether in the attempt, but the ultimate success in 1897 justified this expense. To-day indigo is only cultivated in small quantity, while huge quantities of the synthetic product are manufactured each year.

The dyeing industry has benefited very materially by these efforts to beat Nature. Not only are the synthetic colouring matters always purer, more reliable and cheaper, but the knowledge obtained in establishing the processes of their manufacture has always suggested methods for preparing compounds of a similar type, and many of these have proved to be valuable dyes. In this way, not only indigo but a whole class of synthetic dyes similar to indigo have become available to dyers. The same is true in regard to madder.

As will be explained later, dyes differ considerably among themselves in their behaviour towards the different textile fibres. A dye which is very fast on wool may yet be easily removed by washing when applied to cotton. So that it was a serious matter to dyers and dyemakers that, while nearly all the new synthetic dyes could be applied directly to animal fibres such as wool and silk, none of them had a direct affinity for cotton. Of course, the dyes were used for dyeing cotton fabrics, but these had first to undergo a special preparation. So that it was a most important discovery in 1884 when a German chemist—Bottiger—prepared the first dye in a solution of which ordinary unprepared cotton could be dyed. This first cotton dye was a red one—Congo Red—and it belonged to the Azo group. It was not very fast, but a consideration of its molecular structure indicated how other direct cotton dyes might be produced. The clue so obtained was followed up, and to-day the direct cotton dyes are very numerous and are extremely important.

Nine years after the discovery of the first direct cotton dye a French chemist, Vidal, found that valuable black and brown dyestuffs could be obtained by fusing together at a high temperature various coal tar products with sulphur and sulphur compounds, such as sodium

sulphide.   Something of this nature had been discovered twenty years previously, when a greenish yellow dye had been produced from organic materials such as bran and sawdust by the same method, but Vidal's discovery was much more important, since it showed that coal tar products could be used.   Several dyes made by this new process were quickly discovered, and they were particularly fast, and their direct application to cotton could be carried out by a simple process. To-day dyes of this type are very numerous, and are known as sulphur dyestuffs.

The discovery of the first dye of a class which is now known as vat colours was made in 1901, and some of the fastest dyes known to the dyer are contained in this class.   Nearly all these are extremely resistant to light, washing, acids and alkalis.   They are made from anthracene—a substance which is present in considerable quantities in coal tar.   But, although this raw material is extremely cheap, the methods for making the dye are so complex that the dyes themselves are very expensive.   Still, owing to their excellent qualities, they are being more and more used.

During the past fifteen years a tremendous amount of research work has been carried out, but on the whole this work has been directed along well recognized channels, so that no very startling discoveries have been made.   Yet, at the same time, the processes of manufacture have been so improved that, while in most cases they are almost economically perfect, they enable huge quantities of dyes to be produced having absolute uniform quality and shade.   Dyers can thus rely on the quality of the dyes which they use and in consequence are able to obtain uniform results in their dyeing processes.

In concluding this necessarily brief sketch of the

manner in which the coal tar dyestuff industry has
been developed, the following scheme will be found
interesting—

		Intermediates	
		Benzene	7 lbs.
Distillation		Toluene	3 lbs.
Coal ⟶ Coal tar ⟶		Phenol	3 lbs.
20,000 lbs. 1,000 lbs.		Cresol	7 lbs.
		Naphthalene	6 lbs.
		Anthracene	3 lbs.

CHAPTER II

IT is probable that at the present time about one thousand dyes are in commercial use. Yet it would not be a difficult task for the average chemist to catalogue ten times this number of coloured compounds. So it is evident there are more fundamental properties which dyes must possess other than that of colour. In this chapter an attempt will be made to show exactly what a dye is, and why it is.

One of the best known green dyes is termed Malachite Green. If wool is boiled in a solution of this dye it quickly absorbs colour and becomes green. Further, after thoroughly washing with water the wool still remains green. Under similar circumstances silk behaves like wool. On the other hand, if cotton is treated in the same manner it will be found that by washing the colour is easily removed and the cotton becomes white. A further experiment, however, can be performed. It is a well-known fact that when cotton is steeped in a solution containing tannin—the same substance that gives tea its astringent flavour—it absorbs a considerable quantity of this substance. If the cotton treated in this manner is now immersed in the solution of Malachite green, the dye will rush on to the fibre so as to leave the solution almost colourless. Moreover, the green colour of the cotton is not removed even by repeated washing. So that, although the first experiments might have been interpreted as showing

12

that Malachite green is capable of dyeing wool and silk but not cotton, it is now seen that it is a cotton dye provided that the cotton has been suitably prepared.

It is thus evident that a dyestuff does not necessarily have an affinity for the textile fibre towards which it is used as a dye. It is sufficient if there is some method by which the dyestuff can be attached to or deposited within the fibre. So that any substance which may be made to adhere to a textile fibre, thereby giving it a definite colour which is reasonably fast to washing and other mild cleansing treatment, can be called a dye. Its commercial value as a dye is, of course, dependent on its all round degree of fastness to many other influences such as light, alkalis, acids, oxidizing and reducing agents, heat and rubbing.

In general, it is found that while some dyestuffs are capable of dyeing several fibres such as wool, silk, cotton and linen, in most cases dyes are very selective in their effect. But more will be said about the classification of dyes in a later chapter.

Although the dyeing properties of any substance must always be determined by direct experiment, it is only natural to expect that the accumulated experience of colour chemists, obtained by searching for new dyes, would have led to the recognition of some characteristics which are to be associated with substances having dyeing properties. In other words, that there is some connection between the colour of a dyestuff and its molecular structure. This is indeed the case, for it has been found that, if the atoms within the molecule of a substance are grouped together in certain recognized forms, then that substance in all probability is a dye stuff. Moreover, from a consideration of molecular structure of a dye, a colour chemist is able to draw

fairly accurate deductions as to its colour, its suitability for various fibres, and its fastness to light, washing, and other influences. How is this possible ?

Although the reader may know but little of chemistry, by an easy descent to the level of atoms and molecules it is possible to answer this question and at the same time show him something of the romantic world in which the dye chemist labours.

Practically all dyes are composed of carbon, hydrogen, and oxygen, together with sulphur or nitrogen or both. A relatively small proportion of dyes contain the halogen elements such as chlorine, bromine and iodine. A very much smaller number contain metallic constituents, and even in these the metal has only a subsidiary effect on the colour. Dyestuffs are essentially organic substances.

If one starts with a small amount of a dye (the principle can be applied to any other substance) and divides it into halves, then quarters, eighths, and so on, a point will be reached at which the portion of the dye is so small that it cannot be further divided by simple means. It will in fact consist of one particle or granule, and this is termed by scientists—a molecule. This molecule will, of course, be composed of all the elements (carbon, hydrogen, etc.) which go to make up the dyestuff. Their relative proportions can be determined by analysis of the dyestuff. A molecule is in fact the smallest representative sample that can be taken of any substance. Moreover, it must be made up of a number of the indivisible particles—called atoms (the building bricks of Nature)—of the elements of which the dye is composed. Now, since chemists are able by special methods to look as it were into the molecule of a substance and see how it is built up, the molecule of a dyestuff can

always be expressed in a simple formula such as—
$C_aH_bO_cN_dS_e$.

a = Number of atoms of Carbon (C)
b =   ,,   ,,   ,,   ,, Hydrogen (H)
c =   ,,   ,,   ,,   ,, Oxygen (O)
d =   ,,   ,,   ,,   ,, Nitrogen (N)
e =   ,,   ,,   ,,   ,, Sulphur (S)

Thus referring back to Malachite green, this dye has the composition $C_{23}H_{25}N_2Cl$, or expressed more fully, a molecule of this dye contains 23 atoms of carbon, 25 atoms of hydrogen, 2 atoms of nitrogen, and 1 atom of chlorine. Another dye, indigo, has the composition shown by the formula—$C_{16}H_{10}N_2O_2$.

Chemists, however, were not long content to know merely the number and kind of atoms which went to form each molecule of a dyestuff. They attempted to discover much more than that, so that to-day they are able to go so far as to describe the actual manner in which the atoms within the molecule are linked together. For it is evident that the various atoms must be held together by strong forces ; otherwise the molecule would be unstable and would break up into other yet more stable compounds.

We are now in a position to see how a dye research chemist gropes his way to success, and for this purpose we can refer to the well-known dye indigo. This dye it will be remembered, has been known from very early times, and was extracted from the leaves of the indigo plant which grows in India, China and Egypt.

About 1850 several chemists examined indigo, and from their researches it became generally agreed that each molecule of the dye consisted of 16 atoms of carbon, 10 atoms of hydrogen, 2 atoms of oxygen, and 2 atoms of nitrogen. A chemist would, of course, express this more shortly by saying that indigo had the formula

$C_{16}H_{10}N_2O_2$. The problem then arose as to how these atoms were arranged within the molecule, and the solution occupied over thirty years of patient experiment and research. Foremost among the chemists engaged in this task was a German chemist—Baeyer— and it was he who finally solved the problem.

The first clue was obtained as a result of the discovery that when a molecule of indigo was decomposed by chemical means it split into two equal halves. This showed that within the indigo molecule there were two groups each $C_8H_5N\,O$ symmetrically linked together. It was also proved that each of these halves contained six carbon atoms linked together in the same manner as the carbon atoms in a molecule of benzene. And, as we have previously seen, the arrangement of the atoms in a molecule of benzene is expressed by Kekule's formula—

Benzene
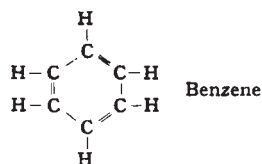
Finally, in 1883, Baeyer had collected together sufficient evidence to show that in the molecule of indigo, the atoms were arranged thus—
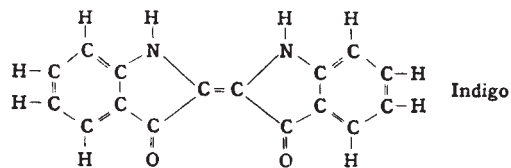
Indigo

And as yet no facts concerning the properties of indigo which have since come to light have failed to

agree with this molecular structure.   Moreover, chemists guided by this formula have been able to devise no fewer than five different methods by which indigo can be successfully made from coal tar products such as toluene and naphthalene.   A wonderful achievement this :   the manufacture from a gas works by-product of a dyestuff identical in all respects with the natural indigo dye as formed within the plant leaf.

But subsequent developments are even more interesting.   The excellent dyeing properties of indigo led chemists to attempt the preparation of substances whose molecules were similar in form to that of indigo but yet slightly different.   In this way it was hoped to produce dyes having the valuable properties of indigo but differing from it in colour.

In one of these attempts a substance was obtained whose molecule had the following structure—

Ciba Violet
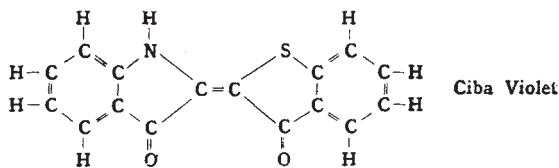
This differs from indigo only in so far as two atoms—one of nitrogen and one of hydrogen—have been replaced by one atom of sulphur.   Yet, whereas indigo is a blue dye, the new substance yields violet shades and has proved to be a valuable dyestuff, and is known as Ciba Violet.

The next obvious development was, of course, to

prepare an indigo substance having two atoms of sulphur, thus—
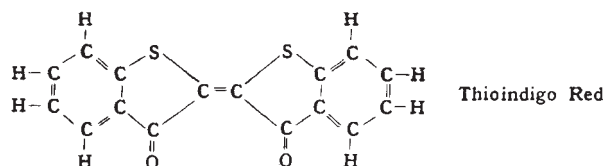
Thioindigo Red

This also is a valuable red dye, and is called Thio-indigo Red.

Another effort yielded a curious reshuffling of the true indigo molecule, but the substance produced—indirubine—though a dyestuff (redder than indigo) is not very important.

Indirubine
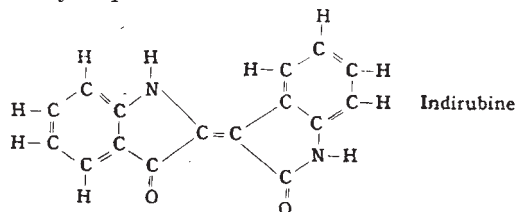
By introducing naphthalene into the indigo molecule in place of the benzene groupings thus—
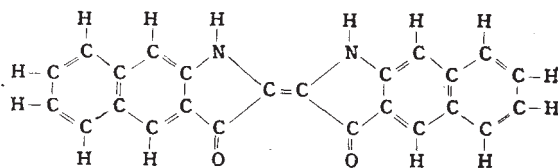
a green dye was formed.

One more example will suffice.   In 1909 the discovery was made that the purple of the Ancients was constituted similarly to indigo.   Previously two chemists had

succeeded in preparing a compound related to indigo but containing bromine (Br.). Its structure was decided to be—

Purple of the Ancients
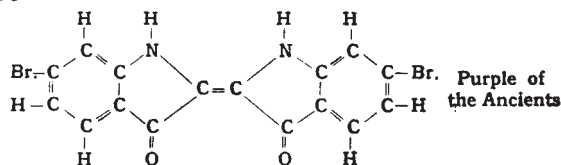
Then Friedlander extracted from about twelve thousand molluscs the purple colouring matter which the Ancients at one time used, and from experimental evidence conclusively proved it to have the same composition and molecular structure as indicated in the above formula.

Of course, the dyes just described are only a few taken from the great number which have been made since the first synthesis of indigo. They are all classed together as the indigoid dyestuffs. And to this class new dyes (all made from coal tar products) are being added each year.

From what has now been stated, it will be inferred that the general method by which the dye industry develops is this : By some chance experiment or as a result of patient chemical investigation a substance having the properties of a dyestuff is produced. This is then carefully examined by many methods until the structure of its molecule is revealed. In this way the dyeing power of the substance can be attributed to a certain peculiar arrangement of the atoms within its molecule. Thus the tinctorial properties of indigo and dyes related to it are ascribed to the presence in their molecules of the atomic grouping CO. CC. CO. Then attempts are made to produce different but related compounds each containing the same peculiar arrangement of the atoms.

By such a method many dyes having the same general properties of the original dye are produced. Some of these will be worthless, but others will have considerable commercial value.

It is thus evident that the progress of the dye industry is limited only by the amount of energy that mankind is willing to devote to research.

Now, why is indigo a dyestuff ? A similar question has, of course, been applied to every known dye, and as a result, various theories have been put forward. Many of these have had to be abandoned, but it now seems generally accepted that the properties of a dyestuff are due not to the molecule as a whole but to the presence in the molecule of certain atomic groupings. Thus the dyeing properties of indigo are ascribed to the presence of the group CO. CC. CO, and it will be noticed that all the dyes related to indigo as described above contain this grouping. The other atoms within the molecule exert an influence on the actual colour of the dyestuff, but the fact that the dye has dyeing properties at all is due essentially to the one particular atomic grouping.

Of course, these groupings also involve the chemical forces which hold the atoms together. But, without going more deeply into this question, it is pointed out that each dye is a dye because of a particular grouping of atoms within its molecule, and that its colour is dependent on the influence exerted on this particular grouping by other groupings also present within the molecule. Moreover, all chemists are able to classify dyestuffs very conveniently, not only according to their behaviour towards the various textile fibres, but also in accordance with the peculiar atomic groupings which they contain.

CHAPTER III

HOW DYES ARE MADE

MANY people unacquainted with the dye industry frequently make the mistake of supposing that the greatest task of the dye manufacturer is to make dyes. In point of fact, the actual manufacture of a dye is usually simple. The difficulties which do arise are nearly always in connection with the production of the necessary intermediates. Given intermediates of good quality it is in most cases easy to produce a good dyestuff. This is borne out by the fact that about two-thirds of the plant of a modern dyeworks is devoted to the manufacture of dye intermediates, the remaining third being sufficient to produce the dyes.

In these days when the share capital of the largest dye-making firms reaches several million pounds, it is not surprising that everyone outside of the industry imagines that a modern dyeworks is one wonderful hive of concentrated industry. And it is true to say that it always is. But to explain to a non-technical reader the processes which are there carried out, the difficulties that arise and even the successes which are obtained, is somewhat difficult Yet, without knowing something of the manner in which dyestuffs and their intermediates are produced, no one can appreciate the wonderful achievement which is represented by a beautifully dyed silk blouse or even a brightly coloured sports jacket. So that an attempt will be made to show quite simply the operations which are involved in the manufacture of one dyestuff—methylene blue.

Methylene blue is a very important colour. It is

largely used for producing bright blue shades on cotton goods which are quite fast to light and soaping. It can also be used for dyeing wool and silk, and in addition is frequently employed for staining animal and vegetable tissues.

Methylene blue is made from coal tar intermediates only. Of course, a dye maker could buy these and just convert them into the dyestuff, but he could scarcely justify his name by doing this, since he would have avoided all the most difficult operations. So that we will consider the manufacturer who starts from the very beginning using benzene as his raw material. It is correct to consider benzene as the starting point, for the extraction of such substances as benzene, toluene, naphthalene, anthracene, etc., from coal tar is rarely carried out at a dye works, but nearly always by the coal tar distillers. These specialize in the working-up of the crude coal tar obtained directly from the gas works.

In the manufacture of methylene blue, the following stages are necessary—

Benzene ——→ Nitrobenzene ——→ Aniline ——→ Di-methyl-aniline

Amino-di-methyl-aniline ←—— Nitroso-di-methyl-aniline

———→ METHYLENE BLUE.
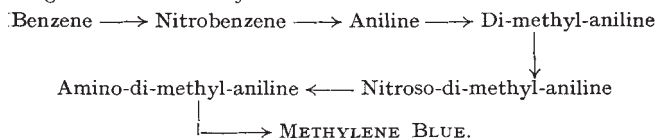
The formation of nitrobenzene is always brought about by *nitration*, that is, the action of a mixture of concentrated nitric and sulphuric acids on benzene. Nitrobenzene itself is a heavy liquid having a slightly yellow colour. It is also known as " oil of mirbane," and having an odour of almonds it is sometimes used in perfumes.

Usually very large quantities of nitrobenzene (about 6,000 lb.) are made in one operation.

The benzene is first placed in a cast iron vessel called

the " nitrating pan." Then the mixed acids are cautiously run into the benzene while it is being mechanically stirred. A reaction occurs almost immediately between the benzene and the nitric acid, and much heat is evolved, but by means of lead pipes arranged within the nitration pan through which cold water is circulated the rise in temperature is controlled. Otherwise there would be a great risk of explosion. When all the acid has been added and time has been allowed for the reaction to be complete, stirring is discontinued, and after a time the contents of the nitration pan separate into two layers. The bottom layer consists of the " used-up " or " spent " acid, while the nitrobenzene separates as an oily upper layer. The benzene has, of course, been almost completely converted into nitrobenzene, and practically all the nitric acid has also been used up for this purpose. So that the layer of spent acid consists largely of water and sulphuric acid. The purpose served by the sulphuric acid is to aid the reaction.

It is then usual to run off the spent acid from the bottom of the nitrating pan, transfer the nitrobenzene to another iron tank, and there wash it with water until it is free from acid. Nitrobenzene is almost insoluble in water, so that in the washing process it is easily separated from the water, since it is heavy and readily forms a bottom layer.

The spent acid is sent to another department and there concentrated so that it can be used again.

In the nitration process the following chemical change takes place—

$$C_6H_6 \longrightarrow C_6H_2N O_2$$
Benzene Nitrobenzene
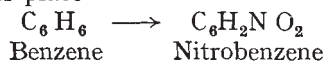
That is, the elements oxygen (2 atoms) and nitrogen (1 atom) have been introduced into the molecule of

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benzene which previously contained only the elements carbon and hydrogen.

The nitrobenzene as thus obtained is then ready for conversion into aniline, one of the most important of coal tar intermediates.

The most important part of the plant for this purpose consists of the " reducing pan," which is made of thick cast iron and is fitted with a powerful mechanically driven agitator or stirrer. Into this pan is first placed about 10 gallons of hydrochloric acid, some water, and 1 cwt. of iron borings or filings. A vigorous reaction takes place, the iron dissolving in the acid with liberation of gaseous hydrogen. Then nitrobenzene is gradually added in a thin stream and also further quantities of iron. By continuing the cautious addition of both of these substances the contents of the pan which are constantly stirred are just maintained at the boil. All the vapours arising from the seething mixture are led through a condenser (a thick lead coil immersed in flowing cold water), and it is arranged that the condensed liquors flow back into the reaction mixture. After about twelve hours, when some 10 cwt. of iron and 1,000 lb. of nitrobenzene have been added, all the nitrobenzene is converted into aniline, and the reaction is complete.

The next procedure is to separate the aniline from the tarry sludge which contains all the iron in the form of a brown oxide. This may appear difficult, but as a matter of fact the operation is easily performed by simply blowing steam (superheated) into the mixture.

The contents of the pan are thereby made to boil vigorously, and the escaping steam carries with it a small proportion of aniline, the iron and other impurities being left behind in the pan. The escaping steam and aniline vapours are led into the condenser, but this time the condensed water and aniline are run into another

tank from which they are later pumped into other
tall and narrow iron tanks. This process for removing
the aniline is known as *steam distillation*, and it is
continued until no aniline remains in the reducing pan.

After a few days, the aniline separates from the water
and forms a lower layer which can then be drawn off.
The top water layer contains only a small amount of
aniline in solution, but this is so used that the aniline
is ultimately recovered.

The crude aniline so obtained is a liquid, dark brown
in colour. By distillation it is purified to a water white
product. The iron sludge remaining in the reducing
pan has but little value, but it is often sold to gasworks
where it is useful for purifying the gas.

All the labour, steam and energy used about the
aniline plant produces the following subtle change in
the molecules of nitrobenzene—

$$C_6H_5N\,O_2 \longrightarrow C_6H_5N\,H_2$$
Nitrobenzene   Aniline
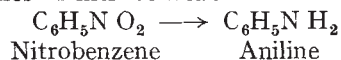
In other words, the two oxygen atoms in each molecule
of nitrobenzene are replaced by two atoms of hydrogen.

In the next stage aniline is converted into dimethyl-
aniline which is also a liquid much resembling aniline
in appearance and odour. The conversion is brought
about by heating a mixture of aniline and methyl
alcohol (this is a liquid very similar in composition to
the alcohol present in wines, spirits, etc.), to which a
small amount of sulphuric acid is added in order to
facilitate the reaction.

The desired action between these two substances
does not take place if the mixture is simply boiled.
It is necessary to raise the mixture to a temperature of
about 230° C., which is much above its boiling point.
So that in order to prevent the escape of the boiling
vapours, the operation is carried out in airtight pots,

known as autoclaves. These autoclaves, of course, have to withstand the very high pressures (about thirty atmospheres) generated by the vapours of the boiling reaction mixture and are made of iron.

When the operations are commenced the autoclave is partly filled with a mixture of aniline, methyl alcohol and a little sulphuric acid. The cover is then made airtight, and the autoclave heated over a gas fire. As the reaction proceeds, the temperature and pressure within the autoclave increases, but after about fifteen to twenty hours, all the aniline will have been converted into dimethylaniline. So the heating is then discontinued.

After cooling, a tap in the autoclave is opened and the pressure within is relieved. The contents are then run into a distillation pan and distilled. At first, unchanged methyl alcohol (this has a lower boiling point than water and dimethylaniline) distills over, and this is collected separately for re-use in the process. Finally superheated steam is led into the remaining liquor and the dimethylaniline is steam distilled just as in the manufacture of aniline. The vapours are condensed and allowed to settle. Dimethylaniline being insoluble in water, separates out as an oily layer, which being quite pure is then run into iron storage tanks.

The molecular changes involved in this third operation are—

$$C_6H_5N\,H_2 \longrightarrow C_6H_5N\,(C\,H_3)_2$$
$$\text{Aniline} \qquad\qquad \text{Dimethylaniline}$$
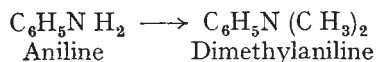
Two atoms of hydrogen in each molecule of aniline have been replaced by two groups of atoms each containing one atom of carbon and three atoms of hydrogen.

As yet the processes for converting one intermediate
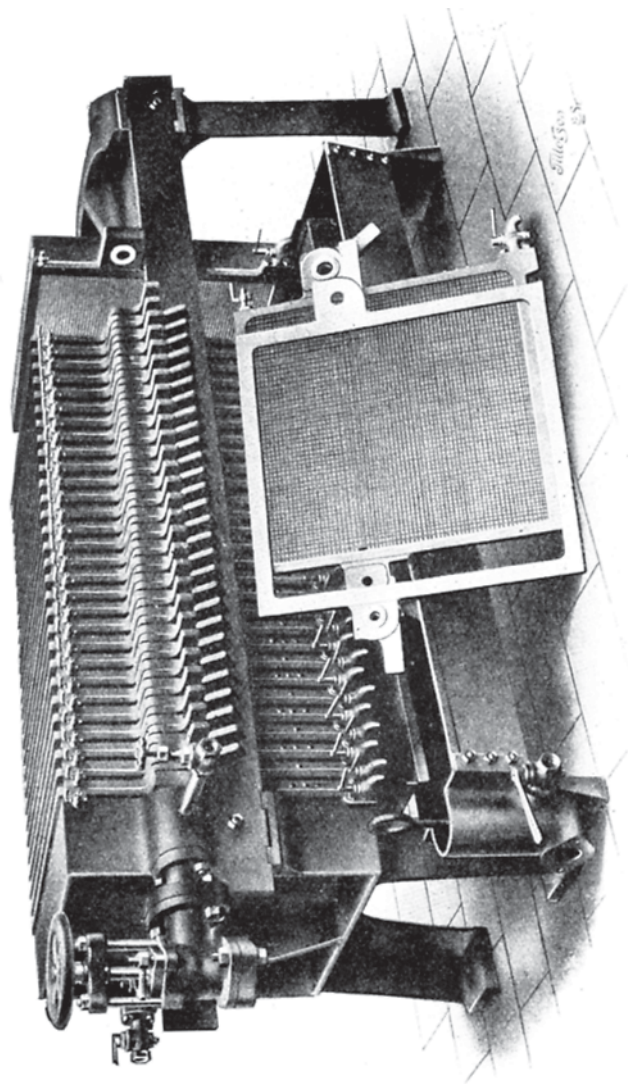
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into another have involved more or less high temperatures. In the next stage, the formation of nitroso-dimethylaniline, which is a crystalline solid, resort has to be made to the use of ice.

In a wooden vat a mixture of dimethylaniline and hydrochloric acid is cooled by the addition of ice. The mixture is thoroughly stirred and a solution containing sodium nitrite (a white solid very largely used by dye-makers for the manufacture of Azo dyes) is gradually added. A reaction ensues, and the dimethylaniline changes into nitroso-dimethylaniline which remains dissolved.

The molecular changes are—

$$C_6H_5N (C H_3)_2 \longrightarrow N O . C_6H_4(C H_3)_2$$
Dimethylaniline   Nitroso-dimethylaniline
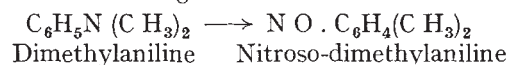
One atom of hydrogen in the molecule of dimethylaniline has been replaced by one atom of nitrogen and one atom of oxygen.

In order to save expense it is not usual to isolate the nitroso-dimethylaniline in a pure state, but to the reaction mixture is added zinc dust in small quantities at a time. A further reaction commences, the zinc dissolving in the hydrochloric acid present and at the same time the nitroso-dimethylaniline is converted into amino-dimethylaniline, thus—

$$N O . C_6H_4 . N (C H_3)_2 \longrightarrow N H_2 .^r C_6H_4N (C H_3)_2$$
Nitroso-dimethylaniline   Amino-dimethylaniline
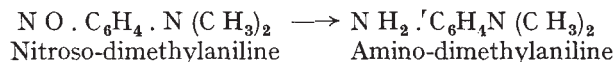
One atom in each molecule of nitroso-dimethylaniline is thus replaced by two atoms of hydrogen. This change is somewhat similar to that involved in the formation of aniline from nitrobenzene.

Thus after five distinct processes, amino-dimethylaniline is obtained from benzene, and from this the dyestuff methylene blue can be directly made.
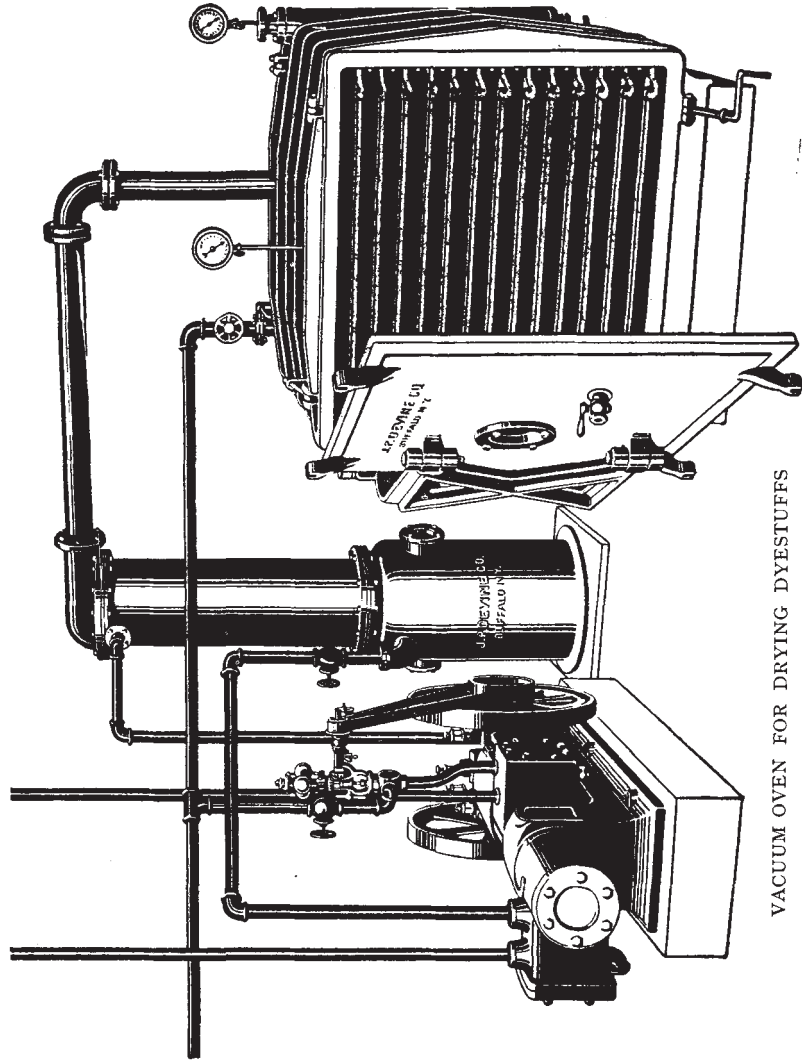
VACUUM OVEN FOR DRYING DYESTUFFS

Again, there is no necessity for isolating the inter-
mediate amino-dimethylaniline.in a pure form, so the
reaction mixture in which it is contained is used directly.
To this is added just sufficient caustic soda to neutralize
all excess of acid. Then sulphate of alumina is added,
and after stirring for about half an hour solutions
containing sodium thiosulphate (the *hypo* of the pho-
tographer) and sodium bichromate are quickly added
in succession. A further addition of dimethylaniline
and sodium bichromate is then made, followed by a
solution containing zinc chloride. Finally, the whole
reaction mixture is boiled for about an hour.

When the heating is discontinued and the mixture
allowed to cool, bronze coloured crystals of the dyestuff
—methylene blue—separate. These are filtered off
by means of a filter-press, and after being purified by
recrystallization are dried.

The reaction in which the methylene blue is formed
is a complex one, but it results in the union of two
molecules of amino-dimethylaniline with one atom of
sulphur which is derived from the sodium thiosulphate.

The difference between the molecules of benzene and
methylene blue is shown in the formulae—

Benzene   Methylene Blue (hydrochloride)
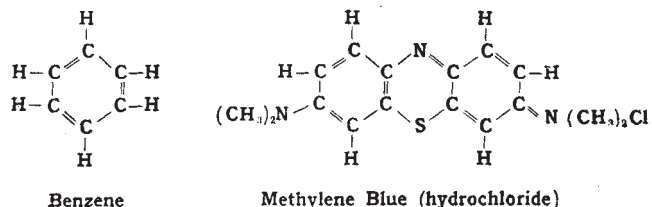
From the above description some idea can be formed
of the difficulties which have to be solved before a single
dyestuff can be manufactured. Yet over a thousand

dyes have to be made before dyers consider that they have an adequate range of colours. The reader will thus appreciate the task of those pioneers who are endeavouring to establish a dye-making industry in England.

CHAPTER IV

MANY methods are used in the dyeing of fabrics, and although dyes which can be bought in shops for purposes of dyeing at home are usually applied by simply dissolving them in water and steeping the fabric in the solution so obtained, it is seldom that so simple a method is used in dyeing on the large scale.

It is the task of the dyer to dye as much cloth as he can with as little dye as possible. So that after the dyeing operation is completed, the used dye liquor must be almost exhausted of its colour. For this purpose then, various substances are added to the bath which have the effect of rendering the dye less soluble, and so forcing it into the cloth. According to the circumstances, these substances are neutral, acidic or alkaline.

Furthermore, not all dyes are soluble in water alone, so that special chemicals have to be added in order to aid the solution of the dye. And since these additional substances are often of a corrosive nature the dyer has always to take into consideration the nature of the fabric being dyed. This, of course, must be injured as little as possible.

It is thus evident that the methods used for dyeing fabrics are largely dependent on the fabrics themselves. It will, therefore, be useful to consider some of the characteristic features of those textile fibres such as cotton, wool, silk and linen, which are commonly used for clothing.

Cotton fibres consist of the hairs which are attached

to the seeds of the cotton plant. And, although this plant will grow anywhere within 2,000 miles of the Equator and is largely grown in Egypt, China and Brazil, it is in America that more cotton is grown than in any other country. When Columbus discovered America he found that cotton clothing was in common use.

In America, the cotton seed is usually sown about April in elevated ridges of ploughed land which are some 5 ft. apart. The cotton plants appear about one week later, and are then thinned with a hoe until they are about 15 ins. apart. During the next two months, the hoe is constantly used so as to check the growth of troublesome weeds while the cotton plant attains a height of 8 ft. and bursts into bloom.

The flowers are coloured with white and red, and after lasting about four days, they drop off, leaving a small boll or capsule. This grows on into August, when it reaches the size of a hen's egg and bursts so as to expose a fluffy mass of cotton. Each boll contains thirty-two to thirty-six seeds, and the cotton fibres are attached to these.

Cotton picking is then commenced, and this is mostly done by hand since machinery is not entirely satisfactory. All the bolls do not ripen together, so that it is necessary to pick over the fields three times. The average yield of cotton is 200 lbs. per acre.

Freshly gathered cotton contains only about one-third of its weight of fibre, the remainder consisting of seeds. These are separated by passing the cotton through ginning machines which comb the seeds from the fibres. The ginned cotton is then compressed into bales so as to save space in transport, and then some months later may be spun and woven into fabric.

Linen is also a vegetable fibre, and is obtained from the best fibres of the flax plant. It has been known

from time immemorial, and many Egyptian mummies are covered with linen wraps.

Although grown like wheat and oats, flax plants are never harvested with a reaper ; they are always pulled up by the roots. Moreover, since the mature plant yields coarse fibres, flax is gathered when it is scarcely two-thirds grown. Each flax stem is then about 25 ins. long, and consists of a woody core surrounded with a layer of long linen fibres held together by means of a glutinous substance.

On the harvest field it is usual to separate the flax seeds by drawing the stems through coarse combs. The stems are then ready for *retting*. In this process fermentation of the stems takes place and the glutinous matters are destroyed. The linen fibres are thus sufficiently loosened so that they can be easily separated from the wood by mechanical means.

In Ireland *water-retting* is usually employed, the flax stems being tied together in bundles and placed in baskets which are left for about twenty days in running or stagnant water. But in Germany and Russia *dew-retting* is preferred. In this method the stems are spread out over a grass meadow for a week or fortnight, and are occasionally turned and moistened if necessary.

The retted stems are then dried, crushed in a stamping mill and afterwards passed between rollers. They are then drawn through finer and finer combs until the pure linen fibres suitable for spinning are obtained. These are then woven into fabrics.

Italian linen is very lustrous, but the best linen is produced in Ireland and Belgium. Linen from other countries is usually strong but coarse.

As is well known, wool, of which about 1,000,000 tons are produced each year, consists of the hairy covering of the sheep. The greater quantity is obtained by the

annual shearing of sheep, but a certain amount is also taken from sheep which have been slaughtered. Since, in the latter case however, it is customary to treat the skins with lime or sodium sulphide so as to aid removal of the wool, the fibres obtained are much inferior to those obtained from the live animal.

Various qualities of sheared wool are known ; some being distinctly lustrous. Again, in some wools, the fibres are relatively short—1 to 2 ins.—while in others the length of the fibre sometimes extends to 6 ins. These two classes are known as short and long stapled wools, and different methods are used for making them into fabrics. Unlike cotton and linen, the natural wool fibres contain a large amount of fat and other impurities, which, of course, have to be removed before dyeing.

Silk was probably first utilized in China over some four thousand years ago. Since then the industry has spread to India and Japan, and in later years to France and Southern Europe. The manner in which silk is obtained is very interesting.

The eggs of the silk worm, which resemble turnip seeds and are yellow in colour, are placed in incubators kept at about 70° Fahrenheit. At the end of thirty days the silkworms hatch, and they are then removed to wickerwork shelves and there fed with freshly dried cut-up mulberry leaves. Each silkworm then lives for about thirty days, during which time it eats about an ounce of leaves, sheds its skin four times, and attains a length of $3\frac{1}{2}$ ins., and finally weighs about one-sixth of an ounce.

After the fourth moult, a silkworm climbs upon twigs which are provided, and there encloses itself within a silken cocoon which is often one and a half inches long and three-quarters of an inch across, and takes three days to spin. The cocoon actually consists of a

continuous double silk fibre from 500 to 4,000 yards long, and which is discharged from two glands situated underneath the silkworm's mouth.

The best cocoons are selected for breeding, and for this purpose are placed in a warm room. In about two weeks time the dirty white moth which has developed within, moistens one end of the cocoon with saliva, forces the silk threads apart and creeps out. The moths immediately begin to pair, after which each female lays about 400 eggs and then dies. These eggs are collected, and those free from disease are used for future breeding.

All the other cocoons are steamed so that all life within them is destroyed. Then after steeping them in hot water so as to soften various gelatinous matters, the silk thread is reeled, and is ready for manufacture into fabrics.

It has, of course, always been recognized that there are very definite differences between fibres derived from vegetable sources, e.g. cotton, linen, hemp, jute, etc., and those obtained from animals, e.g. wool and silk. In the simple act of burning, say wool and cotton, it will be noticed that whereas wool burns difficultly and emits a strong odour resembling that of burning horn, cotton will burn easily but no distinctive odour is produced. This is mainly due to the fact that cleansed vegetable fibres are almost solely composed of cellulose consisting of carbon, hydrogen and oxygen, while animal fibres, though varying much among themselves in composition, nearly always contain nitrogen and sulphur in addition to the elements present in cellulose. It will be seen that these differences in composition manifest themselves very distinctly in the operations of dyeing.

Under the microscope, wool, cotton, linen and silk fibres can be easily distinguished from one another. Cotton fibres resemble short lengths of twisted ribbon;

wool fibres appear as flexible rods covered with scales (overlapping like the scales of a fish) ; linen fibres are round but are notched at regular intervals, while silk threads are extremely long and have a slight longitudinal twist.

A most important difference, however, between the animal and vegetable fibres is shown in their resistance towards liquors of an alkaline character. Such liquids have no deteriorating effect on cotton and linen. But on the other hand wool and silk are converted into a gelatinous mass, and finally dissolve when treated with caustic alkalies. So that, as will be subsequently seen, those dyes which can be applied only when dissolved in strongly alkaline solutions cannot be used for dyeing animal fibres.

Wool, however, is able to resist the action of acids much better than cotton and linen. Consequently, the dyeing of wool can be effected, as is often necessary, with dye liquors having an acid character. If it was attempted to dye vegetable fibres under similar conditions, they would be so deteriorated as to be almost worthless.

The two classes of fibres also differ considerably in their activity towards dyestuffs. Wool and silk appear to have a peculiar combination of basic and acidic properties which enables them to unite with a large number of dyes. That is, in numerous instances these fibres can be dyed directly by simple immersion in a solution of the dye. Cotton, however, is very inert, and only with a relatively small number of dyes can it be dyed directly.

This difference between the animal and vegetable fibres is also evident in the behaviour of the dyed fabric. Thus, indigo is faster on wool than when dyed on cotton. Many Azo dyes also have a superior fastness on wool

and silk. On the other hand aniline black which is so fast on cotton, can only be applied with great difficulty to wool, and the resulting shade is by no means fast.

Wool and silk also have widely differing properties, the former being usually somewhat more reactive towards dyestuffs than the latter.

Mention should also be made here of artificial silks, since these textile materials are becoming increasingly important. There are many varieties of these silks, but they are all composed of cellulose, and are all inferior to real silk. At the present time, three kinds of artificial silk — Chardonnet, viscose and cellulose-acetate — are being extensively manufactured.

Chardonnet silk is made from collodion, a nitrated form of cotton, while cellulose-acetate silk is made from a product obtained by heating cotton with acetic acid under special conditions. Viscose silk differs from both of these varieties, since it is usually made from the cellulose present in wood pulp, and the manufacturing process involves the use of caustic soda and carbon bisulphide.

All these varieties are produced by forcing a solution of the cellulose through small orifices into a coagulating liquid. A soft pliable thread is thus obtained, and this is well washed in water in order to remove the solvent and is then dried.

As might be expected, the dyeing properties of these artificial silks vary considerably. Thus Chardonnet silk has acidic properties which cause it to resemble wool in its behaviour to certain dyestuffs. On the other hand cellulose-acetate has even less affinity for dyestuffs than ordinary cotton, although methods have now been discovered by which its reactivity in this respect can be much improved. Viscose silk resembles cotton in all its properties except that it is usually somewhat more reactive towards certain chemicals and dyestuffs.

CHAPTER V

THE PREPARATION OF FABRICS FOR DYEING

IT is, of course, obvious that for dyeing clear and bright shades the fabric must first be thoroughly cleansed and bleached. Only in those cases where fabric is to be dyed in black or drab shades can unbleached cloth be used. So that from the dyer's standpoint, the removal of the impurities in textile fabrics is a most important operation.

The chief impurities in raw cotton consist of the natural colouring matter, wax-like substances, and a small amount of mineral matter. During the processes, however, by which cotton is spun and woven into fabric various sizing compositions containing oils and starches (wheat flour is generally used) are added as assistants. So that when cotton fabrics reach a bleaching and dyeing works they may contain about 10 per cent of impurities, which must be removed before dyeing.

Linen contains more impurities than cotton, but raw wool and silk are perhaps the most impure of the textile fibres.

It is only intended to deal here but briefly with the various processes adopted for the cleansing and bleaching of fabrics, since fuller information can be obtained elsewhere. But, by doing so, we shall the better be able to understand how faulty and careless bleaching can add very considerably to the difficulties of the dyer.

The first process in preparing cotton fabrics for dyeing is to remove the substances which have been added

39

during spinning and weaving. For this purpose, the fabric, usually after singeing off the loose fibres adhering to the face side, is passed through a solution containing diastase and then allowed to lie in a heap overnight. Diastase is a curious organic ferment which is manufactured from barley after it has germinated under suitable conditions, and it has the power quickly to convert a thick starch paste into a thin fluid. Consequently, on the following day, all starchy impurities and most of the loosened mineral matters in the fabric are easily removed by washing. The cloth is then ready for what is known as the *alkali boil* or *kiering*.

This alkaline treatment can be carried out in slightly different ways, but in all the principle remains the same. The cotton fabric is evenly packed inside the kier, which resembles a steam boiler placed on end, and is there subjected to a boiling liquor containing lime. So as to ensure that the fabric is uniformly treated in this process, arrangements are fitted to the kier, so that the liquor is continuously withdrawn from the bottom, returned to the top of the kier, and so sprayed on to the fabric within. The treatment lasts for several hours, and the fabric is then withdrawn from the kier and well washed in water so as to remove much of the lime and the loosened impurities. The remaining lime is then completely removed by treating the fabric with a weakly acid solution, and then, after another washing with water, the fabric is returned to the kier and boiled as before.

This time, however, a liquor containing either caustic soda or sodium carbonate or both is used. After another wash in water most of the impurities originally present in the fabric have been removed. Under certain circumstances the boiling with lime is omitted. The natural colouring matter of the cotton, however, is not
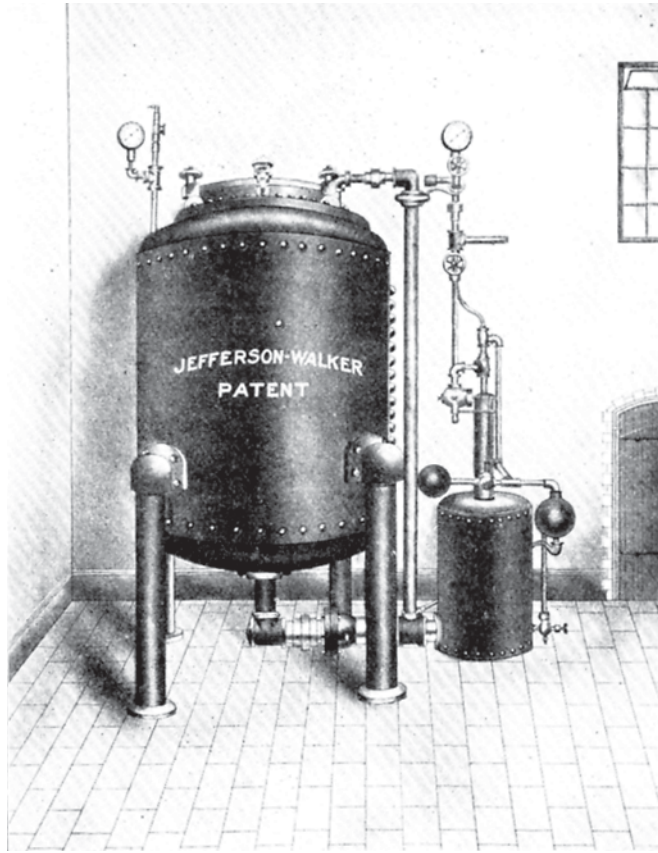
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affected by kiering so that this has to be destroyed by a further bleaching operation.

In this bleaching process proper, the cotton fabric is thoroughly saturated with a weak solution of chloride of lime and then allowed to lie for a short time. It is then washed and passed through water to which some acid has been added, and finally washed completely free from all traces of the bleaching powder. After this the fabric usually has a pure white appearance and is ready for dyeing. As is to be expected, cotton fabric loses considerably in weight during bleaching.

The methods used for bleaching linen are very similar to those employed for cotton. But the details of the processes are somewhat modified so as to allow for the fact that linen contains more impurities and is less resistant to acids, alkalis and bleaching powder than cotton.

Wool is so easily affected by alkalis, and, moreover, it contains so much impurity of a fatty nature that its treatment is quite different from that of the vegetable fibres. Also, since the difficulties of spinning raw wool are so great, wool is always cleansed or scoured in a loose state. Furthermore, the actual bleaching of wool is a much less important process than it is in the case of cotton.

Scouring is carried out by treating the wool with a soap solution to which sodium carbonate is often added. But the scouring must not be conducted at too high a temperature since the wool would acquire an unsatisfactory harsh feel. After treatment the loose wool can be dyed directly without further treatment, but, if before dyeing it is woven into cloth, then this must be again scoured.

However efficiently wool is scoured it still retains a slight yellow colour, and this must be removed by

bleaching if the wool is to be dyed with pale or pure shades.

The bleaching of wool cannot be carried out with bleaching powder, since this, under the conditions which would be necessary, would have a harmful effect on the fibre, so that wool is usually bleached by means of burning sulphur. In some cases, however, wool is bleached by means of special chemicals such as hydrogen peroxide or peroxide of sodium, but this is more expensive than the sulphur bleach.

In the sulphur bleach moistened woollen yarn in the form of hanks is suspended on rods within a chamber, which is connected with a smaller chamber. In the latter is an iron pot in which sulphur is slowly burnt. The fumes of sulphur dioxide pass into the large chamber and there bleach the wool. When the bleaching is complete the chamber is opened and the wool being exposed to fresh air gradually becomes freed from the sulphur fumes. Wool, however, retains sulphur dioxide very persistently, so that it is sometimes found necessary to remove the remaining traces of this gas by immersing the wool in a solution containing hydrogen peroxide.

For the bleaching of woollen piece goods a continuous process is used. The fabric enters the bleaching chamber (often known as the sulphur stove), and passes over a number of wooden rollers, so that when it leaves the chamber it is thoroughly bleached.

In all cases, since dry wool cannot be satisfactorily bleached with sulphur dioxide, the wool entering the stove must be damp. Usually about seven pounds of sulphur are used for each hundred pounds of wool.

Like the other textile fibres, raw silk requires considerable cleansing treatment before it acquires the soft lustrous properties which are possessed by silk garments which may be purchased in shops. It has been pointed

out previously that raw silk consists of two silk fibres cemented together by means of a gummy substance known as sericin, so that scouring is the first process to which raw silk is subjected, and has for its object the removal of the sericin.

As a result of scouring silk loses very considerably in weight. Usually Chinese and Japanese silks lose about 20 per cent, and European silks 30 per cent. And since silk is always sold by weight this loss is not desired by the silk merchant, so that much silk is given only a moderate scouring treatment, in which the loss of weight amounts to about 8 per cent only. This treatment, however, is just sufficient to deprive the raw silk of its harsh handle. Partially scoured silk is known as " souple " silk.

But whether silk is thoroughly or only partially scoured the operation is carried out in the same manner. The raw silk is immersed for about one hour in a boiling solution containing 20-30 per cent of soap. The sericin softens and ultimately dissolves in the soap liquor, while at the same time the silk fibres separate and gain in lustre and suppleness. Sometimes this treatment is repeated in a weaker soap solution, but finally the silk is well washed in water and then dried.

For the production of souple silk only weak soap solutions are used in the scouring, and they are maintained at a moderate temperature.

The scouring liquors can be used several times until they contain so much sericin that they fail to function properly. The spent liquor, however, is not thrown away but, as will be described later, is used as a valuable assistant in the processes by which silk are dyed.

Silk by scouring alone acquires a very satisfactory appearance, but for the production of delicate shades such silk must be further bleached. For this purpose

the silk is subjected to the fumes of burning sulphur under much the same conditions as used for wool. To some extent, however, the bleaching of silk is also affected by treatment with solutions containing oxidizing substances such as hydrogen peroxide or sodium perborate.

Souple silk, is often bleached in a solution containing sodium nitrite and sulphuric acid or a weak *aqua regia*— a mixture of nitric acid and sulphuric acid.

Artificial silk is bleached by methods similar to those used for cotton. Owing, however, to the serious loss of strength which occurs when artificial silk is immersed in water, the bleaching operations demand much care and attention.

Mention must also be made here of the process known as Mercerization, which is very extensively carried out on cotton yarns, but more particularly on cotton fabrics. The process is named after John Mercer, the discoverer, and it confers on cotton a lustre which approaches that of true silk. At the same time, however, after mercerization, cotton has an increased affinity for most types of dyestuffs, and cotton is often mercerized for this purpose alone.

In the mercerizing process, the cotton (pure cellulose) is thoroughly impregnated with a strong solution of caustic soda maintained at ordinary temperature. The cotton forms with the alkali a comparatively unstable compound, for, when the so treated cotton is thoroughly washed under tension, acidified and again washed, it assumes its original form, has an increased lustre, and consists of pure cellulose. If, however, fibres of mercerized and unmercerized cotton are compared under the microscope, it is seen that mercerization has caused the natural twisted flat ribbon-like cotton fibres to shrink in length, swell, lose their twist, and

take the form of cylindrical rods. The gain of lustre is undoubtedly due to these physical changes, but experience also shows that unless during the washing the fabric saturated with caustic soda is stretched out to its original width and length, a satisfactory increase of lustre is not obtained.

The mercerization of cotton fabrics is usually carried out by means of a specially designed machine and the illustration shows one of the most modern and perfect type (made by Sir James Farmer Norton & Co., Ltd.) at present designed by textile engineers. It is the result of considerable scientific research and practical experience. The mercerizing range consists in the first place of an impregnating mangle, with a caustic soda impregnating tank underneath. Here the cloth receives a thorough impregnation and immersion in caustic soda. After being immersed twice and receiving two powerful squeezes with the mangle rolls, the cloth is led on to the clip stenter frame, where it is gripped by automatic clips. These clips hold the cloth under tension whilst at the same time it is sprayed with hot water or weak solution of caustic soda. The washing on the stenter is arranged progressively, clean water being sprayed on to the cloth at the delivery end of the stenter, the washings becoming progressively stronger at each spray. The washings are collected underneath in a tank and pumped to a separate storage tank.

Connected with this machine is a patent caustic lye recuperator, by which a large proportion of the caustic soda used may be recovered and used again. Where this is used the cloth on leaving the stenter passes over a compensator, which regulates the tension of the cloth, and then enters the steaming box, which is divided into twelve compartments. In each of these compartments a jet of steam plays on the cloth, and the caustic soda
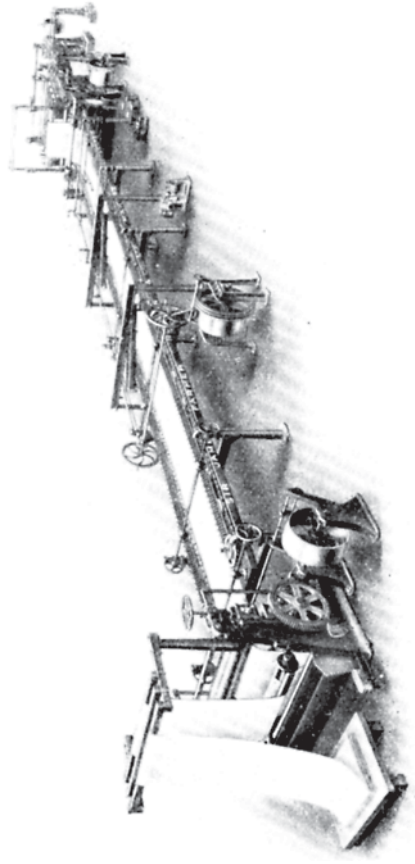
MERCERIZING MACHINE

is dissolved by it and collects at the bottom of each compartment. These compartments are arranged on an incline so that the caustic soda collects at the bottom of the lowest compartment, from which it is pumped to the collecting tank. The cloth is now reasonably free from caustic soda and passes through a compound levered nip into the washing-off tanks. Here it can, if necessary, be treated with a weak solution of acid in the first tank and thoroughly rinsed and washed in the remaining two. As a rule, however, where the caustic lye recuperator is used the cloth is so perfectly freed from caustic on leaving the recuperator that a treatment with acid is unnecessary. On leaving the washing-off tanks the cloth is then ready for bleaching, or if already white, for dyeing.

CHAPTER VI

DYEING : PRELIMINARY CONSIDERATIONS

BEFORE describing the methods actually employed in the dyeing of fabrics it is necessary to consider briefly the principles on which these methods are based. For, to a large extent, the dyer's art is fashioned by circumstances dependent on the properties of the dyes and textile materials used.

It has previously been pointed out that dyestuffs may be classified by their molecular structure, but this classification, although very useful to dyemakers, is not satisfactory to all dyers. For even in these times many skilled dyers, although perfectly familiar with the tinctorial properties of the various dyes and able to produce perfectly satisfactory dyeings, know little about the chemistry of the dyes which they use. So that dyers have adopted a classification of dyes which is largely dependent on their constitution and partly on their properties. The following classes are those which are generally recognized—

1. Acid dyestuffs.
2. Mordant dyes.
3. Basic dyes.
4. Direct cotton dyestuffs.
5. Sulphur dyestuffs
6. Vat dyes.
7. Ingrain dyestuffs
8. Natural dyestuffs.
9. Mineral dyes.
10. Miscellaneous dyes.

Acid Dyes are largely used for wool and silk, but are seldom applied to cotton since no satisfactory method for fixing them on this fibre is known. These dyes chiefly consist of Azo compounds, and being reasonably cheap they are largely used for ladies' dress materials, gentlemen's suitings, and for carpet and knitting yarns. An important consideration affecting their application to animal fibres is that they are *substantive* dyes. That is, no preparation of the fabric is necessary before dyeing, and wool and silk are dyed by merely steeping them in a warm acidified solution of the dyestuff.

Mordant Dyes, on the other hand, are not applied to unprepared fabrics, since they have but little affinity for textile fibres and would not, therefore, be fast to washing. Yet, when applied by suitable methods, these dyes yield shades which are generally very fast. As a rule, mordant dyes are not used for cotton except in printing, but are very largely employed for the better class of woollen fabrics and to a lesser extent for silk.

With metallic salts mordant dyes readily form insoluble and permanent coloured compounds which are known as *lakes*. It may generally be considered that a metallic salt is formed by the union of an acid with the oxide of a metal, and that the lake is produced by union of this metallic oxide with the dyestuff. So that mordant dyestuffs are always applied to fabrics which have been so treated (mordanted) that they contain an insoluble metallic oxide. When such a mordanted fabric is immersed in a solution of a mordant dye, the metallic oxide within the fibres of the fabric attracts the dyestuff, and the insoluble colour lake so formed becomes intimately fixed within the fabric which thus becomes dyed.

Usually it is not difficult to mordant animal fibres such as wool and silk. When these fibres are boiled

in a solution of a metallic salt they have the power to decompose the salt and absorb the metallic oxide. This oxide being insoluble is thus fixed within the fibres and is very fast to washing. Frequently, however, various substances are also added to the mordanting liquor with the object of assisting the decomposition of the metallic salt.

Cotton, however, cannot be mordanted so easily, since it is of itself unable to absorb a metallic oxide. So that, in mordanting this fibre, it is usual first to thoroughly saturate the cotton fabric with a solution of a metallic salt, and then immerse it in a solution of an alkali or other substance capable of decomposing the salt with the formation of the metallic oxide. In this manner the oxide of the metal becomes intimately deposited within the fabric, and it is then merely necessary to wash the fabric thoroughly free from all soluble substances.

In another mordanting process the cotton is saturated with a mordanting substance consisting of a salt derived from a volatile acid such as formic or acetic acid. The cotton is then partially dried and steamed so that the acid is driven off, leaving the metallic oxide within the cotton.

It is thus evident that the mordanting of cotton with metallic substances is somewhat troublesome, and for this reason the mordant dyes are not often used in cotton dyeing.

The metals most commonly used for mordanting fabrics are chromium (the same metal as enters into the composition of stainless cutlery), aluminium, iron, tin and copper.

In the **Basic Dyes** are included many of the most brilliant dyestuffs yet discovered. Perkin's mauveine was a basic dyestuff. Unfortunately this brilliancy is

also associated with a certain lack of fastness to light
and washing. But nevertheless these dyestuffs are of
great value.

Basic dyes are not largely used for wool since they
can be replaced in most instances by the faster acid
and mordant dyes. However, they are frequently
applied to silk in cases where fastness is of less impor-
tance than brilliance. For the dyeing of cotton,
however, these dyes are largely used.

Basic dyes cannot be applied directly to cotton
since this fibre has no affinity for them. But cotton
which has been mordanted with tannic acid is able to
retain them firmly. So that for cotton, basic dyes
really belong to the *mordant* dyestuffs. But whereas the
latter, as already indicated, are used on metallic mor-
dants, the basic dyes are almost exclusively used on a
tannic acid (an organic substance) mordant, although
this is nearly always finally fixed more strongly by means
of antimony salts.

Direct Cotton Dyes, as their name implies, are especially
suitable for the dyeing of cotton. For this purpose they
are very popular since they can be applied directly to
the unprepared fabric. With no other class of dyestuffs
is it so easy to carry out the operations of dyeing.
Moreover, direct cotton dyes, on the whole, have a
good fastness to light and washing.

Direct cotton dyes are, however, not solely used for
cotton. They are frequently used for wool and silk,
and especially for union fabrics (those composed of
more than one kind of fibre, e.g. cotton-wool, cotton-silk,
wool-silk). The annual consumption of direct cotton
dyes is greater than that of all the other classes together.

Among **Sulphur Dyes** are many important dyes for
cotton. During the Great War they were very much
employed for producing khaki shades. Owing to the

fact that these sulphur dyes are soluble only in strongly alkaline solutions, they cannot be used for wool and silk without deterioration of the fabric unless special precautions are taken. So that, in practice, fabrics composed of animal fibres are seldom dyed with sulphur colours.

A peculiarity of this class is that it contains no true red dyestuff, and all attempts during the past twenty years have failed to produce one. Moreover, the yellow members are not very fast to light. On the other hand, for brown, drab, blue and black colours, sulphur dyes are exceptionally suitable since the shades obtained by their use are very fast to all influences except bleaching. Hundreds of tons of sulphur black dyes are used each year for the dyeing of black cotton fabrics.

All sulphur dyes contain sulphur, and their properties are entirely dependent on its presence. In their usual state they are extremely insoluble in water. However, by means of reducing agents they can be converted into a soluble form (often more or less devoid of colour) which allows them to be applied to cotton fabric. If the fabric is then exposed to the air oxidation takes place and the dye takes up its original coloured insoluble state. The fabric thus becomes coloured by the dye which is thus intimately fixed within the fibres. On these facts the methods for dyeing with sulphur dyes depend.

Vat Dyes include many of the fastest dyestuffs known. At the same time, however, they suffer from the disadvantage that they are expensive. Hence these dyes are not very extensively used. Many dyemakers have spent much money and labour in research upon them, but it has yet to be seen whether vat dyes are going to be what is claimed for them—the dyes of the future.

In their methods of application vat dyes resemble

sulphur dyes. Thus vat dyes in their usual form are insoluble and cannot be applied to fabrics until brought into a soluble state. This is accomplished by means of reducing processes so that aerial oxidation of the dyed fabric is an essential part of the dyeing process. Moreover, the dye liquor is generally required to be strongly alkaline, so that with few exceptions, as in the case of indigo, vat dyes are almost exclusively used for cotton.

The **Ingrain** dyestuffs differ from those dyes described previously since they are not prepared apart from the fabric, but are actually formed during the dyeing process. Moreover, all ingrain dyes are Azo dyestuffs, since this type of dye can be easily and rapidly produced without involving the use of solutions which would have a deteriorating effect on the fabric being dyed.

In the usual process fabric is saturated with one component of the dyestuff which is to be ultimately produced, and is then treated so that when it is passed into a solution containing the other component, immediate combination takes place, the insoluble dyestuff being intimately distributed within the fibres of the fabric.

It is obvious that these dyestuffs can have only a limited use, but by their use certain shades which are very bright and fast to washing can be obtained.

Nearly all **Natural** dyestuffs are mordant dyes. But though at one time extensively used, they have now lost most of their importance. Their mode of preparation from plants and berries prevents them from being available to dyers in a uniformly pure state, and but few natural dyes have any superiority over the more reliable coal tar dyes. Moreover, those natural dyes such as indigo and madder which were of special value have been synthesized, and are now made from coal tar

products. However, while logwood and fustic are still used, the former being particularly useful for dyeing black silk, other natural dyes such as Persian berries, cutch, cochineal, weld and safflower are only employed to a trifling extent.

As will be inferred, **Mineral Dyes** have no connection with the coal tar dyestuffs. They are really pigments such as are used for paints and enamels, and are metallic compounds. Like the ingrain dyestuffs, however, they are always produced within the fabric. Mineral dyes are only used for the colouring of fabrics in special circumstances. Heavy qualities of khaki coloured army cloth are produced by means of iron pigments.

Finally, in the term **Miscellaneous** are included dyes which are applied to fabrics by special methods. Among these dyes aniline black has the greatest importance.

As will be seen in the next chapter, the dyeing process is usually carried out by immersing the fabric for a suitable period in a solution of a dyestuff maintained at a suitable temperature. But such a simple procedure is not often possible, and anyone can discover the reason if he cares to carry out a few experiments with any dye such as is sold cheaply for purposes of dyeing at home.

Thus, if to a solution of a cotton dyestuff is added a considerable amount of ordinary table salt, it will be noticed that a large amount of the dyestuff will fall out of solution. This is in agreement with the fact that most dyes are sparingly soluble in brine solutions. So that, in dyeing, the rate of dyeing can be increased by the addition of salt, the dyestuff then being precipitated within the fibres of the fabric. Instead of salt, Glauber's salt and many other substances can be used for this same purpose.

It is also not difficult to discover that a fabric is

dyed more quickly in a hot dye liquor than in one which is cold. On the other hand, careful experiments would indicate that some dyes dye less rapidly in boiling solutions than in those which are merely hot.

Further, when hard water is used it will be noticed that in dissolving the dyestuff a scum is formed. This scum is formed by union of the dyestuff and mineral matters which are present in the water, and which are the cause of its hardness. The formation of scum, of course, implies a waste of dye.

Moreover, while it is common knowledge that some dyes are sparingly and others easily soluble in water, perhaps only a few amateur dyers have ascertained that the solubility of a dyestuff can be much altered by the addition of alkalis or acids.

Some dyes show a great tendency to rush on to fabric which is being dyed so that it becomes unevenly coloured. Yet, by the addition of substances to the dye liquor which render the dye more soluble, this undesirable behaviour can be corrected.

It is thus evident that the dyeing process is largely dependent on the condition of the dye liquor. So that, as will be seen later, experienced dyers are able by additions to the dye bath to considerably control the operation of dyeing. The various substances which are added to the dye liquors for this purpose are called *assistants*, and their selection depends on the class of dyestuff being used.

Although over a thousand dyestuffs are in use, it is seldom that dyes are used singly. For almost all the colours which at present appeal to the public require the use of mixed dyestuffs. And the production of compound shades demands a considerable amount of skill on the part of the dyer.

Thus, while dyes of the same class can be mixed in solution, and a compound shade obtained by one process of dyeing, it is seldom that dyes belonging to different classes can be so used. For generally when solutions of dyes of different classes are mixed, the dyes combine to form insoluble compounds which are, of course, totally unsuitable for dyeing purposes. So that for compound shades it is generally necessary to select dyes of the same class ; the choice of the dyer is thus limited.
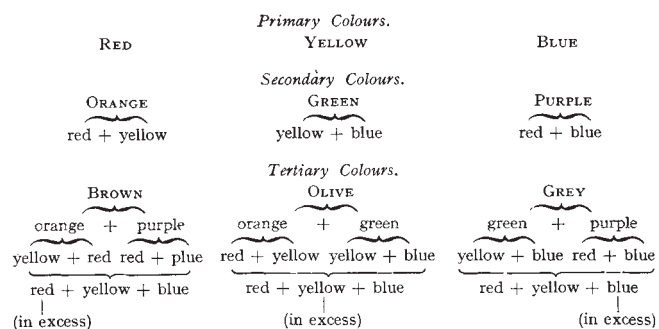
Again, for compound shades it is also necessary to use dyes which have about the same degree of fastness to light and washing. How disappointed would be the wearer of a green fabric if the blue component of this colour faded so that the fabric ultimately became of a dirty yellow shade !

But, while the above factors influence the dyer's choice, the fundamental principles underlying colour mixture must also be observed. For only in this way can the matching of a compound shade become an easy problem.

It has long been recognized among artists that for the production of any coloured pigment not more than three colours, red, yellow and blue are necessary. These colours are termed *primary* colours, and are characterized by the fact that they cannot be produced by the mixture of any other colours.

By mixture of the primary colours two at a time, three so-called *secondary* colours, orange, green and purple, are obtained. On the other hand, by mixture of three primaries one being in excess, by mixture of one primary with a suitable secondary or by a mixture of two secondaries, the *tertiary* colours, brown, grey and olive are produced.

These facts are summarized thus—

Primary Colours.

RED	YELLOW	BLUE

Secondary Colours.

ORANGE	GREEN	PURPLE
red + yellow	yellow + blue	red + blue

Tertiary Colours.

BROWN

orange + purple

yellow + red   red + plue

red + yellow + blue

(in excess)

OLIVE

orange + green

red + yellow   yellow + blue

red + yellow + blue

(in excess)

GREY

green + purple

yellow + blue   red + blue

red + yellow + blue

(in excess)

The shade of any secondary or tertiary colour can be modified by varying the proportions in which its primaries are combined.

Further consideration explains the characteristic subdued tone of a tertiary colour. For whenever three primaries are mixed a certain amount of black is produced ; the depth of the black being dependent on the relative proportions of the constituent colours. All tertiary colours, therefore, contain a certain amount of black.

CHAPTER VII

THE APPLICATION OF DYES TO TEXTILE MATERIALS

THE methods of dyeing textile materials are extremely varied, since they are dependent on the characteristics of the dyestuffs and also the nature of the textiles. Moreover, much cotton, wool and silk is dyed before being woven into cloth, so that dyeing processes are adapted for textile materials in three forms: loose, yarn and fabric.

With the object of reducing costs, dyeing is carried out wherever possible by means of machinery, and manual labour is reduced to a minimum. For the same reason, those machines which are continuous, the fabric entering at one end and emerging fully dyed at the other, are especially favoured. But such machines can be used only for the production of standard shades, such as Para red, aniline and sulphur blacks. So that at the present time, there are a limited number of standard types of dyeing machines which experience has shown to be reliable, and these are commonly used throughout the dyeing industry.

All dyeing machines have a common feature in that they are constructed so that within them textile material is continuously moved through a dye liquor, or a dye liquor is continuously circulated through the textile material, which is maintained stationary or which may also be moving. Further, all machines have arrangements by which the dye liquor can be cooled or heated.

Generally, in machines for the dyeing of textile material in loose form, the dye liquor is circulated.

59

Yarn in the form of hanks or skeins is generally moved through the dye liquor. For piece (fabric) dyeing the machines are arranged so that the fabric is passed backwards and forwards or continuously forwards through a dye liquor.

It is not proposed to describe these machines in detail
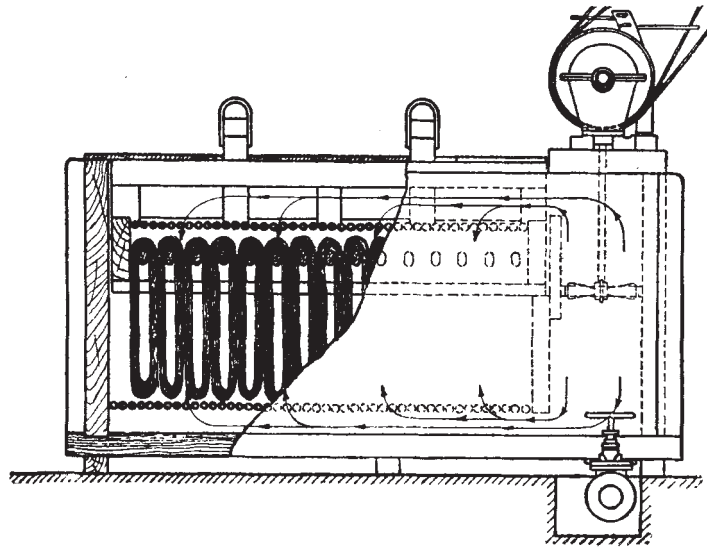
SKEIN DYEING MACHINE

as no good purpose would result, but the illustrations show all their essential features. Fuller mention, however, will be made of the *jig*, a dyeing machine which is to be found in every dye house, and although used only for piece dyeing it suggests the principles underlying most other machines.

Before the commencement of the dyeing operation, some 300 to 500 yds. of fabric are wound on one of

the top (larger) rollers. The dye liquor is then placed
in the bottom of the jig so as to cover the lower (small)
rollers, and is brought to the desired temperature and
state of dilution by means of the attached steam and
water pipes. The necessary dyeing assistants are also
added. The machinery is then started when the fabric
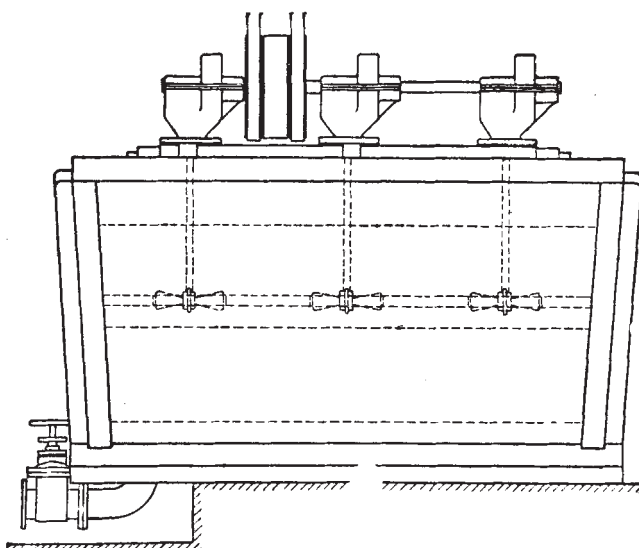
SKEIN DYEING MACHINE—END VIEW

is drawn through the dye liquor and wound on the
opposite top roller. The motion is then reversed and
the fabric is again wound on the first roller. With each
passage through the liquor the colouring of the fabric
becomes more intense, and the process is continued until
the desired shade is obtained.

In order that one end of the fabric may not be more
heavily dyed than the other, the dyestuffs are not all

added in the beginning, but are added from time to time. Moreover, in order that the dyeing may be followed, small pieces of the fabric are occasionally cut out from the bulk of fabric and washed and dried. From their appearance the dyer directs any additions of assistants or dyestuffs which may be necessary. Usually dyeing is completed by four to six passages through the liquor, and this takes about an hour.

After dyeing, the spent liquor is then run into the drain, the jig filled with water, and the fabric washed by one or two passages through this. Finally, the fabric is wound on to a removable roller which is then carried to a mangling machine. After being mangled the fabric is then dried by passing over a series of hollow cylinders through which steam is circulated.

In the case of loose textile materials, these, after dyeing, are dried in chambers with hot air.

A feature essential to all dyeing processes is that all parts of the textile material must be uniformly impregnated with the dye liquor. That is, during dyeing the relative motion between fabric and liquor must be maintained. Otherwise uneven or patchy dyeing will result.

Before describing the methods of dyeing in detail, mention should be made of a practice familiar to all dyers which is known as *shading* or *topping*. It has been previously pointed out that dyes of one class frequently have an affinity for those of another and therefore readily combine with each other. It is evident therefore that a dyed fabric may be considered as mordanted, for, on immersing it in a solution of a suitable dyestuff, the fabric will absorb some of the dissolved dye. The colour of the fabric will, therefore, be modified according to the colours of the dyes used. Under these
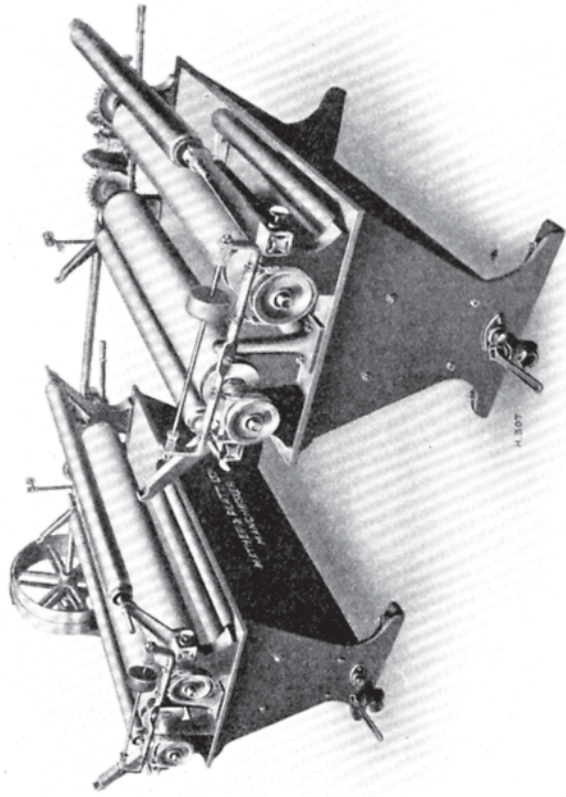
DYEING JIGS

circumstances the dyed fabric is said to be shaded or topped.

This operation is utilized by the dyer when he wishes to correct a dyed fabric which differs slightly from the desired shade. Also it sometimes happens that a dyed fabric appears too dull and requires to be brightened. Under such circumstances, the fabric is passed through a very weak solution of a suitable dyestuff.

For purposes of topping, basic dyes are very useful. They are very bright, and are readily absorbed by fabrics which have been dyed by means of direct cotton or sulphur dyestuffs. During the war, when indigo was scarce, an indigo blue shade was obtained by topping with methylene blue and methyl violet (basic dyestuffs) fabrics which had been dyed with a weak shade of sulphur black.

The Dyeing of Wool. More dyestuffs can be applied to wool than to any other fibre, so that it is not surprising to find that wool can be dyed with six classes of dyestuffs. In actual practice, however, sulphur and vat dyes (indigo excepted) are rarely applied to wool since they involve the use of strongly alkaline solutions. Moreover, basic dyes are only used to a limited extent, since on wool their fastness is not entirely satisfactory. Basic dyes are fugitive to light and but moderately fast to washing.

All the most important dyes for wool are contained in the acid, mordant and direct cotton dyestuffs.

Acid dyestuffs are very largely used and are easily applied. The assistants used with these dyes are almost invariably Glauber's salt and sulphuric acid, and both of these are cheap. In the dyebath the Glauber's salt renders the acid dyestuff more soluble, and in fact, wool which has been dyed with an acid dye can be largely stripped of its colour by immersion in a boiling solution of

this substance. On the other hand, the acid has the opposite effect and tends to precipitate the dye, and therefore tends to force the dye into the textile material. It is by balancing these two opposite tendencies that the rate of dyeing can be controlled.

Sulphuric acid is a strong acid so that when the
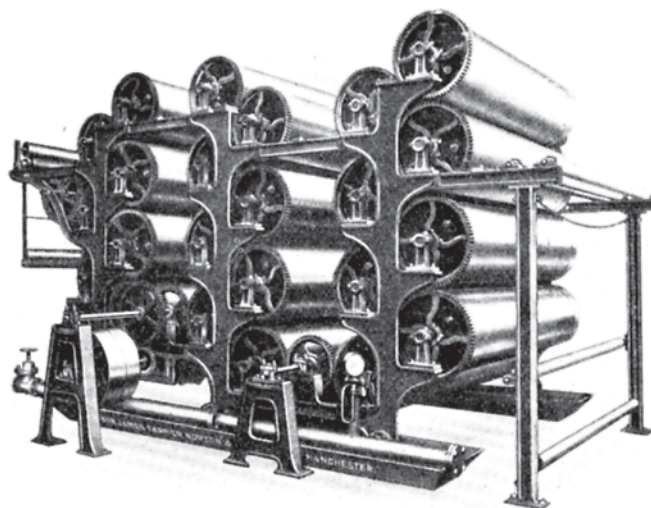
VERTICAL DRYING CYLINDERS FOR FABRICS

wool is dyed in the presence of cotton, weaker acids such as acetic (present in vinegar) and formic (present in stinging nettles and honey) acids are used as substitutes. But as these are less effective than sulphuric acid, larger quantities of them must be used.

The dye liquor usually contains 10–20 per cent[1] of

[1] All such percentages are calculated on the weight of textile material being treated.

Glauber's salt, 2–4 per cent of sulphuric acid, and 1–5 per cent of the dye according to the depth of shade required. Generally, it is made warm before the wool is entered. The dye liquor is then gradually raised to the boil and dyeing continued for about one to one and a half hours. In order that the dye liquor may be completely exhausted, further quantities of acid are often added towards the end of the dyeing operation.
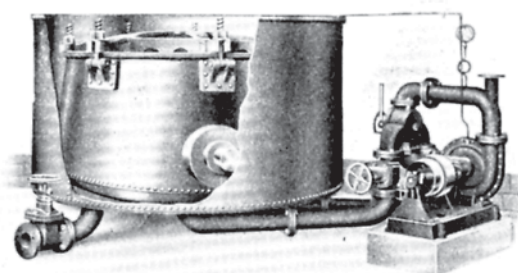
DYEING MACHINE FOR LOOSE MATERIAL

Finally the wool is thoroughly washed free from the acid dye liquor and is then dried.

While it will be noticed that the dyeing of wool with acid dyes is performed in one process, two operations are necessary in the application of the mordant dyestuffs. Sometimes, however, the operations of mordanting and dyeing can be carried out at the same time, but not always.

It has already been explained that mordant dyes are held within the fibres by means of insoluble metallic oxides, and they are, therefore, generally very fast to washing. It is for this reason that mordant dyestuffs are largely used for the better class of woollen materials.

In practice a chromium mordant is nearly always used, since chromium salts are cheap. Moreover, they can be applied to wool quite easily and yield excellent dyeings. Sodium bichromate is the mordanting substance which is almost universally used.

When wool is boiled in a solution of sodium bichromate, decomposition of the bichromate takes place, and some chromium in the form of chromium oxide becomes
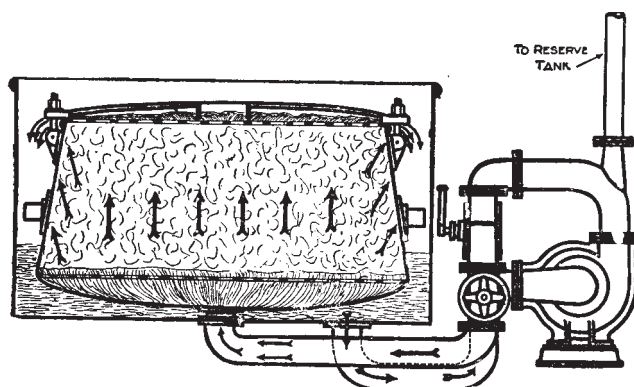
DYEING MACHINE FOR LOOSE MATERIAL—SECTION

deposited within the fibres. This deposit cannot be removed by simple washing in water, so that the fabric is thus mordanted with chromium. To assist the mordanting process, various substances such as cream of tartar, sulphuric, oxalic, acetic and formic acids are frequently added to the solution of the bichromate, but in all cases the result is the same—the deposition of chromium oxide within the fibres. When the chrome mordanted wool is then dyed, the dyestuff is attracted by the chromium and forms with it a fast colour pigment.

In practice, the application of the mordant dyes to wool is carried out by three methods—

1. Dyeing after mordanting.

2. Mordanting after dyeing.   (Top chroming method.)

3. Dyeing and mordanting together.   (Metachrome method.)

Wherever possible, the second and third methods are used, as they are easier and cheaper to carry out.

In the first method, the wool is boiled for one or two hours in a liquor containing 2-4 per cent[1] of sodium bichromate.   If formic acid is also added as an assistant, then less bichromate is required.   About 1–2 per cent of bichromate and 1–2 per cent of formic acid are the usual quantities employed.   The wool acquires a greenish colour and, when mordanting is complete, it is thoroughly washed in water.   The washing is important, since otherwise it will be possible to rub colour from the surface of the material after dyeing.

Dyeing is carried out by boiling the wool for one to two hours in a liquor containing the necessary quantity of dye, and usually a small amount of acetic acid.   The initial temperature of the dye liquor and the duration of boiling are, of course, dependent on the particular dyestuffs and the condition of the textile material being used.

Thus, for dyes which are known to give uneven dyeings, it is preferable to enter the textile material in a cold dye liquor.   Dyes of an easy levelling character may be used in a dye liquor whose initial temperature is comparatively high. ·

In the second method, the wool is first dyed by entering it in a warm liquor containing the dyestuff, Glauber's salt and some acetic acid as assistants.   This dye

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[1] The reader is again reminded that all such percentages are calculated on the weight of textile material treated.
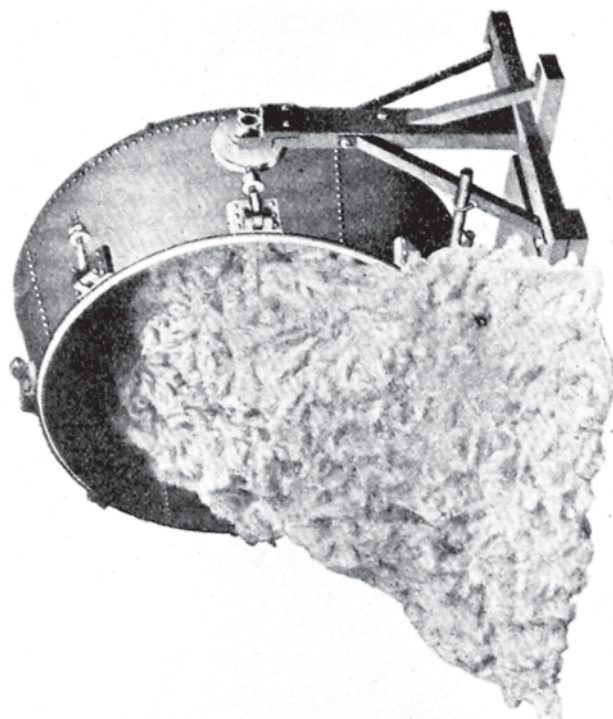
REMOVAL OF LOOSE MATERIAL AFTER DYEING

liquor is then gradually raised to the boil, and after boiling for about half an hour it is usual to add $\frac{1}{2}$-1 per cent of sulphuric acid, which has the effect of exhausting the dye liquor, that is causing the wool to take up the dye more completely whereby the dye liquor loses most of its colour. As soon as the liquor is exhausted sodium bichromate is added and the boiling is continued for another half an hour. The wool is thus chrome mordanted in the same liquor as was used for dyeing. As soon as possible the dyed and chromed wool is then washed and dried.

A disadvantage of this top chroming method is that the dyer finds some difficulty in dyeing the wool to exactly match his pattern, since the shade as determined by the dyeing process is often considerably modified by the subsequent mordanting. This disadvantage can often be overcome, however, if loose wool is being dyed, for if a batch of the wool is dyed slightly off shade, the dyer can so dye the next batch that when the two batches are mixed, as they must be before spinning and weaving, the resultant colour is correct. For this reason the top chroming method is more suitable for loose wool than for woven fabric, which being in the last stages of cloth manufacture must be exactly dyed to shade (that is, match a given pattern).

It is, however, the metachrome method which particularly appeals to dyers. For, by this process, the mordant dyes can be applied in one operation, so that a great saving of labour, time and steam is effected. Under the usual conditions, if sodium bichromate were added to the dye liquor at the commencement of dyeing, most of the dye would be precipitated and the liquor would be thus rendered unsuitable for dyeing purposes. If, however, sufficient of an alkali is added to the liquor, such precipitation is prevented, but with such a liquor

no mordanting or dyeing of the wool could be effected. If, however, during the dyeing, this alkaline dye liquor gradually became acid, then dyeing and mordanting of the wool could take place simultaneously. The metachrome method is a satisfactory process in which this ingenious reaction is carried out.

The wool is entered into a liquor which is just warm and which contains the dyestuff, sodium bichromate
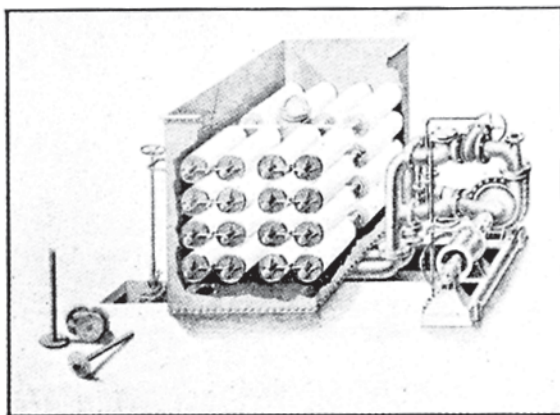
MACHINE FOR DYEING WOOL-TOPS

and a suitable amount of ammonia and ammonium sulphate or ammonium acetate. This dye liquor is then gradually raised to the boil and maintained at that temperature for about an hour. During that time ammonia gas is gradually liberated from the liquor so that it loses its alkalinity and becomes more and more acid. The dye and the chromium are then simultaneously absorbed and fixed by the wool. The simplicity of the process is obvious. Unfortunately

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not all mordant dyestuffs are suitable for this method, but it is employed wherever possible.

Although the direct cotton colours, as their name implies, are most important for cotton, they are also largely applied to wool. In fact, from a chemical standpoint the direct cotton dyes are so closely related to the acid wool dyestuffs, that they are used in much the same manner as previously described for those dyes, except that the dye liquor is made only slightly acidic. For this purpose, acetic acid is preferable to sulphuric acid.

An important application of the direct cotton dyes, however, is in dyeing of mixed fabrics such as those containing wool and cotton, or cotton and silk. This, however, will be dealt with later.

The Dyeing of Cotton. The large number of dyestuffs which are used for dyeing cotton are largely drawn from four classes : Direct cotton dyes, basic dyes, sulphur dyes, and vat dyes. Except in printing and special cases the mordant dyes are seldom applied to cotton, and no satisfactory method for fixing the acid dyes on this fibre is known.

Although many of the Basic dyestuffs are not very fast to light and washing they are, owing to their brilliance, extensively used on cotton. Before dyeing, however, this fibre must be mordanted with tannic acid.

Tannic acid exists as a white powder and can be handled without risk since its acid properties are so very feeble. Hence it can be dried into cotton fabric without this being in any way damaged.

If a solution of a basic dye is added to another containing tannic acid, the two substances immediately unite to form a coloured precipitate. Furthermore, it has been discovered that tannic acid can also unite with metallic salts (those of antimony are almost
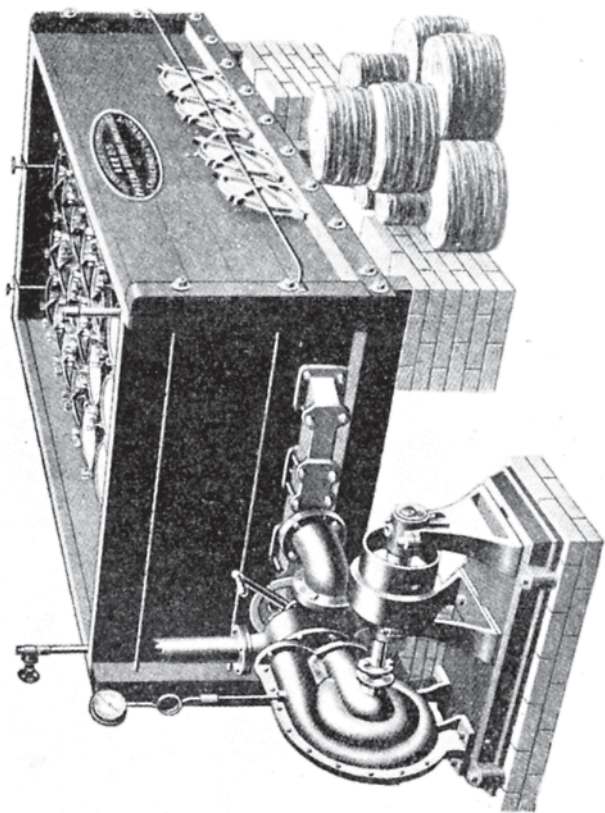
MACHINE WITH VITRALITE CANS FOR DYEING WOOL TOPS

exclusively used although iron, lead, chromium and aluminium salts can also be employed) to form insoluble compounds, and these retain the power of attracting dyes. But the compounds containing tannic acid, metal and dyestuff are more stable and insoluble than the similar ones in which the metallic constituent is absent.

Moreover, cotton itself has the power of absorbing tannic acid from solution. So that in large scale dyeing the following method, based on the above facts, is very largely used for preparing cotton cloth for dyeing with basic dyes.

The cotton is first steeped for two or three hours or even overnight in a hot solution containing 1–3 per cent of tannic acid. It is then lightly rinsed free from the unabsorbed tannic acid and immediately treated with a cold solution containing a salt of antimony— usually tartar emetic (potassium antimony tartrate). In this way an antimony tannate compound is fixed within the cotton and withstands the further light rinsing to which the cotton is subjected before dyeing.

The mordanted cotton is then entered into a cold solution of the basic dye which should be preferably slightly acidified. The acid prevents the dye from rushing too quickly on to the fabric and so leads to level dyeing. Under these circumstances the dye is attracted to the cotton, and this quickly reaches its full shade. Often it is unnecessary to heat the dye liquor at all, but when it is gently warmed a better exhaustion of the dye bath is obtained. Finally the cotton is lightly rinsed with water and dried.

The sulphur dyestuffs being in their usual form insoluble in water, require special methods for their application. For it is impossible to dye fabrics except with substances in a state of solution.

It appears that while under no circumstances can a sulphur dye be dissolved in an acid liquor, it is possible to obtain alkaline solutions. Thus when a sulphur dye is heated with a solution containing sodium sulphide or sodium hydrosulphite it immediately dissolves. If now air is bubbled through this coloured solution it will be found that after a short time the dye is precipitated and the solution loses most of its colour. The reason for this is that by the action of the sodium sulphide the sulphur dyestuff is reduced to a substance of a more oxidizable nature. This modification has less tinctorial power, but is soluble in dilute alkaline solutions such as those containing ordinary washing soda or caustic soda. Such a solution, however, is able to absorb oxygen rapidly from the air, and in doing so the fully oxidized form of the dye is regenerated, and this being insoluble is immediately precipitated. This behaviour is characteristic of all sulphur dyestuffs, and on it is based the method for their application to textile materials.

The dye liquor is prepared by dissolving the sulphur dye in a hot solution containing sodium sulphide (this is universally used since it is many times cheaper than sodium hydrosulphite). Usually, equal quantities of sodium sulphide and the dyestuff are used. Also, since the solution must be alkaline, a further addition of sodium carbonate or even caustic soda is made. The cotton is then treated with the dye liquor usually at or near boiling temperature. Since, however, the reduced sulphur dye has not a very great affinity for cotton, an assistant (having the power to reduce the solubility of the dye and able, therefore, to force it into the cloth) such as common salt or Glauber's salt must be added. Then the cotton is exposed to the air. The dye absorbs oxygen, reverts to its original state, and

is thus very intimately fixed within the fibres as an insoluble pigment.

Usually the oxidation takes place so quickly that the exposure which the cotton receives in the operation of dyeing and washing is sufficient. Where, however, cotton fabric is dyed continuously and therefore would receive less exposure to the air, it is necessary to make certain of the oxidation, and for this purpose the dyed fabric is run through a small steam-air chamber.

As might be expected, fabrics dyed with sulphur dyes are extremely fast to washing and most other influences. Sulphur dyes are very largely used, particularly for black shades. There is only one other superior process (aniline black) for dyeing black cotton, and this will be dealt with later.

The direct cotton colours which are very popular among dyers, are mostly made from the coal tar intermediates, benzidine and tolidine. By the use of these dyes almost any shade can be matched, and they are exceptionally easy to apply.

The dyeing procedure merely consists of treating the cotton with a hot or boiling solution of the dyestuff. Usually the dye liquor is first made slightly alkaline (so as to correct any hardness of the water and also to aid the solubility of the dye) by the addition of sodium carbonate, although in some instances the liquor may be slightly acidified. As the dyeing proceeds, common salt is gradually added in order that the dye liquor may be more completely exhausted.

After dyeing, the cotton is usually lightly washed and dried.

Although in most instances the shades obtained by means of the direct cotton colours are reasonably fast, various methods of after treatment have within recent years been adopted with the object of improving them
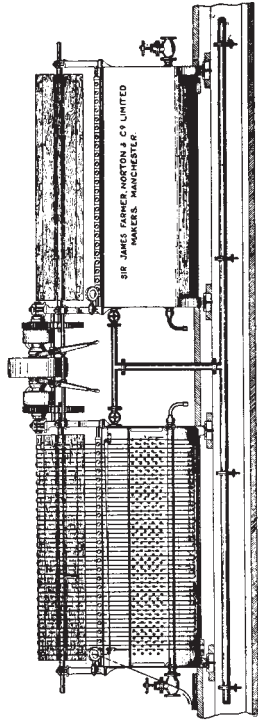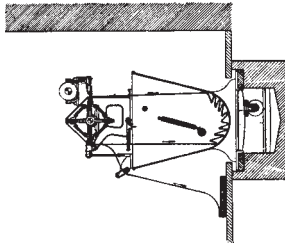
MACHINE FOR DYEING FABRICS IN ROPE-FORM

SIR JAMES FARMER, NORTON & C.º LIMITED
MAKERS, MANCHESTER.

in this respect. Thus it has been discovered that if the dyed fabric is worked for about thirty minutes in a warm liquor containing 1 per cent of copper sulphate, its fastness to light is considerably increased. On the other hand, a similar treatment in which chromium salts, e.g. sodium bichromate, are used, renders a dyed fabric faster to washing although its fastness to light is
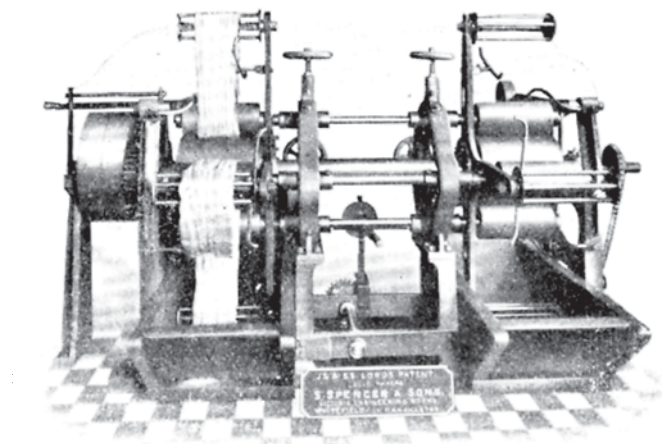
MACHINE FOR DYEING AND TREATING YARN

not greatly affected. A solution of formaldehyde (formalin) is often used for the same purpose. So that these after-treatments are frequently applied to cotton fabrics which have been dyed with direct cotton dyestuffs.

Other processes of after-treatment of an entirely different character are also used. In these, however, the shade of the dyed fabric is generally changed.

It has already been mentioned that the simplest

process by which a dyestuff can be formed is that discovered by Peter Griess in Allsop's brewery at Burton. In this process termed *diazotization*, a suitable dyestuff intermediate is treated with an acidified solution of sodium nitrite (a substance now largely produced by fixation of atmospheric nitrogen). The intermediate thereby becomes changed into a very reactive type of substance, termed a *diazo* compound, so that when another suitable intermediate is added, immediate union or *coupling* takes, and a dyestuff is produced. This reaction is easily controlled and involves the use of no solutions which would harm any kind of fabric.

As, perhaps, might be expected, many dyestuffs can be considered, and are in fact actually used, as intermediates for the preparation of other dyes. For dyes differ from the usual intermediates only in being coloured, and there are several intermediates having a more complex constitution than many dyes. So that, in these special methods of after treatment of direct cotton colours, use is made of the above described *diazo* reaction to convert dyestuffs already fixed on textile materials into more complex dyestuffs.

There are two methods of treatment depending on the types of dyestuff present in the fabric

In one method, the fabric is immersed in an acidified solution of sodium nitrite in order to diazotize the dye which even in its diazotized form is still retained by the fabric. Then the fabric is lightly rinsed and passed into a solution containing a suitable intermediate, which immediately couples with the diazotized dyestuff on the fabric. It is then merely necessary to wash the fabric and dry it in the usual manner.

The other method is used when the dyestuff on the fabric is of a type which is not capable of being diazotized,

but yet is able to couple with a diazo compound. So that in this case, the fabric is passed into a solution containing a suitable intermediate which has been diazotized by addition of an acid and sodium nitrite. Coupling then takes place as in the first method.

It is evident that by either method of after-treatment, the dyestuff finally remaining in the fabric is of a more complex character than the direct cotton dye originally present. And, since such complex dyes are usually but sparingly soluble, it follows that these methods of after-treatment render the coloured fabric faster to washing. Often the fastness to light is also improved. At the same time it must be pointed out that the after-treatment often causes a considerable change in colour, but experience enables the dyer to allow for this.

The vat colours in several respects are similar to sulphur dyestuffs. Thus while they are very insoluble in water they can in a reduced state be easily brought into solution. Moreover, simple exposure to the air is sufficient to oxidize the reduced dyestuff back to its original insoluble form, so that their application is somewhat similar to that of the sulphur dyes. There is this difference, however, that the more expensive sodium hydrosulphite is used instead of sodium sulphide, and also that in most cases the dye liquor must be strongly alkaline.

In the dyeing process the partially dyed textile material is guarded from aerial oxidation as much as possible in order that uneven dyeings may be avoided. Also the final oxidation of the dyed material is effected not only by air but also by chemical means, and for this purpose it is frequently immersed in a solution containing hydrogen peroxide, bleaching powder, or other suitable oxidant.

Vat dyes are especially suitable for fabrics which

are required to withstand the action of sunlight, washing and bleaching.

The Dyeing of Silk.   Silk differs from other textile materials in its much greater cost, lustre and " handle," and for this reason silk fabrics are not generally used for purposes where much wear and tear is involved.   So
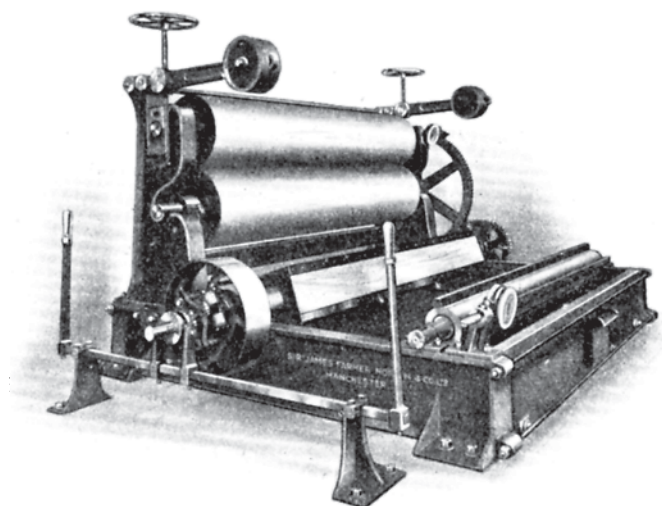
MANGLE FOR FABRICS

that bright dyestuffs rather than fast ones are often preferred for colouring silk.

As compared with cotton and wool, only a small number of dyes are used for colouring silk.   Those most frequently employed are basic dyes, acid dyestuffs and direct cotton dyes.   Mordant, vat and sulphur dyes are not much favoured by silk dyers owing to the difficulties of applying them.   The dyeing of black silk,

however, is extensively practised, and for this purpose logwood, a natural mordant dyestuff, is used.

Silk resembles wool in its strong affinity for dyes, and because of this silk is especially liable to yield uneven dyeings. This fault is corrected by the addition of suitable assistants to the dye liquor.

It has been mentioned previously that in the cleansing treatment (scouring) of raw silk, as a preparation for dyeing, an alkaline soap solution containing the natural silk gum or sericin is obtained. This solution is generally known as "boiled-off liquor," and, when added to liquor in which silk is being dyed, it is found to considerably aid the production of even shades. Boiled-off liquor, then, is the chief assistant used in silk dyeing.

Silk is further distinguished from other textiles in that it is very largely dyed in hank or skein form. Silk fabrics are dyed to a much smaller extent, and loose silk not at all. Moreover, in the dyeing operations it is the constant endeavour of the dyer to preserve the original lustre of the silk.

The dyeing of silk with acid dyes is carried out by much the same method as is used for wool, except that the temperature of the dye liquor is not allowed to rise beyond 85–90° C. Sulphuric acid is used as an assistant, but the Glauber's salt is mostly replaced by boiled-off liquor. On the whole, however, the acid dyestuffs have less affinity for silk than for wool, and in consequence are much less fast.

Silk absorbs basic dyes even from cold solution, so that in dyeing the liquor must be maintained at a moderate temperature—50–85° C. Even dyeings are obtained from dye liquors which have been slightly acidified (the dyestuff is thus rendered more soluble) and to which boiled-off liquor has been added. It is

however, by means of these basic dyestuffs that the most brilliant shades of silk are obtained.

Many direct cotton dyestuffs have but little affinity for silk, especially when cold dye liquors are employed. There are, however, a number of these dyes which can be applied, and with these dyeing is carried out by the same methods as are used for dyeing cotton materials, except that boiled-off liquor is used in the dye liquor and the addition of a small amount of acetic acid is sometimes made.

The large demand for black silk (for umbrellas, linings, etc.) makes the dyeing of this shade a quite important section of the silk industry. For this purpose logwood is the dye most largely used.

Logwood is usually marketed in the form of large blocks, of a deep red colour, which are cut from a species of tree grown in Jamaica, Honduras, and St. Domingo. These blocks are ultimately " rasped " or " chipped " into small fragments which are then moistened and allowed to ferment. The wood becomes much darker in colour, and is finally thoroughly steeped in water, the logwood extract so obtained being then suitable for use in dyeing.

The black dyeing of silk has for its object not only the actual colouring but also the weighting of the silk. That is, by suitably conducting the dyeing process, the weight of the silk is often increased by 100–300 per cent, and this increase is due not to the dye but to the amount of mordant absorbed.

In the usual process, silk in the form of hanks is very heavily mordanted by steeping it alternatively in two solutions, one containing iron compounds and the other tannic acid. In this operation, an insoluble bluish black compound—iron tannate—is deposited within the silk, and this is continued until the silk is weighted

to the desired extent. Often this treatment is followed by immersing the silk in a solution of prussiate of soda. As a result of a reaction between the prussiate and the iron mordant, a quantity of Prussian blue is formed within the silk, and so deepens its bluish colour.

Finally, the silk is dyed in a hot liquor containing logwood extract, iron and copper salts and soap. The whole process is complicated, and requires to be carefully controlled, but it yields a remarkably pleasing black shade.

Dyeing of Linen and Artificial Silk. Linen and artificial silk very closely resemble cotton, since they are all composed of the same substance—cellulose. Consequently the same methods for dyeing cotton are used for these related fibres with but little modification.

Neither artificial silk (except those varieties manufactured from nitrocellulose) nor linen has any useful affinity for basic and acid dyestuffs. Both, however, like cotton, absorb tannic acid readily.

In the case of linen the fibres are difficult to penetrate and, therefore, in the dyeing process allowance has to be made for this. On the other hand artificial silk usually shows, as compared with cotton, a somewhat increased affinity for dyestuffs. So that in dyeing the tendency for the colour to rush on to the fibre has to be carefully restrained.

With both fibres the dyer endeavours to preserve their natural lustre.

The dyeing of mercerized cotton is carried out by exactly the same methods as are used for ordinary cotton, except that allowance is made for the greater affinity which mercerized fabrics show for dyestuffs.

A very interesting but difficult part of the dyer's duty is concerned with the dyeing of union fabrics. Such fabrics sometimes contain three fabrics—cotton,
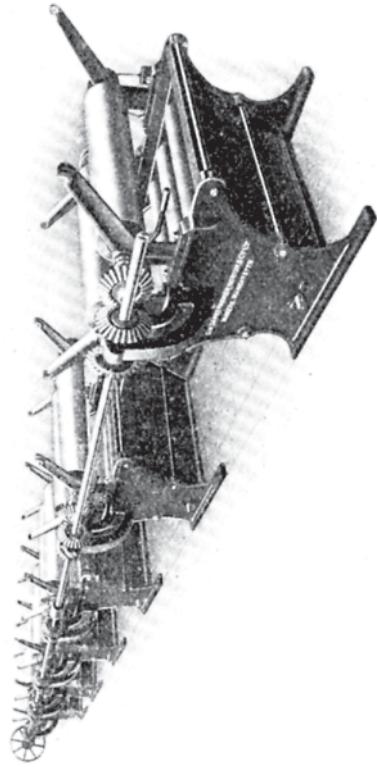
DYEING JIGS IN SERIES

wool and silk—but usually only two, cotton and wool.

In dyeing union goods either of two possibilities may be desired. For it is possible to dye the different fibres to the same shade and so obtain a uniformly coloured fabric, or the fibres may be differently coloured in order to obtain shot effects.

For obtaining shot effects on wool-silk unions, acid, basic and direct cotton dyes are serviceable. It is found that certain acid dyestuffs have an equal affinity for both wool and silk; a few dye wool and not silk at high temperatures, while others dye silk but not wool at low temperatures; also many basic and direct cotton dyestuffs have good affinity for silk but little for wool in the cold. On these facts depend the dyeing methods adopted.

Thus, in one method of dyeing the fabric is first dyed in boiling liquor containing suitable acid dyestuffs. The wool is thus dyed and the silk but slightly stained, and if necessary this can be cleared by gently treating the fabric in a weak soap solution. After this the fabric is dyed in a cold liquor containing a direct cotton or basic dyestuff which is only absorbed by the silk.

For the production of solid shades use is made of the fact that many acid and direct cotton dyestuffs have a strong affinity for silk but a poor affinity for wool at low temperatures, while the reverse is true at high temperatures. So that by dyeing the union fabric at a suitable temperature between these two extremes both wool and silk are dyed alike.

The dyeing of wool-cotton union fabrics is extensively carried out. Much of the fabric which is used for rain coats is made of a mixture of cotton and wool. Fortunately, there are considerable differences in

the dyeing properties of wool and cotton, so that several methods for dyeing this type of fabric are known.

A somewhat expensive method, on account of the many operations involved, will probably suggest itself to the reader. The wool is first dyed with an acid dyestuff, this having, of course, no effect on the cotton. The fabric is then mordanted with tannic acid and tartar emetic, and, since wool has no affinity for tannic acid, it is only the cotton which becomes mordanted. So that on dyeing the fabric in a cold solution of a basic dyestuff the cotton alone becomes coloured. Thus both fibres can be dyed with shot or solid shades.

Instead, however, of filling-up the cotton with basic dyestuffs, the cotton can be dyed in a cold alkaline liquor containing direct cotton dyes which have no affinity for wool under such conditions.

There is a third method favoured by many dyers in which the dyeing is effected in one operation.

The difficulties involved in dyeing cotton and silk union fabrics are much the same as those met with for wool and cotton unions, so that similar methods can be adopted.

Thus the fabric can be dyed with an acid wool colour, the silk alone being dyed, and then, after mordanting with tannic acid and tartar emetic, and subsequently dyeing with a basic dye, the cotton becomes dyed.

On the other hand, an alternative method is practised in which the fabric is dyed with a direct cotton dyestuff under such conditions that the cotton is more strongly coloured than the silk. Then, by suitable treatment of the fabric in a moderately warm bath containing a basic or acid dyestuff, the silk can be brought to

its desired shade with but slight effect on the cotton.

From the above description it will be appreciated that the dyer's task is no easy one, but that the greater his scientific knowledge the greater are his possibilities of success.

CHAPTER VIII

SPECIAL METHODS OF DYEING

ANY industry which is dependent on the fancies of the general public must ever be adapting itself to meet a changing demand. The one who pays the piper has the right to call the tune, and so the dyeing industry must satisfy the public's taste in coloured fabrics. Yet in spite of ever changing fashions certain shades of colour have become so well known, because of their beauty or their fastness, that their production has now assumed something of a routine character. Indigo, Turkey red, and aniline black are well-known standard shades, and the production of these will now be described.

Aniline Black. The fastness of aniline black towards all destructive influences cannot be surpassed by any other colour. Unfortunately, it can be successfully applied only to cotton fabrics, but nevertheless it is a significant fact that about half the world's total production of aniline is used for this purpose.

It has already been mentioned that Perkin discovered the first dyestuff when carrying out some experiments with aniline, and it was with some similar investigations that the process of dyeing aniline black originated. John Lightfoot, a dyer of Accrington, records how he made his important discovery.

" In the year 1859, I was working out some experiments upon aniline for Mr. Richard Dugdale Kay, of Accrington, which he had sent me as oil of naphtha ; the market price of it was then from 15s. to 20s. per lb.

" In November of the same year I found that by mixing an acid chloride of aniline (equal parts of pure

hydrochloric acid and aniline) with starch paste, holding 4 ozs. of chlorate of potash a gallon, and printing this mixture with a wood block, little or no colour was produced after twenty-four hours ageing ; but that, when the same colour was printed in the machine with a copper roller, a green colour was produced in twelve hours.

" My notice of this strange fact was the cause that led me to the discovery of aniline black. I at once repeated this mixture, and added to it various proportions of nitromuriate of copper 88 Tw., and I then found that the intensity of the black was dependent upon the proportions of copper and aniline salt employed, as well as the duration of the ageing.

" The colour, when first printed, was a pale olive, which gradually developed on the fibre to an intense myrtle-green in about twenty-four hours. When washed in water only, without alkali or soap, it became an intense black."

Further on he states—" The high price of aniline at this time prevented me thinking much of the black except as a chemical curiosity, but I had sufficiently developed the colour to print a few pieces of calico in July, 1860, at the Broad Oak Print Works, Accrington.

" Except for a few pieces of single blacks, nothing more was done until the end of 1862, when an offer was made for the process by Messrs. J. J. Muller & Co., of Basle, Switzerland, which resulted in it being patented in January, 1863, and sold to them."

Since the time of Lightfoot, aniline has become plentiful and cheap (its present value is about 1s. per lb.) so that cost, the most formidable obstacle to its use, has disappeared. Moreover, so many chemists turned their attention to the difficulties surrounding the

application of aniline black, that to-day several perfectly reliable processes are known.

It has been found that for the transformation of aniline into aniline black the aniline must be treated with an acid, an oxidant and a catalyst. In other words, aniline black is the product obtained when aniline is oxidized, and it is the function of the catalyst to promote the oxidizing process.

If a mixture of aniline, acid, and an oxidizing substance such as potassium chlorate (this is used in the manufacture of matches) be heated, no change occurs. But, if a mere trace of iron or copper be added, the mixture immediately commences to foam, becomes hot, and is converted into a thick black paste. Iron and copper are thus suitable catalysts, Apparently, without the catalyst, no transference of oxygen from the oxidant to the aniline can take place. On these facts the methods for dyeing aniline black are based.

For dyeing loose cotton it is usual to employ what is generally referred to as the " single bath " method. In this process the cotton is heated in a solution containing a mixture of aniline, hydrochloric acid, sodium bichromate (this oxidant is preferred to sodium chlorate) and iron and copper salts. The black is quickly formed both within and without the cotton fibres, the dye liquor thereby becoming very dirty so that particles of black adhere to their surface.

A thorough after-washing of the cotton is therefore necessary, and even then the dyed cotton is likely " to rub."

The single-bath process has the advantage that the strength of the cotton is not seriously diminished. On the other hand, the black shade obtained is often very bronzy, and when in contact with acids is liable to turn

green.   So that another process which is always applied to cotton fabrics is much to be preferred.

In this second process the cotton fabric is first " padded " or impregnated with a mixture containing
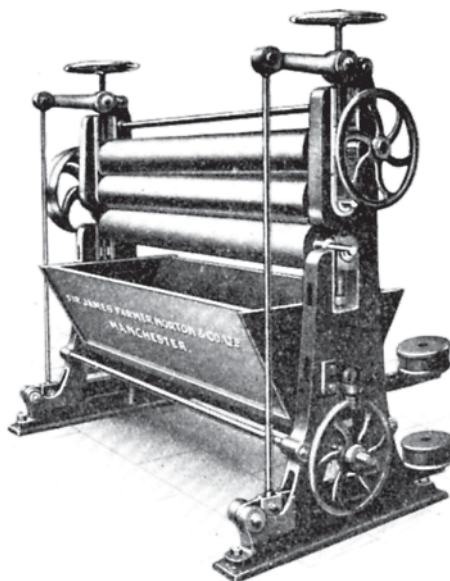
PADDING MACHINE

aniline, an acid (hydrochloric or a mixture of hydrochloric and acetic acids), an oxidant (almost invariably sodium chlorate) and a catalyst (copper sulphate or prussiate of soda).   This mixture at ordinary temperatures is perfectly stable, and shows no tendency to form aniline black.

The fabric which now contains all the substances

necessary for the formation of aniline black is then partially dried by a passage over drying cylinders or through a hot air chamber. During this treatment the fabric acquires a light green colour due to formation of emeraldine—the first intermediate compound produced when aniline is transformed into the black.

In order to carry the oxidation a stage further to nigraniline the fabric is then aged. For this it is led through another heated chamber, the air inside which is also maintained moist by means of small steam jets. The use of steam is necessary since the formation of nigraniline can take place only in the presence of moisture.

The fabric, which by this time has acquired a dark bottle green or almost black shade, is then passed through a warm but weak solution of sodium bichromate (the operation is called after-chroming) in order to complete oxidation. It is then well washed and dried.

In this manner a very permanent and handsome black is produced.

Unfortunately, the acid which it is necessary to use is likely to cause a serious loss of strength in the cotton unless special care is taken. This has always been a difficulty attending the production of aniline black, but experience has shown how to overcome it.

Turkey Red. It has been pointed out that mordant dyestuffs, on account of the difficulties experienced in applying them, are seldom used for dyeing cotton materials. However, the dyeing of cotton with Turkey red is extensively carried out, and from the following description the reader will appreciate the cumbersome nature of the processes required for fixing on cotton this mordant dyestuff—Alizarin.

Methods for dyeing cotton with Turkey red have been practised in India, Persia and the East for several

centuries. But about 1790, Turkey red was started in Glasgow, the natural dyestuff—madder—being used. Towards the end of the nineteenth century we have seen that the dye present in madder was synthetized and finally made under the name of Alizarin from coal tar products.

The older methods of dyeing, in which the natural dye was used, required about four months. Modern methods allow fabric to be dyed within three days, but this gain in speed is accompanied by a slight decrease in quality.

In the modern process cotton fabric is first thoroughly cleansed by boiling it in dilute solutions containing carbonate of soda and caustic soda. It is then partially dried. The fabric is then worked in a 10-15 per cent solution of Turkey red oil—a product which is prepared from castor oil. When the fabric is thoroughly saturated with the oil, it is evenly squeezed and dried at a moderate temperature—40-60° C. After this, a steeping of the fabric in a solution of alum follows, and again it is squeezed and dried.

By these processes a compound, formed between the Turkey red oil and the alum, is deposited within the cotton fibres. In other words, the cotton becomes oiled and also mordanted with aluminium.

For very heavy or brilliant shades, these mordanting operations are repeated once or twice.

At this stage, the fabric usually contains more oil than it could retain firmly after dyeing, so it is well washed in weak alkaline solutions. Also, since the presence of lime is essential to the dye lake which is ultimately formed within the cotton, some chalk is added to the washing liquors, and part of this is absorbed by the fabric. Again the cotton is squeezed, and then it is dyed for about one hour
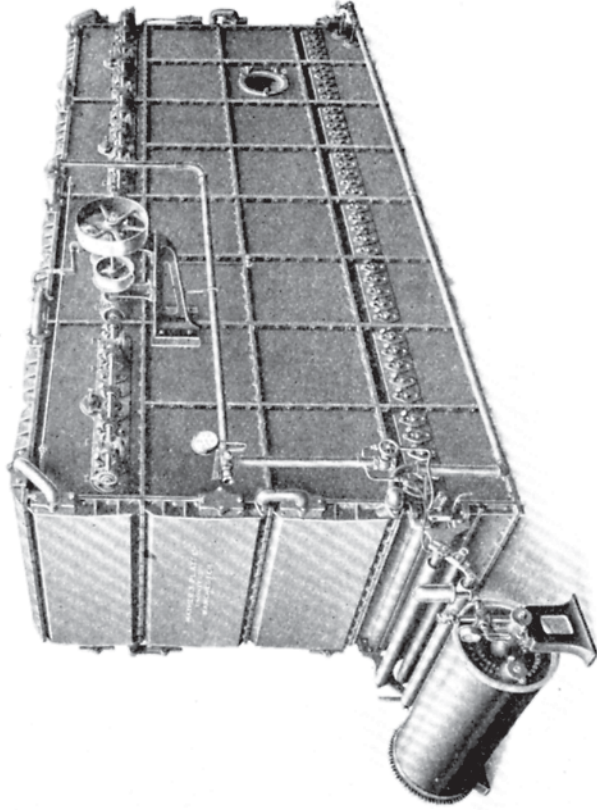
AGEING CHAMBER FOR ANILINE-BLACK DYEING

in a hot liquor containing some 15 per cent of Alizarin.

After dyeing, the shade of the fabric, not being fully developed, is still capable of improvement, and in order to effect this the fabric is once more saturated with Turkey red oil, dried, and then steamed for about an hour. It is in this steaming operation that the complete fixation of the colour lake (consisting of lime, Alizarin, aluminium and oil) takes place. The fabric, however, has yet a dirty tinge, and this is removed by twice boiling the fabric in a weak solution of soap.

Such is the process for dyeing cotton with Turkey red. It is very tedious and difficult, but it is justified by the beautiful, fast red and pink shades which can be produced.

Para Red. There is, however, another standard red shade also dyed exclusively on cotton, and which is known as Para red, or more correctly Paranitraniline red. It lacks the pleasing tone of Turkey red, and is inferior to it in fastness. Yet, because of the ease and rapidity with which it can be produced, Para red is extensively dyed.

Para red is really an ingrain dyestuff. That is, the textile material is coloured by forming a dyestuff within its fibres. The dyestuff so produced has scarcely any affinity for the textile fibres, and is retained merely because it is insoluble and is deposited within them.

In Para red dyeing, use is made of the diazo reaction, which has already been explained in connection with the after-treatment of direct cotton colours. Para red is formed when paranitraniline is diazotized and coupled with beta naphthol. These two substances are well-known coal tar intermediates which are largely used for the production of many dyestuffs.

In the dyeing process, as usually carried out, cotton
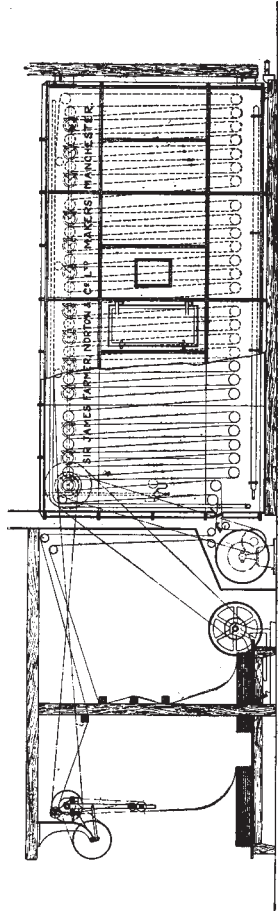
ANILINE BLACK AGER—SECTION

fabric is first evenly padded with a solution of beta naphthol and caustic soda to which Turkey red oil is sometimes added. The fabric is then dried, and immediately after cooling is passed through a solution of the diazotized paranitraniline. In this operation, termed " developing," the red azo dyestuff is formed within the cotton fibres. Finally, the fabric is well washed in dilute boiling soap liquors and then dried.

It is evident that the process is a continuous one, and is capable of a large output. At the same time, however, considerable care is necessary if satisfactory dyeings are to be constantly obtained.

For instance, the diazo solution is somewhat unstable and readily decomposes unless its temperature is maintained low. In summer time the use of ice for this purpose is often necessary. Again, the diazo solution is more stable when it is strongly acid. Yet for the development of the colour it is preferable for this solution to be neutral or slightly alkaline. So that a compromise between these conditions has to be made. Moreover, the acid or neutral state of the diazo solution decides whether the resulting colour will have a yellow or bluish tinge. So that to obtain uniform shades the condition of the developing liquor must be maintained constant.

Although very fast to washing, Para red can be easily discharged or destroyed by suitable chemicals, and is, therefore, largely used in textile printing in cases where coloured patterns are required on a red ground. This will, however, be referred to in a later chapter.

By using intermediates other than paranitraniline, different shades can be obtained by the same method of dyeing. Thus with betanaphthol, α-naphthylamine yields a claret and benzidine a brown shade. Blue shades are obtained by means of a somewhat expensive
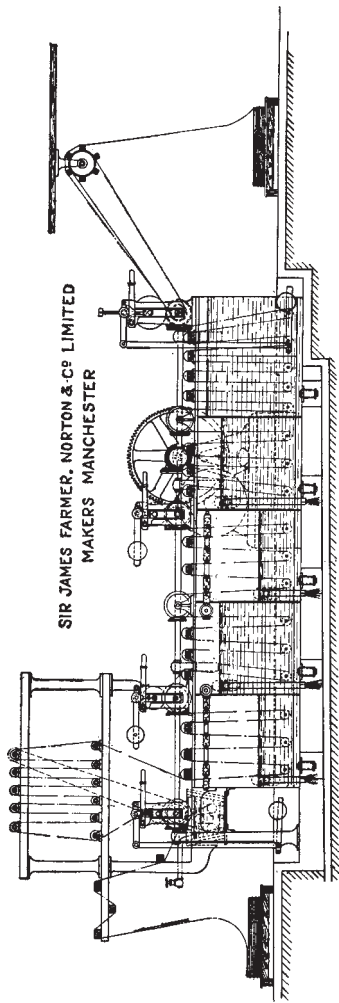
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MACHINE FOR DYEING PARA-RED

intermediate—dianisidine. These other shades are, however, not largely dyed, since they can be obtained more easily by means of other dyestuffs.

German dyemakers have shown much ingenuity in devising improved methods for carrying out this type of dyeing process. They have, for instance, discovered a method for so stabilizing the diazotized paranitraniline that they are able to prepare and sell it in a solid form. Dye users, of course, found this a boon, since they were able to avoid the use of ice and the troublesome operation of preparing the diazo solution by means of sodium nitrite and hydrochloric acid. Also, shortly before the war an excellent substitute for the beta naphthol was placed on the market by German makers.

An interesting difference distinguishing Para red from Turkey red is that when fabrics dyed with the former are heated the dyestuff slowly sublimes.

It is convenient here to mention Primuline—a yellow dyestuff which was discovered in 1887 by Green, the well-known English colour chemist.

Primuline is a direct cotton dyestuff, but it is not fast to light. If, however, the dyed fabric is diazotized by the usual methods, and then immersed in an alkaline solution of beta naphthol, immediate coupling takes place with formation of a red dyestuff. Intermediates other than beta naphthol can be used, and shades fast to light and washing produced. It was in connection with these primuline dyestuffs that the term Ingrain was first applied.

Indigo. Although indigo has been used for many centuries, no satisfactory rival to it has yet been discovered. The qualities which have enabled indigo to establish its position so firmly, are its remarkable fastness to all influences and its handsome and pleasing appearance. Substitutes for it may

possess one or other of these qualities, but lack the combination.

Indigo is applied to wool and cotton but is seldom used for silk. Being a vat dye it requires reduction to
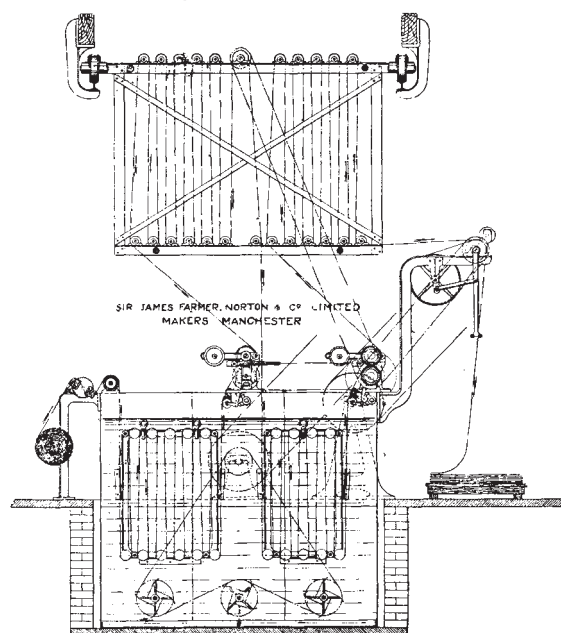
INDIGO DYEING MACHINE

a form which is soluble, and for this purpose several methods are known.

The oldest method of dyeing indigo, and one which is still used for wool, is a fermentation process. In a wooden vat is placed a complex liquor containing woad, bran, indigo and madder, which is warmed and then

allowed to stand. Fermentation sets up, and from time to time lime is added in order to maintain the liquor in an alkaline state. As a result of the fermentation the indigo becomes reduced and ultimately dissolves. The vat is then ready for use.

In the dyeing operation the wool in loose, yarn or piece form is immersed in the vat liquor which is heated to about 50° C. It is then withdrawn, squeezed and exposed to the air. At first the wool has but a pale green colour, but within a short time, owing to aerial oxidation, it rapidly changes to a full blue shade. Indigo in the reduced state is colourless. For very deep shades the wool must be dyed two or three times.

After the dye vat has been used it is strengthened by the addition of more indigo and the other necessary constituents, so that such a vat can be worked for about nine months before being thoroughly cleaned out.

In a second method the so-called *zinc vat* is used. The solution in the vat contains indigo, lime and zinc dust. The latter two ingredients react together and gradually reduce the indigo. When all the indigo is in solution, dyeing is carried out as in the case of the wood vat. The zinc vat, however, is used for cotton goods, and these after dyeing must be passed through a dilute acid in order to completely remove the lime.

In connection with other vat dyes the use of sodium hydrosulphite was mentioned. This excellent reducing agent also finds a use in the indigo vat. It readily reduces indigo to its soluble form, and has the advantage that very little sediment in the vat is formed. The dye liquor must be maintained alkaline, and the dyeing is carried out as with the preceding vats.

Mineral Colours. In these days, when such a large number of easily applied coal tar dyes are available, mineral pigments are not largely used for the dyeing of

fabrics. Yet a few mineral dyes are still used in the production of certain blue, brown and yellow shades on cotton. Such colours are usually formed within the textile fibre itself from mineral salts which are not dyes.

Thus, in the dyeing of *mineral khaki*, cotton fabric is padded with a solution containing the soluble acetates of iron and chromium. It is then dried and steamed in a chamber similar to that used in aniline black dyeing, so that the iron and chromium become fixed in a partially insoluble form within the fabric. Finally the fabric is passed through a boiling solution containing caustic soda and sodium carbonate, the iron and chromium thereby being converted into their most insoluble forms.

Manganese brown is another shade which is produced by aid of mineral dyestuffs. For this, the fabric, after impregnation with a solution of manganese chloride, is passed through a hot solution of caustic soda. An insoluble oxide of manganese is thus precipitated within the fabric, and this is converted into a fast brown shade by treating the fabric with a weak solution of bleaching powder.

For the dyeing of Prussian blue, cotton is first mordanted with an iron salt and is then passed through a solution containing sodium prussiate. A fine deep blue colour at once develops on the fabric, but though fast to acids it is easily destroyed by alkalis and even soap.

On wool Prussian blue can be developed by simply boiling the wool in a solution of sodium prussiate to which a little sulphuric acid has been added.

In addition to the difficulties of their application, the mineral colours usually give the dyed fabric a harsh handle, and this defect has also contributed to the reasons for their neglect.

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CHAPTER IX

THE EXAMINATION OF DYED FABRICS

ALTHOUGH the attractiveness of a fabric is largely dependent on its colour, fabrics are not always judged by their appearance, and it frequently happens that the durability of a fabric is its most important property. So that, in the application of dyestuffs to fabrics, the dyer has to take into consideration the probable uses to which the finished fabric will be put.

It is, of course, most important in a dyeing works that the cost of dyeing, which depends on the methods and dyestuffs used, should be reduced to a minimum. Thus, mordant dyestuffs would not be used where a direct dye could be employed with equal satisfaction, since the cost of the mordanting operation could thus be avoided. A cheap satisfactory direct cotton dyestuff would be used in place of a dear basic colour. So that for any particular fabric the dyer is obliged to use the cheapest combination of dyes which will yet be fast under the conditions to which the fabric will ultimately be exposed. The dyestuffs chosen must have a durability comparable to the durability of the fabric when in use.

In these days it is becoming the custom for manufacturers and cloth merchants to guarantee the fastness of the coloured fabrics which they sell. The responsibility for these guarantees is, of course, ultimately passed on to the dyer, so that in dyeing works these increased responsibilities have led to the adoption of standardized methods by which the behaviour of the variously dyed fabrics is tested.

104

It will at once be seen that, in general, dyed fabrics should be fast to light, washing (washing soda and soap), alkalis, acids, perspiration, and that their colour should not be liable to rub off.

Of course, it is not often possible to dye fabrics so that they are fast to all these influences, but this is seldom necessary. Thus, dyed carpets must be fast to light, their fastness to acids and perspiration being of little importance. It is most important that coloured linings of garments should be fast to rubbing and perspiration. Coloured underwear must not only withstand perspiration and rubbing, but it must also be fast to washing and soap, although not necessarily fast to light. Curtain fabrics must be fast to light, washing and alkalis. So that the tests for fastness are adapted to the purposes of the fabric.

The methods by which coloured fabrics are tested are given here not only because of their interest, but that the reader also might be tempted to test the qualities of the dyes with which his own garments are coloured. The quantity of fabric required for these tests is quite small—a square inch is usually sufficient.

For testing the light fastness of a fabric, a small area of the fabric, part of which is covered with a piece of black or other non-transparent paper, is exposed in the open air to direct sunlight. Each day the exposed portion is compared with the covered part. Thus a piece of fabric dyed with Turkey red will not show any sign of fading before the end of three weeks. Under the same circumstances, indigo will begin to fade in less than two weeks. Some dyes have, however, a much inferior fastness, and many brilliant basic dye-stuffs at the end of three hours exposure to full sunshine will have so faded as to appear ugly and dirty.

It will be appreciated that such a light fastness test,

dependent as it is on sunlight, sometimes occupies, in England particularly, considerable time. So that artificial sources of light are sometimes used instead of sunlight. The rays of sunlight which are most destructive to dyestuffs are those which are invisible— the ultraviolet rays. Hence gas and electric light would not be satisfactory illuminants as they are partially deficient in these rays, so that usually a quartz mercury vapour lamp which produces ultraviolet light is used. With these methods, the tests for light fastness can be carried out more quickly and conveniently, since they are independent of the weather.

The majority of dyed fabrics are required to be fast to washing. Needless to say, however, these requirements are not always satisfied.

In the usual method of testing this property, the fabric is frequently squeezed during about five minutes immersion in a solution containing $\frac{1}{2}$ per cent of soap; is allowed to remain in this solution for a further fifteen minutes, and is then washed in water and dried. The test is sometimes rendered more severe by adding $\frac{1}{2}$ per cent of washing soda to the soap solution. The fastness of the colour is then measured by the difference in shade of the fabric before and after the test.

In another test frequently used, the coloured fabric is plaited with some of the undyed fabric, and the two are then squeezed and allowed to steep in a weak soap solution. The tendency of the dye to bleed is then measured by the degree to which the white fabric has become stained.

In these days when soap contains so little free alkali, the fastness of coloured fabrics to caustic alkalis is not of very great importance to the wearer. However, in the processes whereby fabrics are prepared for the market, it frequently happens that they are subjected

to strong alkalis.   Thus, it not infrequently occurs that fabrics are mercerized *after* dyeing. So that the degree to which a dyestuff will remain unchanged when in contact with alkalis is important to dyers.

In testing this property the coloured fabric is usually steeped in a 1 per cent solution of caustic soda or, in some cases, ammonia, and is then dried without previously rinsing. The change in colour can then be noted.

Human perspiration is acidic, since it contains formic and acetic acids.   So that a fabric's fastness to perspiration is measured by the change of colour which occurs when the fabric is quickly immersed in a 10 per cent solution of acetic acid and dried. A method seldom practised, but otherwise satisfactory, consists of placing the coloured material underneath the saddle of a horse and noting the effect after a hard gallop.

Many ladies' dress materials are required to be fast to mud stains.   Since street dust is usually of an alkaline character, the fastness to mud is tested by sprinkling the fabric with a little lime and water, drying, and noticing the change in colour after brushing.

Such are the general methods for determining the fastness of coloured fabrics. They can be usefully applied by anyone. If your attractive sports' garment becomes dull after a month's wear, you will probably find that the sparsely scattered but brightly coloured threads which gave the garment its " sparkling " character have faded—an example of a dyer's lack of foresight or an attempt to cut price at the expense of durability.

CHAPTER X

TEXTILE PRINTING

In the previous chapters an account has been given of the various processes by which textile materials in their various stages of manufacture are dyed in plain shades. It now remains to give a brief account of the allied art of " textile printing," by which fabrics are ornamented with wonderful and beautiful coloured patterns.

Although methods for printing fabrics have been known for many centuries, it is on the efforts of a Scotchman—Robert Bell—that modern methods of textile printing are based. It is, of course, obvious that designs can be imparted to fabrics by simply impressing them with a " block " on which a pattern is either engraved or raised. But experience has shown that the engraved block is the most useful.

Printing by means of blocks, however, has obvious disadvantages, so that Bell's introduction in **1783** of the engraved copper printing roller is of outstanding importance. By the use of such rollers, the printing process became much more adaptable and speedy. So that to-day Bell's machine has been so improved that it is not difficult in one day to print some ten thousand yards of fabric with a design utilizing a dozen different colours.

In order to understand the principles on which modern printing machines are constructed, reference must be made to Fig. 1. This is a diagrammatic representation of a printing machine capable of printing designs in one colour only.

A is the copper roller on whose surface is an engraved pattern. This printing roller revolves in contact with an iron cylinder, *C*, and also a wooden roller, *B*, covered
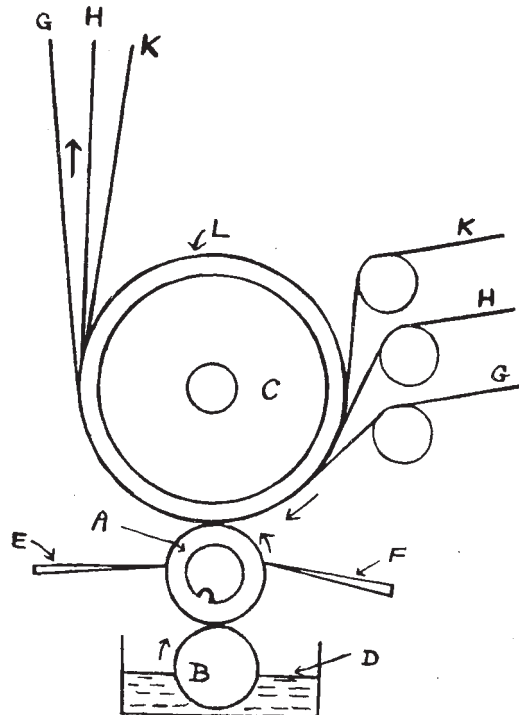
FIG. 1. DIAGRAMMATIC VIEW OF ONE-COLOUR
PRINTING MACHINE

with cotton or woollen fabric. *A*, *B*, and *C* revolve as the same speed. *D* is a " colour box " in which is maintained a constant supply of the colour paste to be printed on the fabric.

In order that the cylinder might have sufficient elasticity, it is covered with several layers of fabric or lapping L. K is an endless revolving woollen blanket. H is a length of ordinary grey fabric—known as a " back grey "—and G is the fabric being printed. The purpose of H is to prevent the woollen blanket K from becoming stained by the colours printed on G. When it becomes too dirty for this purpose it is replaced by another piece, and is then scoured and bleached and so prepared for being printed upon itself. G, H and K pass over the cylinder, C, at the same rate.

F is a strip of steel which is just arranged to scrape the surface of A, and is known as a " cleaning doctor." It is a very important part of the printing machine, while the " lint " doctor, though often desirable, is sometimes dispensed with.

The working of the machine proceeds thus: The printing roller, A, and the " furnisher," B, are both positively driven in the directions indicated, so that the cylinder, C, which is pressed against A is also caused to revolve through friction. As the printing roller comes in contact with the furnisher, its engraved surface is uniformly smeared with the colour paste, the excess of colour being scraped off by the cleaning doctor, F, and the coloured pattern is then impressed on the travelling fabric, G. Any loose fibres or " lint " adhering to the printing roller are then removed by the lint doctor, E, and so the pattern on A can be continually repeated on the fabric being printed, without smudge or defect.

It will be seen that the output from such a machine can be very large and easily speeded-up. But it is limited to the production of a pattern in one colour. For designs of several colours, a more complex machine

is used, and the essentials of its construction are shown in Fig. 2.

In a multicolour printing machine a separate printing
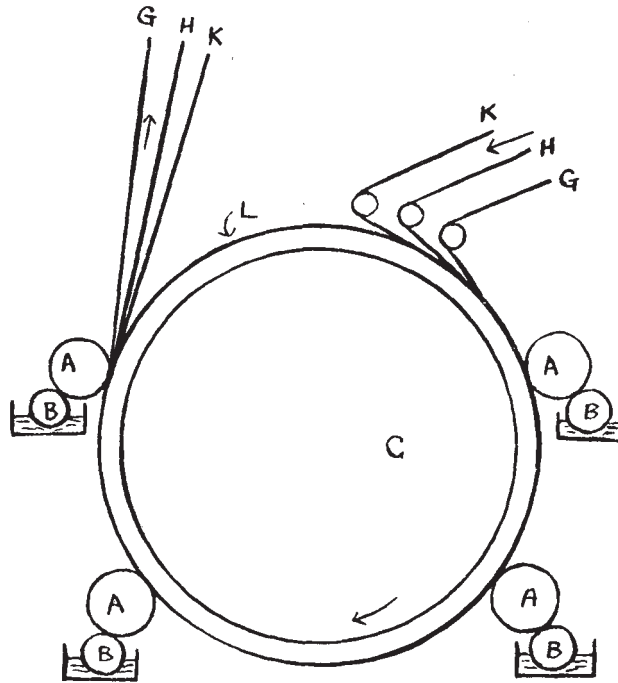
FIG. 2. DIAGRAMMATIC VIEW OF FOUR-COLOUR PRINTING MACHINE

roller and its adjuncts are required for each colour, so that the printing rollers, colour boxes, furnishers and doctors are arranged around a central lapped cylinder. The printed fabric with blanket and back greys passes round this central cylinder just as in the one colour

machine, and each printing roller is adjusted in order to impress on the travelling fabric its particular portion of the colour pattern at the right moment.

An obvious feature of the machine as described above is that it prints fabrics on one side only, so that, in those instances where it is essential that both sides of the fabric should be coloured, a Duplex machine must be employed. This machine is really a combination of two ordinary printing machines, each having its separate arrangement of printing rollers, furnishers, etc., and also its own blanket and back greys. Fig. 3 shows the principles on which such a Duplex machine is worked.

The fabric passes through the one printing machine, A, where a colour pattern is impressed on one side, and then through the second printing machine, B, where all the printing rollers are similarly arranged and the same pattern is exactly repeated on the reverse side of the fabric.

After printing the fabric is usually dried on the usual arrangement of steam heated drying cylinders or in a hot air chamber. But it must not be supposed that the fabric is then ready for " making-up " and dispatch. Such, indeed, is often far from being the case, for, with some styles of printing, the most important treatment of the fabric is carried out after printing.

There are many methods or " styles " of printing, but they are all based on the same principles which are utilized in the ordinary methods of dyeing. Thus, the textile printer makes use of acids, alkalis, mordants, reducing and oxidizing agents, and nearly all the coal tar dyestuffs. It is merely by ingenious machinery and methods for utilizing the properties of dyes and textiles that the printer is able to obtain his wonderful results.

It is impossible to give here more than a bare outline of the methods of printing which are usually adopted.

In what is known as the Direct Printing style, the fabric is first printed with a paste containing one or more dyestuffs (basic, mordant, sulphur and direct cotton
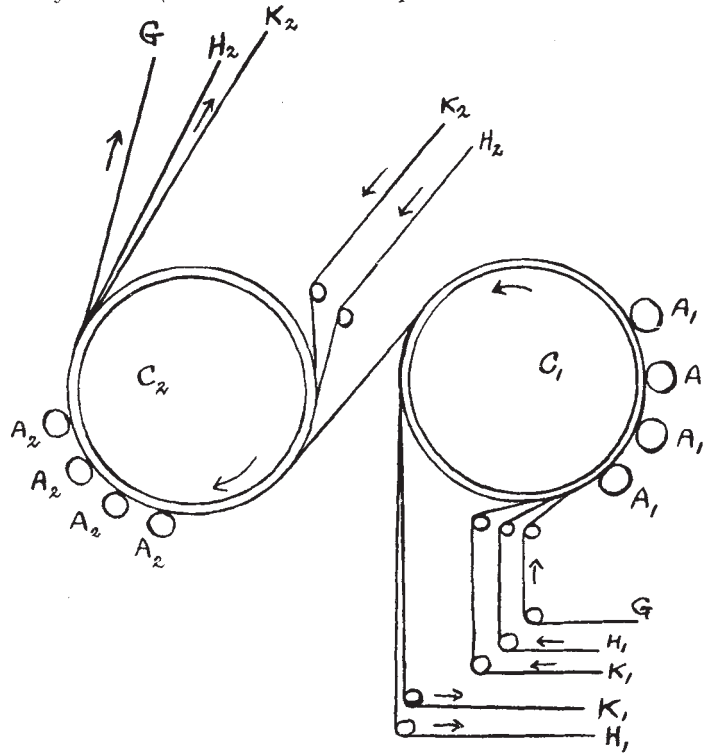
FIG. 3. DIAGRAMMATIC VIEW OF FOUR-COLOUR DUPLEX PRINTING MACHINE

dyestuffs are used) and thickening substances such as starch paste, gum tragacanth or albumen, together with any metallic salts (mordants) which may be necessary for the full development of the colour. The fabric is

then dried, but since at this stage the coloured design is not sufficiently fixed and developed within the fabric, it is then subjected to the action of steam in a chamber specially designed for this purpose. It is during this steaming that the dyes and their mordants become firmly attached to the fabric. Then, in order to clear the unprinted portions, the fabric is washed in boiling solutions containing a small proportion of soap, and is then finally dried.

This method is quite straightforward and is widely used, although in some instances, better results are obtained when the fabric is padded with a solution of Turkey red oil and dried before printing.

It will be seen that the direct printing style allows the production of almost any colour design upon a white ground. But the production of colour patterns upon coloured grounds can be easily accomplished by two other processes—the Discharge and Resist styles.

In the Discharge style, the fabric is first uniformly dyed with a plain shade, and then after drying is printed with a paste—known as a discharge paste—containing substances which are able to destroy the dyestuffs present in the ground colour of the fabric. Such discharging substances are usually of an oxidizing or reducing nature. The printed fabric is then steamed or otherwise treated so as to aid the destruction of the ground colour in the printed parts, and is then thoroughly washed. In this manner, those parts of the fabric which have received the printed pattern will, therefore, appear white.

However, by this same method it is possible to obtain not only white discharges but also coloured ones. For this, dyes which are not affected by the discharging substances are incorporated with the discharge paste. So that after printing, what would otherwise be a white
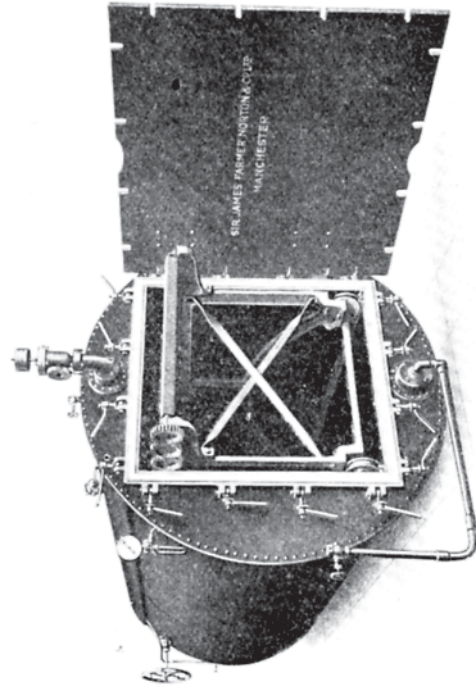
STEAMING COTTAGE

discharge is tinted with the dyestuff which has been added to the discharge paste.

In the Resist style, the fabric is printed and dried with a paste which contains substances which are able, when the fabric is afterwards dyed as for a plain shade, to prevent the fixation of the dyestuff. Also, as in the previous method, various dyes not affected by the resisting substances can be added to the Resist paste, so that coloured resist patterns instead of white ones can be obtained.

Probably the oldest method of printing is that known as the Dyed style, since it involves the use of mordant dyestuffs. In this method the fabric is first printed with a paste containing a suitable metallic mordant, which is then fixed by steaming the fabric. It is then dyed as for a plain shade, with mordant dyestuffs. These, of course, only adhere to those parts of the fabric which have received the printed mordant. This style again is thus adopted for the easy production of coloured patterns upon white grounds.

These four styles of printing, described in their most simple character, allow almost any colour effect to be printed on fabrics with such astonishing ease, rapidity and accuracy, that it is difficult to imagine that any great improvements can take place in this section of the dyeing industry. Yet many keen intellects are always patiently searching for possible improvements, and it is seldom that patience is denied her reward.

INDEX

117

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